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# The effect of treating farm dairy effluent with varying rates of poly-ferric sulphate on reducing phosphate leaching through agricultural subsurface drains.

A thesis submitted in partial  
fulfilment of the requirements  
for the Degree of Master of  
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by

Marion Dumaine

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By Marion Dumaine

The application of farm dairy effluent (FDE) to land is a significant source of phosphate entering waterways. Studies have shown that treating FDE with 250 mg Fe/L of poly-ferric sulphate (PFS) solution can significantly reduce phosphate leaching, however it remains unknown if this can be achieved at lower rates of PFS treatment. A lower treatment rate would reduce cost, which could increase farmer use, and thus potentially help to reduce overall phosphate loss to water. The objectives of this study were therefore to: 1) determine the effect of different poly-ferric sulphate treatment rates on the reduction of phosphorus leaching from subsurface tile drainage systems; and 2) determine the effect of land application of treated effluent on GHG emissions, by quantifying nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and methane (CH<sub>4</sub>) emissions from the soil lysimeters receiving effluent treated with a range of rates of poly-ferric sulphate.

A field trial was conducted to evaluate the impact of different PFS treatment rates on the concentrations of dissolved reactive phosphate (DRP), total dissolved phosphate (TDP), and total phosphate (TP) in drainage water. This water was collected from soil drainage units that underwent two effluent applications over a one-year period. The study investigated the efficacy of three PFS rates (250 mg Fe/L, 167 mg Fe/L, and 83 mg Fe/L) and compared the results with those of untreated FDE, relative to background (control) leaching losses. Treatment rates of 250 mg Fe/L and 167 mg Fe/L proved equally effective, reducing the DRP leaching loss factor by 111.13% and 107.77%, respectively. The 250 mg Fe/L and 167 mg Fe/L treatment rates reduced the TDP leaching loss factor by 115.47% and 112.85%, respectively, and the TP leaching loss factor was reduced by 85.02% and 90.72%, respectively. Reductions greater than 100% indicated that the treatment reduced leaching losses to levels below those of the control (no effluent applied). The 83 mg Fe/L rate reduced the DRP and TDP leaching loss factors by 80.56% and 80.17%, respectively, and did not cause a significant reduction in the TP leaching loss factor. This suggests that P leaching can be significantly reduced using a lower rate of PFS than previously reported.

The results were attributed to the reactions which occur between the phosphate in effluent and the ferric hydroxides formed in the PFS-treated effluent. These reactions reduce the concentration of DRP in the treated effluent and reduce the mobility of phosphate within the soil matrix when PFS-treated effluent is applied to land.

Greenhouse gas emissions of N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> showed no significant difference between the untreated FDE treatment, PFS treatments, and the control.

Keywords: EcoPond, DRP, Total-P, subsurface drainage, poly-ferric sulphate, eutrophication, waterways, farm management

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## Chapter 1 General Introduction

Pastoral agriculture is the predominant land use in New Zealand and has significantly increased since the expansion of dairy farming in the 1990s (Toor et al., 2004a; Journeaux et al., 2017). Dairy farming is of great importance in New Zealand and the country is ranked 7<sup>th</sup> in the list of the top ten major producers of cow milk worldwide with 21 million metric tonnes of dairy products produced (Shahbandeh, 2023). In the year ended December 2022, the dairy products milk powder, butter, and cheese made up 28% of New Zealand's total exports, contributing an export value of \$20.6 billion. This combined export value was an increase of 21% from the year prior (StatsNZ, 2023).

With the global population increasing, the demand for the production of food and feed for livestock has created a pressure on land resources and an intensification of farming practices (Hunter et al., 2017; Kopittke et al., 2019; Beltran-Pena et al., 2020). Although numbers of NZ dairy herds have been dropping since 1975, the average herd size has been increasing, showing a decrease in small dairy farms and a trend towards more intensive dairy farming (DairyNZ, 2021) (Figure 1-1). Intensifying farm production increases reliance on imported fertilisers and increases the amount of manure produced which must then be managed. In turn, this increases the need for the improvement of nutrient-use efficiency and good management practices of farm dairy effluent (FDE).



**Figure 1-1.** Trend in the number of dairy herds and average herd size for the last 30 seasons in New Zealand (DairyNZ, 2021).

The combined application of mineral-P fertilisers and FDE to land is a common practice in New Zealand dairy farms to maintain high levels of pasture and animal production. It allows for the recycling of nutrients, while being more economically efficient (Di et al., 1999; Minogue et al., 2010; Laubach et al., 2015). FDE is composed of cattle excreta (dung plus urine), milk, detergents used at the parlour, mixed with water from the washing of the dairy parlour or other hard surfaces stock is kept on for long periods at a time, such as feeding pads or barns. Usually, FDE contains less than 2% solids (Toor et al., 2004a; Cameron & Di, 2019). Barkle et al. (2000) and Roach et al. (2001) have shown that regular applications of FDE provide further benefits to the soil than just the addition of plant nutrients. FDE can increase soil structural stability which improves the microporosity of the soil and thus drainage flow and air flow. This is beneficial for microbial activity and natural processes in the soil.

Longhurst et al. (2000) reported volumes of effluent ranging between 40-136 L/cow/day with concentrations of phosphorus (P) in the effluent between 40-80 mg/L. This effluent is mostly stored in effluent ponds, then applied by irrigation. While the application of FDE can be beneficial, it can also lead to the soil P retention capacity of the soil becoming saturated, reducing its capacity to retain P, and causing an increase in P leaching (Toor et al., 2004b; McDowell et al., 2019). P saturation occurs when all the sorption sites on soil particles become occupied and the Ca, Al, Fe, and other

such elements which precipitate P, are used up (Zhang, 2017). This is most likely to occur in soils which are already low in P sorption capacity or soils which are shallow and free draining (Cameron et al., 2002). McDowell and Wilcock (2008) surveyed 37 catchment-scale studies in New Zealand and found that P losses from dairy-dominated catchments were the greatest, ranging from 1-10 kg P/ha/y compared to sheep farmland and sheep and beef farmland-dominated catchments which range from 0.1-2.2 kg P/ha/y. The range of values was dependent on geographical features including soil type, topography, and climate, and management factors including irrigation practices, use of effluent, and cultivation practices.

In New Zealand, almost half of GHG emissions come from agriculture (48.1%) of which methane (CH<sub>4</sub>) makes up about 71% (NZAGRC, n.d.). After enteric methane production, manure management is the second largest source of agricultural greenhouse gas emissions (Aguirre-Villegas & Larson, 2017) and accounts for approximately 10% of agricultural GHG emissions globally (Owen & Silver, 2014). Most emissions from manure management are emissions of CH<sub>4</sub> during storage in effluent ponds or tanks. Methane is produced under anaerobic conditions that exist in effluent ponds by the activity of methanogenic archaea (Petersen et al., 2013). Compared to stored manure, CH<sub>4</sub> emissions from manure deposited by stock or applied onto land are significantly lower and generally represent about 10% of the manure management category vs 90% from the effluent storage pond (Collins et al., 2011).

In response to the increase in GHGs worldwide, the New Zealand Government has set targets for reducing CH<sub>4</sub> emissions in its Climate Change Response (Zero Carbon) Amendment Act 2019. By 2030, CH<sub>4</sub> emissions must be reduced to 10% below the 2017 levels and by 2050 they must be reduced 24-47% below 2017 levels (MfE, 2021; MPI, 2023). In 2017, CH<sub>4</sub> emissions were at 3.4 MtCO<sub>2-e</sub> (excluding land use, land use change and forestry – LULUCF) (MFE, 2022). The NZ Greenhouse Gas Inventory (NZ GHG Inventory) represent the top three largest contributor to NZ agricultural GHG emissions as ‘Enteric Fermentation’, ‘Agricultural Soils’, and ‘Manure Management’ respectively (Cameron & Di, 2021).

A new technology called EcoPond<sup>®</sup> has been developed to treat FDE to reduce methane emissions and mitigate environmental concerns from the application of FDE to land. The technology uses the chemical coagulant poly-ferric sulphate (PFS) with the purpose of specifically reducing methane emissions and phosphate losses from land application of treated effluent (Cameron & Di, 2021). Cameron and Di (2021) showed that there was a reduction in CH<sub>4</sub> emissions of up to 99% and a strong relationship between the rate of PFS used to treat FDE and the reduction in CH<sub>4</sub> emissions. Che et al. (2022) found that treating FDE with the maximum rate of PFS to achieve clarification (250 mg Fe/L as described in Cameron and Di, 2019) reduced P leaching losses following application onto artificially drained soils.

However, it is unknown whether lower rates of PFS treatment would also have a similar effect reducing P leaching losses. This is a gap in the current literature and the primary focus of this project.

## 1.1 Objectives

Therefore, the objectives for this study are:

1. To determine the effect of different application rates of poly-ferric sulphate (PFS) on the reduction of phosphorus leaching from subsurface tile drainage systems. This will be done by identifying the rate of PFS that is most efficient for reducing phosphate leaching from treated effluent.

2. To determine the effect of land application of treated effluent on GHG emissions, by quantifying N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> emissions from the soil lysimeters receiving effluent treated with a range of rates of poly-ferric sulphate.

## 1.2 Hypothesis

The hypotheses of this research project are:

- That the P leaching reduction is affected by the rate of PFS;
- That phosphate leaching losses can be reduced by treating effluent with a poly-ferric sulphate rate lower than 250 mg Fe/L; and
- That greenhouse gas emissions from the effluent application area are not affected by the different rates of PFS used to treat the effluent.

## Chapter 2 Literature review

### 2.1 Introduction

Globally, it is a common practice for farmers to supply nutrients to their paddocks via the application of effluent, to compliment or replace fertiliser application (Di et al., 1998; Wang et al., 2004; Tzanakakis, 2011). This provides economic benefit by saving on fertilisers, especially nitrogen (N), phosphorus (P), and potassium (K) (Norris et al. 2019). However, FDE is often applied to land in relation to the N requirements of the plants, resulting in a high rate of P being applied. This becomes a problem when the P concentration in the soil reaches a level higher than the plant requirement because it enhances the potential for leaching losses of P to occur (Sharpley et al., 2000). Many studies have shown that when FDE is applied to shallow free-draining soils or soils with artificial drains, the risk for P leaching into waterways is greatly increased (Toor et al., 2004a; Toor et al., 2004b; Cameron & Di, 2019; McDowell et al., 2019). Furthermore, in soils where there is a high stone content, high preferential flow, a coarse structure, or soils with low amounts of P-fixing material, the risk of leaching is greater due to reduced number of sites in the soil matrix with which FDE can interact (Sims et al. 1998; Monaghan & Smith, 2004; Houlbrooke & Monaghan, 2009; McDowell et al., 2019).

In New Zealand, there are around 2 million ha of poorly drained or imperfectly drained soils (Monaghan, 2014). In Southland, about three-quarters of agricultural land was once poorly drained or imperfectly drained soil which has now been amended by installing artificial subsurface drainage (Pearson, 2015). Subsurface drainage systems ('tile-drains' and/or 'mole pipe drains') aid the productivity of agricultural soils which have high water tables or imperfect drainage by altering the rate and route of water movement through the soil (Ballantine & Tanner, 2013). This allows for better drainage and aeration of the soil; however, it also increases the risk of nutrients leaching due to the shallow depth of soil through which nutrients travel before reaching the drains, compared to areas where soil layers are deeper and nutrients have a greater chance of being retained within the soil matrix (King et al., 2015).

When P enters surface waters, degradation of the water quality can occur. Eutrophication is a growing problem for rivers and lakes in New Zealand and has been identified as being the primary problem for the health of waterways globally (Smith and Schindler, 2009). Most waterways in New Zealand have high nitrogen concentrations (Scarsbrook & Melland, 2015), and the limiting factor for the growth of aquatic algae is most often phosphate (Abell et al., 2010). McDowell et al. (2009) reported that 68% of monitored freshwater sites were P limited, 15% were N limited, and 17% co-limited (N and P). Hence, to prevent further degradation of the health of waterways, it is necessary to reduce phosphate leaching into rivers and lakes. Recent research has discovered that most of the phosphate that leaches from dairy farms with shallow free-draining soils or soils with artificial drainage comes from effluent application areas (Cameron & Di, 2019; McDowell et al., 2019). Therefore, improving effluent treatment before application is the focus of this research investigation.

Greenhouse gas emissions are also of interest in this study due to the many recent regulations in New Zealand targeting the reduction of GHGs. The New Zealand Government has set targets for reducing methane emissions in its Climate Change Response (Zero Carbon) Amendment Act 2019. By 2030, methane emissions must be reduced to 10% below the 2017 levels and by 2050 they must be reduced 24-47% below 2017 levels (MfE, 2021). Furthermore, section 215 of the Climate Change Response Act 2022 has been published by New Zealand's Climate Change and Agriculture Ministers based on the farm-level split-gas levy outlined as part of He Waka Eke Noa, Primary Sector Climate Action Partnership. This describes how prices will be set for farmers and growers for emissions of

methane and nitrous oxide, based on a range of factors. The prices will be low initially and increase after the first five years of the plan being in action. Sequestration systems and the implementation of mitigation technologies will be incentivised and rewarded (MfE & MPI, 2022).

## 2.2 Phosphorus cycle in agricultural systems

Figure 2-1 shows the various inputs, transformations, and losses of P which occur in the soil. This is commonly referred to as the phosphorus cycle.



**Figure 2-1.** The soil phosphorus cycle (Hyland, 2006).

### 2.2.1 Inputs

Soil phosphorus can be found in two general forms, organic P and inorganic P. While P reserves can be high, with concentrations in the soil ranging from 200 to 7000 kg/ha, 80% of this phosphorus is immobile and not readily available for plant uptake (Prasad & Chakraborty, 2019). P inputs to soil come from inorganic mineral-P fertilisers, effluent application, plant and animal returns, and the weathering of rocks.

#### 2.2.1.1 Inorganic fertiliser

A major source of inorganic phosphorus comes from inorganic fertilisers applied by landowners. The most widely used in NZ is single superphosphate (SSP), but the use of diammonium phosphate fertilisers (DAP), monoammonium phosphate fertilisers, and triple superphosphate (TSP) are also common. All these are soluble in water and hence are fast-release mechanism fertilisers. Some countries, including New Zealand, are known to use reactive phosphate rock (RPR) as fertiliser, which is insoluble in water and therefore releases P at a slower rate (White, 1988). Due to the different properties and composition in nutrients of these fertilisers, they will release varying amounts of P to the soil and at different rates (UMN, 2018).

In the 19<sup>th</sup> century, around 1847, it became known that phosphate rock could be mined and used as fertiliser. From then on, its mining and production has grown widely, and agriculture has become heavily reliant on the resources which supply the P used in fertilisers (Cathcart, 1980). The main sources of phosphate used in fertilisers are from mining of deposits. Mining of phosphate rock is currently undertaken in 30 countries: Morocco, USA, China, Russia, Tunisia, Jordan, and Brazil to name a few. USA, China, Morocco, and Russia collectively produce 70-75% of the global production of phosphate rock (Cisse & Mrabet, 2004). China is currently dominating this production, accounting for around 43% of the global production (Garside, 2022).

### 2.2.1.2 Effluent application

It is a common practice to apply effluent to land to compliment or replace fertiliser application (Di et al., 1998; Wang et al., 2004; Tzanakakis, 2011). Effluent is rich in nutrients, which can be returned to the soil, serving as an economic and environmental benefit if done properly. Effluent from an average dairy cow has an economic value of about \$25/year (DairyNZ, 2023a).

Effluent must be applied to land at the correct time and when the soil is not too wet, to ensure that zero/minimal leaching occurs. This will ensure that plants have the best chance of taking up the nutrients they require. The rate of application of effluent and depth at which it is applied will depend on the type of soil as some which have a shallower groundwater table or are free draining will be more at risk of leaching nutrients from the effluent application. Best management practices should be targeted so that the application rate and depth is most effective (Houlbrooke et al., 2011).

### 2.2.1.3 Plant and animal returns

Plants tissues release P during the decomposition and mineralisation of plant litter. In these processes, microbes turn organic P into inorganic P to make it available for plants. This is described further in Section 2.2.2.1.

Of the P ingested, dairy cows return around 70% via dung and urine, which can then be used in the soil in a similar manner to plant litter (DairyNZ, 2023b).

### 2.2.1.4 Weathering of rocks

As a natural process, minerals within soils weather and release phosphorus into the soil solution, for plant uptake. Primary minerals such as apatite are very stable and resistant to weathering and hence will release phosphorus at much slower rates than secondary minerals. Secondary minerals such as calcium, iron, or aluminium phosphates release P at slightly faster rates (Prasad & Chakraborty, 2019).

## 2.2.2 Transformations

Phosphorus transformations include mobilisation/immobilisation, sorption/desorption, and precipitation/dissolution reactions (Figure 2-2).



**Figure 2-2.** Transformations of phosphate in soil (Ballance, 2023).

### 2.2.2.1 Mineralisation/immobilisation

Mineralisation of P can occur through biochemical processes involving phosphatase enzymes which release P from organic compounds into the soil solution. Mineralisation can also occur through other biological processes, where soil organisms oxidise soil organic matter to obtain energy, releasing inorganic P in the process (Bunemann et al., 2007).

During immobilisation, inorganic P is converted back to organic P as soil organisms use phosphate as an energy source. Immobilisation and mineralisation occur simultaneously. The C:P ratio in the soil

determines whether net immobilisation or net mineralisation occurs. When the C:P ratio is less than 200:1, net mineralisation will occur as there is enough P in the soil to sustain both plants and soil microbes. When the C:P ratio is between 200:1 and 300:1, the mineralisation rate and immobilisation rate will be approximately equal. If the C:P ratio is greater than 300:1, there will be net immobilisation as there will not be enough P in the soil to sustain both plants and soil microbes (Dalal, 1977; Deng, 2021). Both processes are greatly influenced by soil moisture, temperature, pH, and aeration.

#### *2.2.2.2 Sorption/desorption*

The sorption of P is the process whereby orthophosphates  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  bind to the surface of soil particles. These particles are aluminium and iron oxides, clays, calcium, and amorphous materials. Soils which contain higher concentrations of these particles will have a greater potential for P sorption. Therefore, soils with a high clay content have a higher phosphorus retention capacity than coarse sandy soils which have the lowest P retention capacity (Ige et al., 2007). Soils with a low pH have greater concentrations of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  and therefore a higher affinity for P sorption.

Parfitt et al. (1975) showed that P is specifically sorbed by Fe oxide surfaces through the replacement of two adjacent surface bound hydroxyl ions. Two oxygen atoms from the phosphate ion bind to two Fe ions, and result in a binuclear surface complex. Rajan (1975) suggested that a similar process occurs with hydrous Al oxide where a binuclear coordination of the phosphate ion occurs with two Al atoms.

The sorption and desorption of P on organic matter is slightly more complex. Moreno et al. (1960), found that organic matter can form complexes with Ca ions, resulting in a release of P into the soil solution from Ca phosphates. Nagarajah et al. (1970), studied the effect of organic acids on the amount of P adsorbed by various clays: kaolinite, gibbsite, and goethite. Their results showed that organic acids could be adsorbed via ligand exchange on the ligand surfaces, competing with P, and therefore reduce the amount of P adsorbed by these clays. Daly et al. (2021), showed a similar effect in peat soils, where organic acids blocked sorption sites. Furthermore, humus can form coatings over the surfaces of aluminium and iron oxides, reducing the amount of P sorption which can occur (Chatterjee et al., 2014). On the other hand, Appelt et al. (1975), showed that in some soils, such as volcanic soils, P was preferentially sorbed over organic acids and therefore the presence of organic acids had no influence on the amount of P sorbed.

Desorption is a process which occurs in response to a decrease in phosphate concentration in the soil solution, most often as a result of plant uptake. Other anions in the soil such as silicates, carbonates, sulphates, arsenate, and molybdate can compete with phosphate for binding sites on anion exchange sites. This can result in the displacement of phosphate ions from those sites, increasing its concentration in the soil solution (Thompson & Goynes, 2012).

#### *2.2.2.3 Precipitation/dissolution*

The precipitation of phosphate is a process whereby phosphate reacts with another substance and forms a solid mineral. This reduces the phosphorus availability in the soil. This process mostly occurs with metal ions such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ca}^{2+}$  which form Al, Fe, and Ca phosphates. This process is a slow one and is almost irreversible. It can be reversed via dissolution, but at a very slow rate (Brady & Weil, 2008). As stated above, the metal ions  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Ca}^{2+}$  form sorption-type reactions with P. It was suggested by Brady & Weil (2008), that at low P concentrations, sorption is the main transformation process which occurs, while at higher P concentrations, precipitation is the dominating process occurring.

Dissolution is a form of weathering where phosphate minerals dissolve and release P back into the soil solution as described in section 2.2.1.4.

### 2.2.3 Losses

Phosphorus is lost from the soil/plant system via plant uptake, leaching, runoff, and soil erosion.

#### 2.2.3.1 Plant uptake

Plant roots absorb P from the soil solution, which is in much lower concentration (0.001 mg/L – 1 mg/L) than other macronutrients found in the soil solution (Brady & Well, 2002). The P which is readily available for plant uptake is the P which is found in the 'labile/soluble pool' in the soil. This is the smallest pool of the three pools of P found in soil and is made up of predominantly orthophosphate anions ( $\text{H}_2\text{PO}_4^-$  and  $\text{H}_2\text{PO}_4^{2-}$ ). This form of P is very minimal in the soil and only found at concentrations of around <1%. P in the soluble pool can be replaced by P in the reactive pool via the processes mentioned in section 2.2.2. Plants mostly take up orthophosphate anions, but can also take up certain forms of organic P. Mycorrhizal fungi develop symbiotic relationships with plant roots and, via extending hyphae through the soil profile, can help plants take up P.

#### 2.2.3.2 Runoff and erosion

Runoff and erosion can occur with rainfall or irrigation events. Water running off the top layer of the soil carries with it both soluble (dissolved) and particulate (attached to other particles) phosphorus from the soil surface. This can be influenced by the soil, slope, and farm management practices such as tillage and cultivation practices, stocking levels, and irrigation scheduling (Withers & Bowes, 2018).

#### 2.2.3.3 Leaching

Leaching of P occurs when water percolates downwards in the soil profile, carrying soluble-P in the soil solution with it. In many soils, leaching is a minimal form of P loss in comparison to runoff, as a lot of the P in the soil is bound and not readily available for uptake or for leaching (Prasad & Chakraborty, 2019). P leaching is likely to occur in soils with lower concentrations of materials that bind P, such as coarse sandy soils, free-draining soils, soils with artificial drainage systems, and soils with high stone content (Monaghan & Smith, 2004; Houlbrooke & Monaghan, 2009). P leaching is also more likely to occur when the soil test P value (i.e., P available for plant uptake) is high (Hooda et al., 1999). Leaching mechanisms and losses will be described in detail in Section 2.5 below.

## 2.3 Sources of P in soils

Phosphate in soil comes from the P fertilisers which are applied to the soil, manure spread on the soil, parent material of the soil, and dead organic matter.

### 2.3.1 Phosphate rock for fertiliser

Phosphorus (P) is one of the most abundant elements on earth, being the 11<sup>th</sup> most common in the crust of the earth and the 13<sup>th</sup> in seawater (Smil, 2000). Most of the phosphate used globally comes from phosphate rock mined from sedimentary or igneous deposits. Sedimentary deposits are the most common, providing more than 80% of the global production of phosphate. Igneous phosphate deposits are mainly mined in Russia, South Africa, Finland, and Brazil. They are often of lower grade than sedimentary deposits, and hence not used as widely. Sedimentary deposits can be found throughout the world in a wide range of chemical compositions and variations in physical forms (Cisse & Mrabet, 2004). However, not all P deposits are suitable for mining, certain conditions need to be met for them to be a good source of phosphate rock (Filippelli, 2011). Marine sedimentary deposits of P make up about 80% of the sources of P production with the rock ores containing about 30-35%  $\text{P}_2\text{O}_5$ . By comparison, igneous deposits only contain about 5%  $\text{P}_2\text{O}_5$  or less (Krauss et al., 1984).

The use of phosphate additions to improve soil fertility began in the early 19<sup>th</sup> century with ground animal bones treated with sulfuric acid, a source of fertiliser devised by Lawes and Gilbert in the UK (Johnston & Poulton, 2019) and simultaneously by Liebig in Germany (Young & Davis, 1980). Around 1830, the industrial treatment of phosphate rock with sulfuric acid began, creating the first superphosphate fertilisers. The first factory for the production of this fertiliser was established in England in 1842, by John Bennet Lawes, when the mining of coprolites began in Suffolk (Cathcart, 1980). By 1853, there were a total of 14 factories producing the fertiliser. The production spread rapidly and expanded into Europe and the USA (Hignett, 1971). The production from large Moroccan deposits only began around 1920, and later, in the 1950s, triple superphosphate was created (Cathcart, 1980). In the 1960s, production of crops was increasing along with the increasing demand for food production and new high yielding crops began to be introduced. These required large increases of nutrient application along with increased irrigation in order to give greater yields (IFA, 1998).

Recently, with growing global population, and an increase in the consumption of meat and dairy products, especially in countries with growing economies such as China and India, demand for phosphate fertilisers is on the rise (Cordell et al., 2009). The phosphate rock produced is mostly used for the production of mineral fertilisers DAP (Diammonium Phosphate), MAP (Monoammonium Phosphate), TSP (Triple Superphosphate), SSP (Single Superphosphate), and phosphoric acid. The main production occurs in the USA, China, Morocco, and Russia which collectively account for 70-75% of the global phosphate rock production (Cisse & Mrabet, 2004). Of those four, China is currently the largest producer in the world, producing around 85 million tonnes of phosphate rock, or 43% of the global production in 2021 (Garside, 2022). By comparison, large parts of the world, such as India, Australia, and many countries in Europe almost completely depend on the imports of phosphate from other countries. The global consumption of phosphate fertiliser from the 1965 to 2019 to is shown in Figure 2-3.



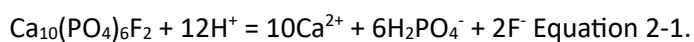
**Figure 2-3.** Global consumption of phosphate fertiliser in million metric tons, from 1965 to 2019 (Statista Research Department, 2023).

Aside from sedimentary and igneous deposits of phosphate, other sources of phosphate include deposits such as guano, residual deposits, and low-grade rocks known to be in the Atlantic and Pacific Oceans. Guano is the dried excrement of sea birds and bats accumulated on islands or in coastal areas with dry climates. It has been used as fertiliser for thousands of years, but is of very limited supply and hence, does not make up a great proportion of the sources of P (Flaten, 2019). The phosphate deposits in the Atlantic and Pacific Oceans are of low-grade and cannot be mined with the current technology at hand (Cathcart, 1980).

The production of phosphate rock is principally used for agriculture, with 80% going towards fertiliser manufacturing, 5% for animal feed additions, and the remainder 15% for industrial applications which include detergents, metal treatment, and high-tech products (Smit et al., 2009). From these proportions, it is clear that agriculture is the main driving force for the production of phosphate rock. However, the amount of phosphate rock mined and rate at which it is consumed is becoming a concern in terms of the over-exploitation of a finite resource (Cordell & White, 2014). “Reserves” of phosphate rock are the resources of phosphate rock which are economically extractable, easily accessible, and have a high content of P<sub>2</sub>O<sub>5</sub>. The long-term continuous extraction of these will eventually lead to an exhaustion of the resources, while the demands for them will continue to rise (May et al., 2012).

Future production may one day be forced to change towards low quality deposits with more impurities and higher production costs and challenges (UNEP, 2011). Various studies have endeavoured to model an estimation of the remaining global phosphate reserves, but these do not seem to agree. The results range between 100-300 years’ worth of reserves if production rates remain the same, to millennia if more reserves are discovered, better mining practices are developed, and methods for the recycling of phosphate are improved (MacDonald et al., 2011; Elser & Bennett, 2011; Cordell et al., 2011; Tirado & Allsopp, 2012). However, the majority of the studies agreed on the fact that a peak in phosphorus (production from mining reaching its maximum) is likely to be coming soon. Once the peak is reached, the phosphorus resources will be harder to access, of lower quality, and more expensive (Cordell et al., 2009). As of December 2024, the price of phosphate rock is at \$152.50 USD/t, up from \$119.50 USD/t in January 2015 (Diversity Times, 2024).

In New Zealand, soils of most pastoral farms are known to be low in phosphorus and sulphur. For this reason, farmers supply these two nutrients through fertilisers (Fertiliser Association, 2023). New Zealand began importing phosphate fertilisers in 1867, with the first manufacture factory of superphosphate beginning in 1881 in Dunedin. Recently, New Zealand farmers have reduced their use of phosphate fertilisers due to the increases in price and growing knowledge around environmental impacts. Fertilisers are used more strategically, alongside the use of nutrient budgets, to learn how to apply less fertilisers while maintaining productivity (Fertiliser Association, 2023). Traditionally, superphosphate has been the most commonly used fertiliser in New Zealand. However, New Zealand is one of the few countries worldwide which has shown more interest in the direct application of phosphate rocks (PRs) to pasture soil, especially reactive phosphate rocks (RPRs) (Bolan et al., 1990). RPRs can be used in places where the annual rainfall is >800mm and the pH of the soil is <6 (Sinclair et al., 1990). Currently, about 5-10% of P fertiliser applied in New Zealand is RPRs, with the addition of fertilisers which contain a significant proportion of unacidulated RPR residue such as SSP-RPR mixtures (White 1988). This can be attributed to the fact that the application of RPRs can be as effective in supplying P to soil as that of SSP or TSP, and to the rising cost of the manufacturing of SSP (Gregg et al., 1987; Sinclair & Dyson, 1988). The phosphate component in RPRs dissolves in moist soils according to equation 2-1 which is shown for fluorapatite but applies to all members of the apatite mineral group (Bolan et al., 1990).



RPRs have a slower release than other P-fertilisers, which makes them useful as maintenance fertiliser. On long-term pastures with high root densities and biological activity, RPRs have been shown to provide great benefit to the soil as a P source (Mackay et al., 1982). The use of RPRs was shown to decrease P losses by around a third in a study done on field plots grazed by dairy cattle and compared with SSP (McDowell, 2010). However, the lag time of the availability of P to plants when applying RPRs may limit the attractiveness of this P source for some farmers.

It is common globally to apply fertilisers to soils when the moisture content of the soil is below 'field capacity' as fertiliser granules only require a small amount of water to begin dissolving. This allows for the most efficient use of the fertiliser in the soil (Sample et al., 1980). Areas where fertiliser granules have landed will be more concentrated in P than the soil water in areas where granules did not land. Therefore, an osmotic potential gradient establishes between the two, resulting in the fertiliser dispersing throughout the surrounding soil. The osmotic gradient continues until dilution by rain or irrigation decreases the concentration, or by the reaction of the nutrients in the fertiliser with soil components (Huffman & Taylor, 1963). The reactions between soil constituents and P in soil which remove P from the solution phase have been known for decades and are well researched (Sample et al., 1980). These are described in section 2.2.

In the past, it was common for farmers to apply P fertilisers at rates greatly exceeding the required amount for crops, resulting in elevated soil test P (STP) levels (Sims, 1992; Sharpley et al., 1994). The intended goal of this was to remove the P limitation for high crop yield, however environmental consequences were ignored or not understood at the time (Sharpley et al., 2000). When soil tests for P became more common, farmers recognised them as an accurate indicator of when to stop applying P fertiliser, resulting in a decrease in the excessive use of P fertilisers. However, high STP levels can take years to decrease due to the slow release of P in the 'stable pool' and benefits from the reduced use of P fertiliser will take time to appear (Sharpley and Rekolainen, 1997).

### 2.3.2 Application of manure

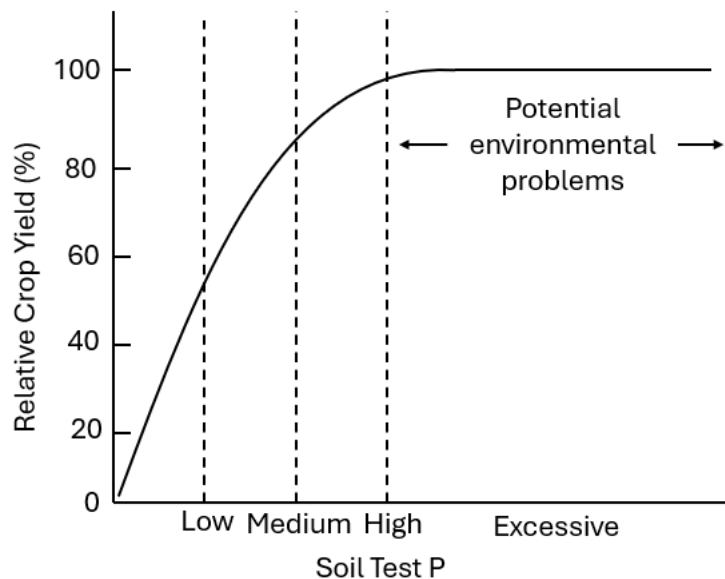
The application of manure to land, as is commonly practiced in New Zealand pasture-based systems, recycles nutrients back to the soil system. The nutrient composition of manure depends largely on animal species and age, the size of the animals, the composition of their diet, and the manure collection, storage, and treatment (Van Faassen & Van Dijk, 1987). The inorganic phosphate compounds in manure react with soil particles by adsorbing onto them or chemically combining with associated minerals to form precipitates (Zhang, 2017).

Research suggests that losses of P via subsurface pathways tend to be greater from organic than inorganic sources, and hence, greater loss occurs with manure application than fertiliser. Eghball et al. (1996) showed that concentrations of P moved deeper into the soil profile under long-term application of cattle manure than under similar rates of inorganic fertiliser. McDowell et al. (2005) and Delgado et al. (2006) compared manure applications to similar rates of P fertiliser superphosphate and phosphogypsum and showed that P losses in drainage water were twice as high under plots receiving manure. Macrae et al. (2007) observed that plots receiving manure applications had greater dissolved P concentrations in drainage water than plots receiving a combination of manure and inorganic fertiliser and plots under inorganic fertiliser only. These results have been hypothesised to be due to organic P being sorbed less strongly than inorganic P in the soil matrix and hence being leached more readily (Frossard et al., 1989; Simard et al., 1995; McDowell et al., 2005). Another suggestion is that organic P sources may increase STP more than inorganic P sources which result in greater P leaching potential (Kinley et al., 2007; Nayak et al., 2009).

High STP levels are found in agricultural soils where manure is repeatedly applied at a higher rate than the rate of plant nutrient uptake (King et al., 1990). The application of manure can therefore increase the available soil P in excess of plant requirements in cases where manure is applied on the basis of crop N requirement (Nelson & Janke, 2007). The average N:P ratio of manure is around 2-4:1 while the N:P uptake by most grains and hay crops is around 4-9:1 (Maguire et al., 2006). Applying manure when considering only the N requirements of the crop results in a P surplus which accumulates in soil. This will have no effect on plants but will increase the potential for

environmental risks (Figure 2-4). Hence, both N and P concentrations of manure should be considered when applying manure to land and fertiliser application should be planned accordingly (Schoumans, 2015).

Toor et al. (2004b) analysed farm dairy effluent and found that the forms of P within it were on average 59% dissolved reactive P and 32% particulate unreactive P. These proportions varied with time over the eight collections: the dissolved reactive P varied from 38 to 76% and the particulate unreactive P from 15 to 56% of total P. Proportions of dissolved unreactive P and particulate reactive P in the effluent ranged from 1 to 3% and 5 to 10% respectively.



**Figure 2-4.** Relationship between relative crop yield and soil P test which can lead to environmental problems (Zhang, 2017).

### 2.3.3 Soil parent material and organic sources of P

Both organic and inorganic phosphates are found in soil and neither can be found without the other present. In contrast to nitrogen, which is about 50 times more present in soils in organic forms than inorganic, neither organic nor inorganic forms of P are predominant in soils worldwide (Addiscott & Thomas, 2000). P in soils is found in a wide range of forms, as shown in Table 2-1.

The starting point of phosphate supply in soils is the parent material that the soils are derived from (Walker & Syers, 1976). Furthermore, while climate is the main driver of N limitation in soil due to its influence on soil microbial activity, P limitation is primarily driven by soil parent material (Augusto et al., 2017). This is further explained in section 2.5.1.

Walkers and Syers (1976) investigated soil chronosequences in various landscapes across New Zealand to determine the pedogenetic pathways of soil P. Their studies revealed that total P, available P, and primary mineral P (apatite, P-Ca) declined in soil with time while occluded P in metal oxides and organic forms of P increased. They determined that total P concentrations were greatest in the topsoil due to the additions of organic P from organic matter while P-Ca concentrations increased down the profile. They further proposed that soils from mafic parent material, namely, basalt, tend to have a greater proportion of occluded P than soils formed from acidic parent material. This is likely due to more oxides and hydroxides of Fe and Al being present in basalt-derived soils, which are important in the immobilisation/sorption of P.

Furthermore, organic P in the form of a range of esters of orthophosphoric acid are constantly released into the soil from dead organisms. Esters are found mostly in the clay and silt fractions of the soil (Anderson, 1980). Humic phosphate is phosphate associated with dead organic matter, but which does not fall into the ester categories.

**Table 2-1.** Categories of phosphate in soil.

Category	Subcategory	Examples	References
Inorganic	Ionic	$\text{PO}_4^{3-}$ , $\text{HPO}_4^{2-}$ , $\text{H}_2\text{PO}_4^-$ , $\text{H}_2\text{PO}_4$	Aslyng (1954)
	Mineral	Apatite, tenticite	Frossard et al. (1995)
Organic	Monoesters	Phytin Inositol hexaphosphate	Anderson et al. (1974)
	Diesters	Phospholipids Nucleic acids	Newman and Tate (1980)
	Biomass P	Microbial P Adenosine triphosphate	Brookes et al. (1984) Jenkinson et al. (1979)
	Humic P		Tiessen et al. (1994)

## 2.4 Phosphorus in waterways

P can enter waterways via soil erosion, surface runoff, subsurface leaching, or direct transmission from stock standing in water bodies. This can become a problem if the concentration of P in the waterway is no longer limiting the growth of aquatic weeds or algae.

### 2.4.1 Sources of P to waterways

P naturally enters freshwater environments through the weathering and erosion of bedrock and soils around the catchment, and through the decomposition of organic material (Correll, 1999). Native forests, although being systems which usually have little or no human interference, also contribute to P loss to waterways. Even small losses of P from systems such as these, while having no measurable effect on the P fertility of the soil, can raise P concentrations in nearby waterways to eutrophication threshold levels (Taylor & Kilmer, 1980). However, the main origin of P loss to waterways remains the P applied to agricultural systems, accounting for more than half of the losses of P to lakes, rivers, and coastal waters (Tirado & Allsopp, 2012).

#### 2.4.1.1 Diffuse and point sources

Phosphorus loss from agriculture can either be from diffuse or point sources. Diffuse sources are usually low concentrations of phosphorus spread over larger areas, which are hard to manage, and can result in high total amounts of P loss (Johnston & Steen, 2001). These diffuse source losses include soil erosion, surface runoff, and leaching of P from the soil.

Point source losses are concentrated in specific locations of the farm and usually comprise high concentrations of P and lower amounts of P loss than diffuse loss sources. Point source losses include direct transfer of animal excreta to waterways, such as when livestock have access to streams and water bodies (James et al. 2007). Farmyards, farm tracks, and roads around the farm can also be diffuse or point sources of P loss from rural environments. In these areas, dung and urine is often deposited, silage transported and stored, and detergents used for cleaning which can all be transported to waterways. To make matters worse, these surfaces are often impervious and allow no or limited infiltration into the soil, decreasing the amount of P which can be retained. Edwards and

Hooda (2007) measured P in farmyard drains and found up to 51 mg total P (TP)/L in flow from two farmyard drains. They estimated that farmyards can contribute up to 25-30% of annual P loads to waterways, depending on management.

#### *2.4.1.2 Fertiliser and manure application*

The overuse of P fertilisers in the past has led to the accumulation of P in many agricultural soils and an increase in diffuse pollution of P to waterbodies (Chardon & Schoumans, 2007). Importantly, the application of manure has been shown to be an even greater source of phosphorus loss than fertiliser when managed poorly over the long-term (Hergert et al., 1981). Toor et al. (2004b) found that the mean total concentrations of P in leachate where both effluent and superphosphate fertiliser (45 kg P/ha) had been applied on free draining soils under grazed pasture were ten times greater than the leachate from plots which had only received superphosphate (45 kg P/ha). They concluded that the application of superphosphate did little to enhance P loss in the effluent treatments. When applied in large quantities and at inappropriate times, phosphate in the manure is likely to leach and cause environmental issues (Tirado & Allsopp, 2012). There is a tendency to apply too much manure due to the limitations of effluent pond storage which result in high nutrient concentrations in runoff water and in soil solution (Allen & Mallarino, 2008; Chardon & Schoumans, 2007).

Current good practice for dairy farms in New Zealand are to abide by regional authority rules to avoid ponding of FDE on the soil surface (Canterbury Regional Council, 2015); apply FDE at no more than a 10 mm depth at a time and not within 24hrs of saturation for shallow soils with < 50% of profile available water in the upper 30 cm of the soil, hence application in winter months is avoided (DairyNZ, 2015b); and testing the soil P to keep its concentration at or below the agronomic optimum and maintaining this level through the application of maintenance fertiliser-P and/or FDE (Gourley et al., 2015). These practices are similar to those of irrigated land globally (USDA-Natural Resources Conservation Service, 2012). However, McDowell et al. (2019) showed that, even with good management practices, effluent irrigation is the main source of phosphate leaching loss from a dairy farm, especially when the farm has free-draining stony soils. Similarly, Carrick et al. (2013) showed that in freely drained, shallow stony soils such as Eyre soils in New Zealand, good management practices according to rules set by the regional council did not prevent P losses from FDE application to land (Canterbury Regional Council, 2015).

Another problem that stems from the over application of P to soils is the legacy of soil phosphorus which occurs via the various mechanisms that retain P to soil constituents within the three soil 'pools'. Accumulated soil P is not likely to be released immediately and can remain stored in the soil for long periods at a time. Therefore, an improvement in P management may take some time to show a decrease in losses to waterways (Withers & Bowes, 2018).

#### 2.4.2 Pathways for loss of soil P to waterways

The two main pathways for P loss from agricultural soils are surface runoff and subsurface leaching (Figure 2-5). These two pathways occur with water flow, either during precipitation or irrigation events. Whether rain falling on the soil infiltrates into the soil or runs off the surface depends on several factors including the intensity of the rain and the infiltration capacity of the soil, the type of soil, the climate, the slope etc. (Addiscott & Thomas, 2000).

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**Figure 2-5.** Transport mechanisms for loss of P to waterways (Bundy, 2014).

Soil erosion is another mechanism which can cause P loss from soils. This can happen due to wind or water, causing soil P to be transferred into waterbodies. In regions with sloping landscapes, erosion and surface runoff are the main mechanisms for loss of P (Sharpley & Smith, 1990). In comparison, areas where the land is flat, leaching of P through the soil profile is the dominant pathway of P loss and can quickly contaminate waterbodies, especially if the groundwater is shallow or if the soil has had artificial drainage system (Chardon & Schoumans, 2007). The P concentration of eroded soil particles is higher than that in the bulk soil due to the erosion processes carrying smaller and lighter soil particles preferentially to larger ones (Wall et al., 1996). These are particles which have a greater sorption capacity for P than the bulk soil and hence carry a greater concentration overall. This mechanism is called P enrichment.

Lastly, another pathway is when livestock have access to waterways and direct deposition of dung and urine occurs when the animals stand in the water (Davis-Colley et al., 2004).

The majority of P loss from effluent runoff and leaching is in the form of particulate phosphate (PP), mostly unreactive particulate P (Toor et al., 2004b). Some dissolved P (DP) is also lost, especially via runoff or erosion. In water, dissolved reactive P (DRP) is immediately available to aquatic organisms and will cause a direct effect (Sharpley et al., 1981). On the other hand, reactive particulate P and unreactive P take longer to become available to organisms when they enter waterways. P in these forms has to be released by enzymatic or physiochemical processes in order to be available for aquatic organisms. These forms of P loss are of greater concern in slow-flowing water systems (lentic systems), where they can have a high residence time, allowing the particles to settle out and P to be released and made available (Chapra, 1997). However, in soils that have had subsurface artificial drainage installed, there is less soil surface area for DRP to react with and hence more leaching of DRP can occur, and this can cause a problem for fast moving water systems (Che et al., 2022).

#### 2.4.3 Impacts of P entering waterways

When light and temperature conditions are not limiting, aquatic algal growth will be controlled by nitrogen and phosphorus concentrations in the water (Schindler et al., 2008). The ratio by which these nutrients have been found to be an indicator of algal growth is carbon (C), nitrogen (N) and phosphorus (P), 100:16:1 (Redfield et al., 1963). As the C supply is generally not a limiting factor, N and P are usually the limiting factors (McDowell et al., 2009). When neither of these nutrients are limiting, phytoplankton and other aquatic plant growth occurs and can cause the deterioration of water quality. It is important to note that phytoplankton species differ, and that they will have different nutritional requirements, therefore the ratio is only used as a guideline (Sterner & Hessen 1994).

Eutrophication is an important problem to waterways as the aquatic plants and algae shade out the waterway, disturbing the habitat of organisms living within it. As the plants and algae die, they decompose and use up the dissolved oxygen within the water while releasing their nutrients along with carbon dioxide. Such conditions can be deadly to fish and invertebrates (Figure 2-6) (Jaworski, 1981). Some algae such as blue-green algae or cyanobacteria also release toxins which make the waterways dangerous for humans and animals and can lead to death if the water is ingested (Kotak et al., 1994; Farley, 2012).



**Figure 2-6.** Process of eutrophication whereby the addition of nitrate and phosphate nutrients allow the growth of phytoplankton and harmful aquatic plants (University of Waikato, 2013).

Eutrophication is a problem worldwide and whether nitrogen or phosphate is the limiting nutrient will depend on the water body type, common farm management practices in the area, and the nature of the nutrient source (whether it is a point source or a non-point source) (Addiscott & Thomas, 2000). P is the limiting factor for algal blooms in most freshwater systems in the US, UK, Australia, and Europe (Ferguson et al., 1996; Herath, 1997; Carpenter 2008). In marine systems, however, it is N that has been identified as the limiting factor in most areas, especially in summer (Anderson & Glibert, 2002).

Transport of P from agricultural soils to waterways sensitive to eutrophication has been an environmental concern globally for greater than thirty years (Sims et al., 1998). Excess phosphorus in soil can become detrimental if it exceeds the soil P retention capacity and leaches into waterways. This can also occur via runoff if P applied via mineral-P fertiliser or effluent runs off during irrigation or heavy rainfall, or during erosion processes. A loss of P to freshwater bodies can cause algal blooms and reduce the water quality (Prasad & Chakraborty, 2019). Only a small amount of P loss to waterways is required to cause a substantial effect to the water quality. Eutrophication is a growing problem for rivers and lakes in New Zealand and has been identified as being the primary problem for the health of waterways globally (Smith & Schindler, 2009). In New Zealand, about 44% of lakes greater than 1ha were found to be eutrophic (Verburg et al., 2010). Most waterways in New Zealand have high nitrogen concentrations (Scarsbrook & Melland, 2015), and the limiting factor for the growth of aquatic algae is most often phosphate (Abell et al., 2010). McDowell et al. (2009) reported that 68% of monitored freshwater sites were P limited, 15% were N limited, and 17% co-limited (N and P). Hence, to prevent further degradation of the health of waterways, it is necessary to reduce the phosphate leaching into rivers and lakes.

## 2.5 Factors affecting Phosphate leaching

Many studies show that the loss of P from soils depends on several factors beside the P content of the soil including soil chemical and physical factors, rainfall and irrigation, drainage, and fertiliser and tillage practices.

### 2.5.1 Soil factors

Research has shown that in most soils where fertiliser P is applied based on soil testing, little P loss should occur. However, significant P leaching can still occur in sandy soils, high organic matter soils, soils with reduced P-fixing capacities, soil with a high pH, stony soils, or due to preferential flow.

#### 2.5.1.1 *P fixing capacity*

Volcanic soils and highly weathered soil have the greatest amount of P-fixing capacity and therefore, a reduced risk of leaching P. Volcanic soils have high amounts of amorphous materials which give them their high P fixing capacity. However, not all highly weathered soils have high fixing capacities. Soils formed from basalt parent material have a high P fixing capacity while those formed from granite have a low P fixing capacity, and metamorphic and alluvial soils have an intermediate P fixing capacity (Toreu et al., 1988). Soils with high amounts of clay have increased P sorption capacity as well due to the greater amount of surface area on which phosphate sorption can take place (CTAHR, 2023).

Some of the soils most prone to leaching P are sandy soils as they tend to have very low P fixing capacities due to being low in clay, low in Fe and Al oxides, and low in carbonates. For example, appreciable P leaching from sandy soils was observed by Neller et al. (1951) in Florida, by Mattingly (1970) in the UK, by Paton and Loneragan (1960) in Tasmania, and by Ozanne and Shaw (1961) in Western Australia. However, Mattingly (1970) reported that P may not be removed completely from the profile as much of it is translocated into the B horizon. This will depend on the type of soil and the textures of the horizons. Lastly, soils high in organic matter may have greater P leaching due to the organic matter components which can block P sorption sites, making P more available for uptake by plants but also susceptible to leaching (McDowell et al., 2008).

#### 2.5.1.2 *Preferential flow*

Other soil factors include the presence of macropores where the subsurface transport of P bypasses the soil matrix via preferential flow through macropores in the soil (Mabilde et al., 2017) (Figure 2-7). Preferential flow refers to water movement through distinct pathways, also referred to as 'bypass flow' (Hillel, 1980). The other type of flow which exists in soils is matrix flow, relating to the uniform movement of water through a soil, wetting the profile homogeneously. Matrix flow is more common in sandy soils where soil pores are mostly homogeneous, and the soils have good drainage capacities (Tindall et al., 1986). Figure 2-8 shows the effect preferential flow has on solute transport in comparison to matrix flow, whereby preferential flow results in a rapid transport of solute (Houlbrook & Monaghan, 2009). Macropores increase the hydraulic conductivity of the soil, so that water moves through the soil profile at a quicker rate and nutrients have less time to interact with surfaces within the soil. This process is exacerbated when the soil has had an artificial drainage network installed (Monaghan et al., 2016). Artificial drainage is discussed in section 2.5.3.



**Figure 2-7.** Two types of preferential flow (not drawn to scale). Left: macropore flow due to high stone content. Right: macropore flow through crack formations in clayey soils, plant roots, or earthworm burrows (Engstrom et al., 2014).



**Figure 2-8.** Illustration of breakthrough curves of solute transport via preferential flow vs matrix flow (Houlbrooke & Monaghan, 2009).

Soils with a high stone content also have a risk of preferential flow. McDowell et al. (2019) reported a 14-year study that measured the P leaching loss from applying FDE to two soils representative of the soils under irrigated dairy farming in the Canterbury Region of New Zealand. One was a shallow stony Eyre silt loam and the other a deep Templeton silt loam. They found that mean leaching losses of P were significantly greater from the Eyre than the Templeton soil. They attributed this to the fact that the Eyre soil had greater porosity and hydraulic conductivity due to being a stony soil. They also reported that the leaching loss of P was six times greater in the Eyre soil that received FDE applications over the 14-year period compared to the same soil that did not receive FDE. They hypothesised that repeated applications of FDE gradually saturates the walls of the macropores resulting in a reduced potential for the fixation of P over time, as was also reported by Simard et al. (2000).

Clay soils are another type of soil which tend to have preferential flow due cracks that form easy pathways for soil solution to travel through. The cracks are due to swelling and shrinking of the clay upon wetting and drying (Beven, 1981; McLeod et al., 2007; McLeod et al., 2008).

#### 2.5.1.3 pH

Furthermore, soils with a low pH, generally around 5.5, have the greatest phosphate retention capacity compared to soils with a neutral pH. Soil pH influences the nature of P reactions which make P available in the soil (Engelstad & Terman, 1980). Lopez-Hernandez and Burnham (1974) studied soils which were pedologically similar with the main difference between the soils being their pH.

Through this, they found that there was a significant relationship between the increase in phosphate retention and the decrease in pH. They related this to the increase in Al oxides in soils under lower pH, as mentioned in Bache (1964). Furthermore, soil pH can affect the growth of plant roots and their ability to take up P, hence maintaining an optimum soil pH is important for good pasture management.

#### *2.5.1.4 Slope*

The slope of the land will affect the amount of P which is lost via surface runoff and leaching. Studies have shown that land which is on a gradient will experience greater losses of P via surface runoff and erosion, while flatland is more likely to experience P loss via leaching through the soil profile (Qian et al., 2014; Xiaoling et al., 2019; Fransen et al., 2021). In terms of surface runoff, a well-structured soil with little or no compaction will have greater water (and P) infiltration than one with a poor structure and low permeability.

#### 2.5.2 Rainfall

Rainfall is one of the primary driving factors of phosphate losses from soil. McDowell et al. (2008) give two different situations which can cause P loss from rainfall; one where rainfall events are of high frequency but low intensity and one where rainfall events are of low frequency but high intensity. With the first, P tends to move via subsurface flow while, in the latter, P tends to move via overland flow due to the soil's infiltration capacity being exceeded. These scenarios will also depend on the topography of the land, the soil type and soil water storage capacity, and the depth to groundwater. Furthermore, on flatlands where soils have a low P sorption capacity (such as sandy soils), soils have high preferential flow, and/or soils have artificial drains installed, these areas will tend to experience more subsurface flow in either rainfall scenario (Haygarth et al., 1999). For hilly areas, it has been widely shown that P loss via erosion and runoff is most greatly influenced by rainfall intensity and frequency (Ding et al., 2017; Prosdocimi et al., 2017; Williams & King, 2020).

#### 2.5.3 Drainage

The drainage of a soil is a function of many factors which have previously been mentioned, including the rainfall of an area, the soil texture, soil structure and pore network, infiltration rate, the slope of the land, and the water table (Asseng et al., 2001; Bah et al., 2009). Soils with finer textures usually have less continuity of pores and hence sandy soils typically have greater drainage capacities than fine-grained silt or clay soils (Hillel, 1980). The permeability of the soil plays a role in its drainage capacity. Permeability is affected by the soil's texture, structure, and density. The amount to which a soil is permeable will affect how fast water moves through it and how much runs off the surface. Different horizons in a soil have varying levels of permeability and the permeability of a soil profile is governed by the permeability of the most slowly permeable layer within the profile (Manaaki Whenua, 2023).

##### *2.5.3.1 Soil drainage class*

Williams and Saunders (1956) studied soils of the same parent materials which were cultivated and cropped in the same way but differed in drainage class. Those which were freely draining showed greater P levels in plant tissues compared to those which were imperfectly drained. This was attributed to the better crop growth in freely draining soils where the roots have good aeration and the soil a good structure. On the other hand, imperfectly drained soils can become waterlogged and cause reducing conditions which have been shown to increase P solubility and, in correlation, P leaching (Sims et al., 1998; Brand-Klibanski et al., 2007).

Gley soils are soils which are formed under high rainfall and have poor drainage due to having impermeable horizons which impede drainage and cause periodic or permanent waterlogging. In

other cases, gley soils form from high water tables where the groundwater causes sub horizons to be seasonally or permanently wet (Thomasson, 1975). These conditions affect their productivity and results in management measures to be put in place, most commonly the installation of artificial drainage systems. The fundamental aim of drains in these soils is to remove excess stagnating water and/or lower the water table to provide suitable conditions for the growth of plants (Armstrong & Garwood, 1991; Nijland et al., 2005; Clagnan et al., 2018).

### 2.5.3.2 Artificial subsurface drainage

Artificial drainage systems are important for increasing plant productivity on soils that are usually prone to waterlogging, ponding, or poor drainage. Soils with artificial drainage systems were shown by Bengston et al. (1988) to reduce P loss compared to poorly drained soils due to reduced surface runoff and erosion. Other benefits of subsurface drains include increased soil aeration and temperature, greater soil strength and an effectively longer growing season (Smedema & Rycroft, 1983; Irwin, 1986; Fausey, 2005; Macrae et al., 2007).

However, the leaching potential from the application of FDE increases when soils have had subsurface artificial drainage systems installed (Sims et al., 1998; Monaghan & Smith, 2004; Houlbrooke et al., 2008; Houlbrook & Monaghan, 2009; Cameron & Di, 2019). Figure 2-9 shows the extent of preferential flow occurring in a soil where subsurface drains used to be.



**Figure 2-9.** Preferential flow occurring in Pallic soil where subsurface mole pipe drains used to be (Houlbrooke & Monaghan, 2009).

Clay subsoils have been shown to be highly impermeable and often require subsurface artificial drainage to be used for agriculture. Other soils may also require systems such as these, including soils that are either naturally impermeable or low draining. However, the loss of P from artificial drainage is very common worldwide and is an even greater risk when the soil has a limited capacity to sorb P. In Scotland, Hooda et al. (1999) found significant concentrations of P in leachate in tile drains after the application of cattle slurry on pasture. Sims et al. (1998) showed that on average, losses of P from artificially drained soils are around 1 kg P/ha but can go up to > 2 kg P/ha in soils with low P-fixing capacities. Hesketh and Brookes (2000) found a significant increase in the concentration of P in tile drainage water (0.15 to 2.75 mg/L) when STP in the soil was above 60 mg/kg Olsen P for a silt loam. They suggested that this level, which is known to be well above the requirements of major crops and plants for optimum yield (around 20 mg/kg; Ministry of Agriculture, Food, and Fisheries, 1994), can be a critical point at which P leaching increases in soils where water can move through preferential pathways.

Monaghan et al. (2002) measured the P losses in mole and tile drains at a site under pasture farming in Edendale, Southland. In terms of agronomic losses, their results showed that the annual P loss

measured in the mole and tile drains was small in comparison to the fertiliser P applied. However, the environmental impacts of this loss are much greater. The measured concentrations represent significant loading of phosphate into surface waters, where phosphate is commonly the limiting nutrient, hence, increasing the potential for the growth of weeds and algae. To prevent excessive growth of aquatic algae, phosphorus levels in water should remain below 0.04 g/m<sup>3</sup> (Waikato Regional Council, n.d.).

The risks for loss of P from soils amended with subsurface drainage systems increase especially when preferential flow paths exist in the soil and provide a direct connection to the drains. This can be through cracks (especially in clayey soils), macropores, and biopores (Stamm et al., 1998; Simard et al., 2000).

#### 2.5.4 Tillage and fertiliser management

Tillage changes the size distribution of aggregates and hence porosity, affecting water movement through the soil. Tillage can also compact the soil at the base of the plough layer, creating an impermeable layer causing consequences for the drainage of water in the soil. However, tillage can break up the smooth surface of a soil or break up a soil cap if it has formed one. On the other hand, forms of tillage and cultivation are most often the cause for soil caps due to the disturbance they cause to the structure of the soil (Addiscott & Dexter, 1994).

When a soil is ploughed, it is inverted and the P on the surface is moved into the soil to a depth of up to 250 mm. This practice can reduce the amount of P vulnerable to surface runoff but is more important on cropping than pasture systems. Ploughing increases aeration and decreases organic matter content due to increased microbial activity, which increases the mineralisation of organic P, releasing it into the soil solution (Addiscott & Thomas, 2000). Ploughing may destroy macropores, which can reduce P lost via leaching, but also impede proper drainage through the soil (Ulen et al., 2012).

However, permanent pastures do not usually undergo regular tillage or cultivation and hence, can be more likely to accumulate P in the topsoil and near the surface. This can increase the likelihood of P leaching through preferential flow pathways in soils where macropores are prominent, rather than evenly being distributed throughout the profile (Toor et al., 2004b). Yet, soils which have not undergone cultivation, such as soils under permanent pasture, were found to sorb more phosphate than those which had due to having a lower pH and a greater concentration of Al oxides. This would reduce the amount of P susceptible to leaching (Mehadi & Taylor, 1988).

The rate of P fertiliser application and how it is applied can also influence P loss to waterways (Dougherty et al., 2011). P fertiliser should not be applied when the soil is saturated, such as after a high precipitation event or irrigation (Garnier et al., 2010). The effectiveness of water-soluble P fertiliser granules will depend on the amount of water-soluble P in the granules (Taylor & Terman, 1964). This in turn influences the volume of soil affected by P, as was shown by Sample and Taylor (1964), who found that fertiliser granules of 6 mm in diameter which had 14 and 70% water-soluble P diffused into 4.2 and 20.6 cm<sup>3</sup> of soil respectively. Therefore, the placement of soluble P is important, as it will quickly react with soil components and become immobile (Engelstad & Terman, 1980). Hence, fertiliser must be spread evenly. One common way to do this is via broadcasting, which spreads the fertiliser over the entire surface of the soil. Another method is to inject or incorporate P fertiliser into the soil, minimising the risk of surface runoff (Hansen et al., 2002).

## 2.6 Farming practices and manure management

### 2.6.1 Management of stock

Grassland systems are most commonly rotational systems where the stock graze on one paddock before being moved to another. This allows other paddocks to recover after having been grazed, and for the stock to gain the nutrients and water they require from each grazing session (Figure 2-10) (Petersen et al., 2013). Therefore, in systems such as these, the majority (c. 90%) of manure is excreted onto the paddocks and a smaller amount (c. 10%) is actively managed (Chung et al., 2013).



**Figure 2-10.** Illustration of rotational grazing to allow plants to recover (USDA, 2023).

Confined animal systems are most common in Eastern Europe and Russia (Petersen et al., 2013). In these systems, all or almost all of the manure produced by the stock is collected and must be stored and managed, increasing the potential for greater CH<sub>4</sub> production (Chadwick et al., 2011; Owen & Silver, 2014). Management of the manure consists principally of treating the manure, storing it, and spreading it onto land. However, many farms do not have sufficient land area for all of the manure to be spread across in a manner which limits risks of loss of nutrients to the environment, and therefore must either store the manure for longer periods of time or transport it to other places where it can be applied to land (Menzi et al., 2010; Petersen et al., 2013).

Systems of confined livestock can vary widely depending on the housing design and manure collection system. These can be slatted or solid floors which are regularly washed down with water, bedding material which is collected with the excreta producing solid manure, or bedding manure with a drainage system and separate collection of liquids (IPCC, 2006). These systems often have a smaller dilution factor than grassland systems due to water restrictions and more manure to manage, resulting in dry matter concentrations (i.e. volatile solids) usually between 5 and 10% or greater depending on whether the farm uses bedding material (MPI, 2014). In Europe, livestock production is becoming increasingly intensive while remaining mostly 'landless' where <10% of the animal feed is produced on farm (Kruska et al., 2003). Therefore, in systems such as these, only about 30% of excreta is deposited during grazing (Petersen et al., 2013) whilst in New Zealand dairy farming systems about 90% is returned to the paddock with c. 10% captured by the effluent collection system (Cameron & Di, 2021).

Ghebremicheal and Watzin (2011) studied the phosphorus balances of three different farms in Vermont, USA. The study showed that all three dairy farms had greater phosphate inputs than outputs. The farm with the lowest surplus of P had 5.5 kg P/ha and was a small organic farm, the typical conventional farm had a surplus of 15.2 kg P/ha, and the one with the greatest surplus was a large intensive farm with 18.7 kg P/ha. The study related these surpluses of P to a number of reasons but primarily the fact that many farms have a high animal density but insufficient land area for the

spreading of manure. In contrast, in New Zealand, animals are kept outside the majority of the year and rotated from paddock to paddock resulting in less effluent collected in storage and more land area for it to be recycled on (Laubach et al., 2015).

In some regions of New Zealand, namely Southland and Otago, the use of animal confinement facilities is a common practice during the winter season. This is to prepare the pasture for spring growth and avoid pugging damage caused during wet conditions (Luo et al., 2008). Furthermore, the housing of animals during wet seasons reduces the amount of nutrients and sediment lost from the soil system (McDowell et al., 2003). Different designs of confinement facilities, with varying methods of manure collection and bedding material, influence the chemical and physical properties of the manure, and hence, the CH<sub>4</sub> emissions it produces. At the end of the winter season, manure is generally kept for at least a further two months before application to land begins (Van der Weerden et al., 2014).

#### 2.6.2 Farming practices for the storage of FDE

The most common form of management of FDE on New Zealand farms is via pond storage and deferred application. The effluent which enters storage ponds comes from the milking platform, animal housing, holding yards, feed pads, and stand-off pads, and the amount will depend on the area of these structures on a farm.

##### 2.6.2.1 *Impervious surfaces on farm*

At least 30% of dairy farms in New Zealand use feed pads (Rollo et al., 2017) where cows spend approximately the same amount of time on the feed pads as in the milking shed, hence there is a greater amount of effluent collected in effluent ponds (Chung et al., 2013). Furthermore, Rollo et al. (2017) reported that at least 25% of NZ dairy farms have a stand-off pad to keep cows off the pasture when the soil is saturated. These are usually used between the drying off season (May) and calving (July/August) and will be used for about 6-12 weeks. Cows will be kept on them typically overnight, about 16 h/day depending on the farm's management system (MPI, 2019). A variation to these is wintering pads on which stock are kept during the wintering period 24 h/day and seven days per week. Silage is fed to the stock during this period, which can last up to 12 weeks (MPI, 2019). Both feed pads and stand-off pads have been reported to be on the rise in NZ dairy farms, as estimated with some uncertainty by the dairy industry (Fonterra) and regional councils (MPI, 2014). Hence, the value of 30% of NZ dairy farms with feed pads and 25% with stand-off pads can be considered as the lower estimate with a likelihood of these numbers being in fact greater. While feed pads and stand-off pads are used by farmers for practical reasons which can be beneficial for mitigating risks to the environment, it is likely that the trend towards greater use of these will result in increasing volumes of manure captured in effluent ponds and therefore greater GHG emissions from manure management. Lastly, a few farmers in New Zealand have adopted the use of winter housing for stock, which perform the functions of a feed pad, stand-off pad, and covered shelter (MPI, 2019).

##### 2.6.2.2 *Gas emissions from stored manure*

During the storage of manure, gaseous emissions consist primarily of methane. Nitrous oxide emissions also occur, but less significantly (MfE, 2022). N<sub>2</sub>O emissions are a direct result of nitrification and denitrification processes in the manure. CO<sub>2</sub> is also produced, simultaneously to CH<sub>4</sub>, by anaerobic bacterial degradation of organic matter and by aerobic microbial degradation at the slurry-air interface (Steed & Hashimoto, 1994; Moller et al., 2004).

##### 2.6.2.3 *Solids separation*

The practice of solids separation in stored effluent is becoming more widely used in New Zealand due to the increasing use of feed and stand-off pads (MPI, 2014). Solids separation can decrease CH<sub>4</sub>

emissions when done correctly through the removal of manure substrates from the anaerobic environment of the effluent pond. These solids are often left to dry and applied to pastureland as compost, while creating a liquid fraction which is easier to pump and handle (Van Horn et al., 1994; DairyNZ, 2015a; Holly et al., 2017). In New Zealand, the most common types of solid separators which are used are screw presses, static screen run-down separators, and weeping-wall systems. As solid heaps are generally uncontrolled with continuous addition of fresh substrate, aerobic and anaerobic conditions are likely to be occurring simultaneously and successively and have an influence on CH<sub>4</sub> emissions (MPI, 2014; Laubach et al., 2015). On the other hand, Hansen et al. (2006) found that effluent storage systems with solids separation were more likely to have an increase in N<sub>2</sub>O emissions. These N<sub>2</sub>O emissions come from the separated solids heaps due to their anaerobic nature, and will vary between 1% and 10% of total nitrogen (TN) depending on the type of manure it came from (Dammgen & Hutchings, 2008; Chadwick et al., 2011; Webb et al., 2012). Once the solids are applied to land, direct N<sub>2</sub>O emissions end (Laubach et al., 2015).

Weeping wall systems, as shown in Figure 2-11, are becoming more widely used in New Zealand and have the potential to result in high direct N<sub>2</sub>O emissions. This is due to being high-nitrogen environments which cycle between aerobic and anaerobic conditions daily, similar to when effluent ponds have surface crusts (Hansen et al., 2009; Chadwick et al., 2011; Laubach et al., 2015).



**Figure 2-11.** Illustration of effluent collection system with weeping wall to separate solids from liquids (Agriculture Victoria, 2020)

#### 2.6.2.4 *Mixing of effluent*

Another management factor for effluent ponds is whether FDE in a pond is mixed. Mixing FDE ponds keeps the solid fraction in suspension with the liquid fraction (MPI, 2014). However, the mixing of stored liquid manure shows an increase in the rate of CH<sub>4</sub> emissions, which decrease to very low CH<sub>4</sub> emissions once mixing stops (VanderZaag et al., 2010; VanderZaag et al., 2014). However, this process is more of a release mechanism whereby the same amount of CH<sub>4</sub> is produced but is released at a quicker rate than if no mixing occurred.

#### 2.6.2.5 *Storage time of effluent*

Finally, the storage time of liquid manure on farm will depend on the application time and rates (Hill et al., 2001; Sommer et al., 2007). This is determined by many factors including the pasture and crops grown, size of the farm and number of cows, area of impermeable surfaces, and fertiliser requirements, as well as the region the farm is located in which will have regional council requirements for effluent storage ponds. Manure that is stored for long periods of time, which can go up to nine months depending on the storage capacity of the pond, have the potential to release considerably greater amounts of CH<sub>4</sub> than if it is applied to land relatively quickly (Petersen et al., 2013; Purath et al., 2017; Petersen, 2018).

#### 2.6.2.6 Temperature of stored effluent

Microbial communities in manure are sensitive to temperature and it has been well established that CH<sub>4</sub> production increases with temperature (Rittman & McCarty, 2001; Dalby et al., 2021). Microbes can be split into three groups based on temperature ranges within which they thrive. These are psychrophilic (5-20°C), mesophilic (25-40°C), and thermophilic (> 45°C) (van Lier et al., 1997). Microbial communities within manure will shift depending on the temperature conditions of the environment they are in. Lindorfer et al. (2008) observed a shift in microbial community during a switch from mesophilic to thermophilic conditions. This initially caused a drop in CH<sub>4</sub> production, which returned to normal levels once thermophilic methanogen populations increased to match the change in temperature. Similar observations were reported by Bouskova et al. (2005). However, drastic changes in temperatures which exceed the limits of the dominant groups of bacteria present in the manure can cause drops in CH<sub>4</sub> production for a longer period of time (Bouskova et al., 2005; Lindorfer et al., 2008; Kovalovski et al., 2020). For example, methanogens produce lower rates of methane emissions at temperatures below 20°C, compared to temperatures above 20°C (Wiegel, 1990; Elsgaard et al., 2016). When temperatures are below 10°C, very little methane is produced (Steed & Hashimoto, 1994; Masse et al., 2008).

There is little information on how storing manure under psychrophilic conditions affects methanogens, however, when manure is stored outside or without a heating system, psychrophilic conditions are the most common temperature range (Dalby et al., 2021). Im et al. (2020) investigated CH<sub>4</sub> emissions from stored cattle manure for 80 days under a temperature range of 15 to 35°C. Their study showed that the greatest CH<sub>4</sub> emissions occurred at 35°C and were almost halved when temperatures were below 20°C. Effects of temperature on cumulative methane emissions from dairy manure are shown in Figure 2-12 (Hilgert et al., 2022). This graph shows that CH<sub>4</sub> production rate decreases with decreasing temperature, hence, lower storage temperatures not only reduce CH<sub>4</sub> emissions but also releases them at a slower rate. In New Zealand, the longest manure storage period without field application is during the winter months and, depending on the region, part of the stored manure can become frozen. This has been shown to reduce gaseous emissions (Park et al., 2006; Masse et al., 2008; VanderZaag et al., 2011).

Seasonal changes in temperature have also been shown to have an effect on CH<sub>4</sub> emissions from stored manure. Cardenas et al. (2021) studied methane emissions from stored liquid dairy manure during a winter season and a summer season. They found that emissions were significantly higher in summer than in winter. As can be seen in Figure 2-13, mean daily CH<sub>4</sub> emission rates closely followed the ambient and manure temperature curves. As the temperature decreased during the winter months, CH<sub>4</sub> emissions decreased alongside. CH<sub>4</sub> emissions remained low over the winter season, with cumulative emissions of 0.0011 kg CH<sub>4</sub>/kg VS, while summer emissions reached a cumulative 0.148 kg CH<sub>4</sub>/kg VS. The low cumulative emissions in winter were related to the cold temperatures impeding or slowing down the start of methanogenesis processes (Sommer et al., 2004; Elsgaard et al., 2016).

Furthermore, Figure 2-14 shows that when temperature dropped below 5°C, CH<sub>4</sub> production decreased to the point of being non-detectable (Cardenas et al., 2021). The summer trial showed that CH<sub>4</sub> emissions were the greatest after a 10-week storage period and decreased after that. On the other hand, CH<sub>4</sub> emissions from the winter trial showed a strong lag phase during which CH<sub>4</sub> production could not be detected. Similarly, Clemens et al. (2006) reported a much greater potential for CH<sub>4</sub> production during summer conditions than winter conditions due to CH<sub>4</sub> emissions being temperature sensitive. These outcomes have been observed in several other studies (Petersen et al., 2013; Sommer et al., 2013; Kupper et al., 2020). VanderZaag et al. (2014) measured hourly methane

emissions from stored manure and showed that there was a distinct diurnal trend with minimum emissions occurring at night (1.3 kg CH<sub>4</sub>/h) and a maximum occurring in the early afternoon (2.1 kg CH<sub>4</sub>/h).



**Figure 2-13.** Temperature and methane emissions from stored dairy liquid manure during summer through to winter (Cardenas et al., 2021).



**Figure 2-14.** Cumulative CH<sub>4</sub> emissions from dairy manure at different temperatures (Hilgert et al., 2022).

### 2.6.3 Farming practices for the application of FDE

In the 1970s, effluent stored in aerobic-anaerobic two-pond treatment systems was the main method of treating effluent. This effluent was then discharged into surface waterways, loading a high concentration of nutrients directly into the water (Longhurst et al., 2000; Sukias et al., 2001). Hence, improved effluent management regulations have been introduced to protect and maintain the health of waterways, whereby effluent must be applied to land rather than discharged into waterways (Laubach et al., 2015).

#### 2.6.3.1 Land application of effluent

The land application of FDE is the preferred and most common treatment option in New Zealand (Heatley, 1996; Cameron & Trenouth, 1999). However, when carried out inappropriately, this method can cause the loss of harmful contaminants to ground and surface waters (Houlbrooke et al., 2004a; Di & Cameron, 2002). This is particularly the case where subsurface drainage systems have been installed (Houlbrooke et al., 2004b; Monaghan & Smith, 2004). In the past, it was considered that soils with these types of drainage should not receive land applications of FDE. However, with best management practices (BMP), FDE application to land can be carried out. BMP recommend that

certain precautions be undertaken for this practice. Primarily, FDE should not be applied to the soil when it is wet. Various studies have shown that P loss in subsurface drains has been greater during late autumn, winter, and early spring and FDE application should therefore be avoided during these periods (Macrae et al., 2007; King et al., 2014). Furthermore, the movement of nutrients increases when an irrigation or precipitation event follows soon after a FDE application. Therefore, it is recommended that FDE application is planned around irrigation and precipitation events (Houlbrooke & Monaghan, 2009).

Farmers must abide by the rules and regulations set in place by the regional council in their area. However, many farmers have limited storage facilities and apply effluent irrespective of the soil moisture conditions, often resulting in direct drainage of the effluent (Laubach et al., 2015). BMPs encourage deferring the application of effluent until the soil moisture content is below field capacity so as to maximise the uptake of nutrients by plants and maximise filtering of potential contaminants by the soil, thus reducing the risk of leaching into waterways.

#### *2.6.3.2 Low-rate and deferred application*

Houlbrooke and Monaghan (2009) recommend two different application methods to reduce the risk of leaching into freshwater. The first of these is 'low-rate application'. This method is especially beneficial where soils exhibit drainage limitations, excessive preferential flow, are situated on sloping land, or have sub-surface drainage systems. These soils have a high leaching risk if FDE application rates are too high (Houlbrooke & Monaghan, 2009). Low-rate applicators deliver rates of approximately 4 mm/hr, applying FDE in smaller amounts and more often in periods of low moisture deficit (McLeod et al., 2007). This reduces the risks of surface runoff of FDE or loss of nutrients via leaching (Houlbrooke et al., 2006; Laurenson et al., 2017).

The other method of FDE application recommended by Houlbrooke and Monaghan (2009) is 'deferred irrigation' developed by Houlbrooke et al. (2004b). This system involves the storage of effluent in a pond, with the capacity of storage depending on the local climate, soil, and farm conditions, and the strategic application of the FDE when there is a suitable soil water deficit. This mitigates the risks for the loss of nutrients and contaminants to waterways and maximises the ability for plant uptake of the effluent nutrients. For example, Houlbrooke et al. (2004b) applied deferred irrigation of FDE to soil amended with mole and pipe drainage, over a 3-year period. The FDE was applied in relation to soil water deficits and the results showed that, with this method, little to no loss of nutrients in drainage occurred. If there is insufficient storage capacity available to implement deferred irrigation practices fully, Houlbrooke et al. (2004b) recommend applying FDE at the lowest possible soil depths (< 10 mm) to minimise risks of nutrient loss to waterways.

Many areas of New Zealand do not achieve regular soil water deficits greater than 10 mm until about October, and this period usually lasts until approximately the month of May. However, FDE production begins with lactation in late winter (late July/Agust), giving a period of two to three months where FDE must be stored until it can be applied (Houlbrooke et al., 2004b). Hence, farmers in New Zealand require large storage pond capacities for FDE to be able to abide by the guidelines of deferred irrigation practices, and this may not always be possible. If the capacity of the effluent pond is reached before soil conditions are favourable for FDE application, the farmer will be forced to apply at an inappropriate time, resulting in the risk of nutrient loss via runoff or leaching (Monaghan & Smith, 2004; Houlbrooke et al., 2008). Laubach et al. (2015) found that regional averages over New Zealand, where data was available, ranged from effluent pond storage capacities of 26 days in Canterbury to 111 days in the Bay of Plenty. The average storage pond capacity was 86 days.

Neither method of low-rate application or deferred irrigation mitigate the risks of nutrient loss to waterways in the case of an unexpected rain event soon after an application of FDE to land, or in the case of insufficient pond storage resulting in a poorly timed application. Houlbrooke et al (2008) compared N and P losses in subsurface drains and overland flow after applying FDE using deferred irrigation and a one-off poorly timed application of 25 mm of FDE at a soil moisture deficit of 7 mm in mid-September. The day following this application, there was 12 mm of rainfall, resulting in further loss of nutrients. The poorly timed application showed a concentration of nutrients in drainage 6-10 times greater than would be expected during events of winter-spring rainfall.

This demonstrates not only the importance for BMP for the application of FDE to land, but also that there remains a need for a tool which would minimise risks of nutrient loss in the case of an unexpected rain event or a poorly timed application. This is a significant research gap in the literature and requires more work to be done to find a solution to the issue. Figure 2-15 shows the comparison of nutrient loss in drainage under BMP and when application is poorly planned (Houlbrooke & Monaghan, 2009).



**Figure 2-15.** Direct drainage losses of N and P from FDE under deferred irrigation compared to a one off poorly planned FDE application (Houlbrooke & Monaghan, 2009).

Furthermore, the storage requirement for deferred irrigation practices whereby FDE is stored for long periods at a time, results in significant greenhouse gas emissions, as described in section 2.6.2. Craggs et al. (2008) showed that deferred irrigation systems accumulate anaerobic solids at the bottom of the pond and therefore have high potential for methane production. Hence, while deferred irrigation is efficient at minimising the risks for loss of nutrients to waterways, it has the unintended consequences of increasing methane emissions from the stored effluent.

#### 2.6.4 Subsurface drainage systems

Subsurface drainage systems, most commonly mole-pipe networks, are widely used in soils where natural drainage is slow, or which have a high water table (Monaghan 2014). These drainage systems alter the soil hydrology by creating preferential flow paths which guide the water flow to the mole drain-pipe network (Hoolbrook & Monaghan, 2009).

##### 2.6.4.1 Use of subsurface drains in New Zealand

There is approximately 18,240 km<sup>2</sup> of agricultural land in Southland. Of this, about 13,870 km<sup>2</sup> (76%) is likely to have been amended with subsurface artificial drainage (Pearson, 2015). Hence, subsurface drainage networks cover approximately three quarters of agricultural land in Southland.

Furthermore, areas where wetlands have been converted to agricultural purposes were found to have a very high density of artificial drainage systems while areas with no or low density of artificial drains were located on well drained gravely soils (Pearson, 2015). In the time between 1840 and

2011, there has been a 90% reduction of wetlands in Southland, highlighting the use of significant subsurface drainage modification to the land in order to make it suitable for agriculture (Clarkson et al., 2011).

The principal type of artificial subsurface drainage in Southland is a mole-pipe system, also referred to as tile drainage. These consist of an extensive fissure network made via a mole plough dragged through the soil, which drain into mole channels connected to a pipe/tile that removes the water (Figure 2-16) (Pearson, 2015). The depth to which tiles are installed varies depending on the depth of the water table, the landscape, the soil type, and the need for drainage in the area. Tiles are typically installed anywhere between 60 and 150 cm depth and mole drains usually at about 45-60 cm depth (Houlbrooke & Monaghan, 2009; Strock et al., 2011; Pearson, 2015). The tiles are usually 20-100 m apart and the mole drains can be as close as 2m apart depending on the soil texture - where a finer soil will require narrower drain spacings (Houlbrooke & Monaghan, 2009).

Artificial subsurface drains are also found in other areas of New Zealand, especially where soil characteristics as mentioned in Section 2.5 exist (Nguyen & Sukias, 2002; Tanner et al., 2003).



Figure 2-16. Diagrammatic representation of a mole-pipe drained soil (Houlbrooke & Monaghan, 2009).

#### *2.6.4.2 Mechanism involved in subsurface drainage systems*

The drains work by removing excess pore water when the water table rises above the depth the drains have been installed at. Excess pore water is the soil water content which exists between field capacity and saturation. Through hydrostatic forces, the soil water is driven from larger pores to the drains (Strock et al., 2011). This benefits the soil by allowing the soil to regain topsoil strength sooner after heavy rain, returning the soil to an aerobic state faster thereby improving plant growth and soil health, and reducing the soil's vulnerability to treading damage (Monaghan, 2004). However, artificial subsurface drains cause soil water to bypass other soil pathways and hence decrease the absorption and retention time of nutrients in the soil (Pearson, 2015). This creates a risk for the losses of FDE contaminants to ground water, particularly the nutrients nitrogen and phosphorus, and *Escherichia coli* (*E. coli*) bacteria (Monaghan & Smith, 2004; Monaghan et al., 2005). Figure 2-17 shows how FDE is applied to land where subsurface drains have been installed.



**Figure 2-17.** Illustration of effluent application to land with subsurface drains. The depth of gravel between the soil and the drainage pipe varies between 35-75 cm depending on the soil properties (Che et al., 2022).

## 2.7 ClearTech and EcoPond

Lincoln University, in conjunction with Ravensdown Ltd, has developed a system of effluent treatment known as ClearTech. The purpose of this technology is to recycle water in FDE for its reuse on the farm, meanwhile reducing the amount of effluent going into storage ponds (Cameron & Di, 2019). Poly-ferric sulphate (PFS) is used to treat the effluent and works by flocculating the colloidal material and leaving clarified water for re-use. In addition, a new technology called EcoPond was developed specifically to reduce phosphate losses when FDE is applied to land, and methane emissions from stored effluent. The EcoPond system treats the effluent before it enters the effluent storage pond (Cameron & Di, 2021) (Figure 2-18). This system is less complex and less expensive than ClearTech and can be used where there is no need to recycle water (Cameron & Di, 2021).



**Figure 2-18.** The EcoPond system, (1) tank where the PFS is kept, (2) receives information from the pond to measure the amount of PFS required, (3) measures the flow rate of the effluent going through the mixing coil (4), coil where PFS is mixed into effluent before entering pond (Ravensdown, 2023).

Experiments were conducted to ensure the safety of using PFS to treat effluent. Poly-ferric sulphate is commonly used to treat drinking water (Hendrich et al., 2001) and is classified as a 'food additive' and affirmed as 'generally recognised as safe' for human consumption by the US Food and Drug Administration (FDA, 2017). When applying treated effluent and untreated effluent to plots, Cameron and Di (2019) showed that there was no difference in P, As, Al B, Cd, Co, Cu, Cr, Mn, Ni, Se, Zn, or Pb concentrations in plants between the PFS-treated effluent and untreated effluent plots. This shows that applying PFS-treated effluent to pasture will not impede typical plant mechanisms of nutrient uptake and will not increase risks of leaching of heavy metals. As expected, a higher

concentration of Fe in plant material was found from plots where treated effluent was applied and was attributed to the Fe in PFS. The concentration remained within the range of concentrations of Fe acceptable for NZ pastures (Gray & McLaren, 2005) and would therefore be unlikely to be a concern (Cameron & Di, 2019). Furthermore, Chilsholm et al. (2021) showed that there was no significant increase in Fe in leachate in the treated effluent treatments compared to the untreated (Chisholm et al., 2020). Chen et al. (2019) reported no significant difference in daily N<sub>2</sub>O emissions, pH of the soil, or effects on nitrification rates and bacterial growth and activity between treatments of PFS-treated and untreated effluent. Wang et al. (2019) reported no significant differences in N<sub>2</sub>O, CO<sub>2</sub>, or CH<sub>4</sub> emissions between land applications of the PFS-treated and untreated effluent.

### 2.7.1 Eco Pond benefits

When applied to pasture, it was found that FDE treated with PFS showed significantly reduced phosphate and *E. coli* leaching losses compared to untreated effluent. Che et al. (2022) reported a reduction in mean cumulative DRP, DTP, and TP concentrations in leachate of 93.1%, 86.9%, and 60.5% in PFS-treated FDE compared to untreated FDE. The reduction in phosphate leaching was hypothesised to be due to the water-soluble P in the FDE being transformed into less soluble forms of iron phosphates, which precipitate out of solution and become less mobile in the soil matrix (Che et al., 2022). Reduced *E. coli* losses were attributed to the acidity of the treatment and the encapsulation of the bacteria into the flocculated colloidal particles (Chisholm et al., 2020; Che et al., 2022).

In terms of GHG emissions, Cameron and Di (2021) showed that treating farm dairy effluent with PFS effectively reduced CH<sub>4</sub> emissions from stored effluent by up to 99%, with these effects continuing for a period of up to 2 months after treatment. This was attributed to three main mechanisms.

The first mechanism, sulphate (SO<sub>4</sub><sup>2-</sup>) reducing bacteria (SRB) and ferric-reducing bacteria (FRB) inhibit methanogenesis by outcompeting methanogens for substrate when SO<sub>4</sub><sup>2-</sup> and Fe<sup>3+</sup> ion concentrations, respectively, are high (Liamleam & Annachhatre, 2007; Plugge et al., 2011; Eriksen et al., 2012; Paulo et al., 2015). Competition occurs as both the reduction of SO<sub>4</sub><sup>2-</sup> to sulphide by SRB and of Fe<sup>3+</sup> to Fe<sup>2+</sup> by FRB yield more Gibbs free energy than the process of methanogenesis and are therefore the preferred terminal electron acceptors during anaerobic respiration in the effluent (Paulo et al., 2015; Wu et al., 2022).

The second mechanism, the direct inhibition of methanogenesis, was caused by increased levels of S<sup>2-</sup>, ferric hydroxide (Fe(OH)<sub>3</sub>) and polynuclear ferric compounds from the addition of SO<sub>4</sub><sup>2-</sup> and ferric Fe<sup>3+</sup> ions. Sulphide is toxic to methanogens (Karhadkar et al., 1987), and Fe(OH)<sub>3</sub> and polynuclear ferric compounds can reduce CH<sub>4</sub> emissions via the activity of dissimilatory iron reducing bacteria (DIRB) (Zhou et al., 2014).

The third mechanism, the anaerobic oxidation of methane (AOM) coupled with SO<sub>4</sub><sup>2-</sup> reduction occurs as shown in equation 2-2:



AOM is the dominant process which prevents CH<sub>4</sub> emissions from marine and wetland sediments (Suess et al., 2014; Segarra et al., 2015). In this case, AOM is catalysed by anaerobic methano-trophic archaea (ANME) and SRB (Segarra et al., 2015; Timmers et al., 2016). This process consumes about 90% of the CH<sub>4</sub> produced in ocean floor seeps (Sivan et al., 2014) and over 50% of the CH<sub>4</sub> produced in wetlands (Segarra et al., 2015). In both wetland and marine sediments, it has been shown that the presence of iron can increase the rate of AOM (Sivan et al., 2014; Suess et al., 2014; Segarra et al., 2015; Timmers et al., 2016). Cameron and Di (2021) therefore hypothesised that there was a high

likelihood that the addition of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  resulted in similar reactions of AOM in the PFS-treated effluent as to those in marine and wetland environments. This would thereby reduce  $\text{CH}_4$  emissions into the atmosphere from the treated effluent.

During the study, Cameron and Di (2021) further found that PFS treatment reduced stored FDE  $\text{CO}_2$  emissions by 52% and reduce hydrogen sulphide ( $\text{H}_2\text{S}$ ) emissions compared to untreated FDE. The reduction in  $\text{H}_2\text{S}$  was attributed to the ferrous iron ( $\text{Fe}^{2+}$ ) and the sulphide ( $\text{S}^{2-}$ ) precipitating out as insoluble ferrous sulphide ( $\text{FeS}$ ) as shown in equation 2-3 (Firer et al., 2008):



### 2.8.2 Other methods for mitigating P leaching

The target value for P in surface waters is  $< 0.1 \text{ mg/L}$ , a much lower concentration than what is typically found in leachate from agricultural fields (Weng et al., 2012; Zia et al., 2023). Previous methods to reduce P leaching from agricultural land have included mixing P-fixing materials in the soil (e.g. Codling et al., 2000; McDowell et al., 2008). Materials which have been used are zeolites, aluminium sulphate, steel slags, and fluidized bed bottom-ash and fly ash (McDowell et al., 2008). The risk of using these materials, however, is their potential for being toxic to the environment. Steel slags often contain heavy metals including arsenate, cadmium, and mercury in much greater concentrations than what is allowed for disposal on land. Furthermore, they can pose a risk to animal health. Dewes et al. (1995) showed that cattle which had grazed paddocks that had had basic slag or fly ash ( $\text{pH} > 12$ ) recently applied, had increased pH in their rumen which impeded fermentation and caused the death of the majority of the cattle. They recommended a lag period between application of such materials and cattle grazing.

Aluminium sulphate (alum) was described as one of the cheapest, safest, and most effective P sorbing material and has been widely used around the world to flocculate P from water columns and decrease the solubility of P in manure applied to land (Smith et al., 2001; Paul et al., 2008). It has no impact on pasture growth (Warren et al., 2006) and animals can ingest it at rates of 10 to 40 kg Al/ha/yr without affecting their health or performance (Moore & Edwards, 2007). McDowell & Houlbrooke, (2009) studied the effects of applying alum to a winter forage crop after grazing and found that the losses of P were significantly lower than those with no alum application. However, McDowell (2010) found no significant decrease in P loss from alum applied to grazed pasture on the West Coast of the South Island, most likely due to the aluminium being washed off in surface runoff. This shows that while alum could be a potential mitigation strategy, it may not be effective in all regions depending on factors such as climate and soil properties.

### 2.9 Conclusions

Soils which are most likely to be at risk of P leaching losses include soils with low P-fixing capacities, soils with coarser textures, soils with high pH, stony soils, and soils with high preferential flow or a high hydraulic conductivity. Furthermore, soils which have been amended with artificial subsurface drainage systems either due to being naturally impermeable, slow draining, or having a high water table, are more at risk of P loss via leaching (Sims et al., 1998; Monaghan & Smith, 2004; Houlbrook & Monaghan, 2009; Cameron & Di, 2019). Subsurface drainage systems create preferential pathways to aid the water movement in the soil and drain excess pore water (Strock et al., 2011). This aids the soil's productivity by mitigating the effects of waterlogged conditions, however, it enhances the risk for leaching of nutrients.

Up until the 1980s, the movement of P in soil systems was widely ignored and it was believed that tile drainage only contained trace quantities of soluble P (Logen et al., 1980; King et al., 2015). Since

then, understanding around subsurface P transport has grown and greater attention has been attributed to this issue. The literature on artificial subsurface drainage systems in soils globally shows that there is a concern that these systems increase leaching of nutrients (Miller, 1979; Jensen et al. 1998; Sims et al. 1998; Sharpley et al. 2000; Chapman et al. 2005; Monaghan et al. 2016). Various methods for the mitigation of P loss have been investigated and it is essential that the chosen method is cost-effective, has no harmful effects on the environment, and mitigates more than one problem (McDowell & Nash, 2012).

As most waterways in New Zealand have high nitrogen concentrations, P is generally the limiting factor and even a small amount of P loss can have a substantial effect on the water quality of a waterway (Abell et al., 2010; Scarsbrook & Melland, 2015).

Furthermore, with the NZ national target to reduce methane greenhouse gas emissions by 10% by 2030 and manure management being the second largest source of agricultural greenhouse gas emissions globally, mitigation options for CH<sub>4</sub> emissions from effluent storage ponds are required (Aguirre-Villegas & Larson, 2017).

The EcoPond system has shown to reduce phosphate loss when effluent is applied to land and to reduce methane emissions during storage in effluent ponds (Cameron & Di, 2021). Preliminary studies showed that PFS treatment of effluent was highly effective in reducing P and *E. Coli* leaching losses (Che et al., 2022). However, there is a gap in the knowledge and understanding about the effectiveness of different rates of PFS treatment on reducing the leaching loss of P or their effect on GHG emissions from land after application of treated effluent versus application of untreated effluent.

Furthermore, although Che et al. (2022) hypothesised on the processes at work to reduce P in drainage, there remain gaps in our knowledge about the relationship between the rate of PFS treatment and transformations of P in PFS-treated effluent. Therefore, the objectives of this research programme and thesis are to:

- Improve knowledge and understanding of the effect of the rate of PFS application on the reduction of phosphorus leaching through soil. Che et al. (2022) reported the effects of a single high rate of treatment of FDE but the relationship between PFS treatment rate and the effectiveness in reducing phosphate leaching remains unknown.
- Determine the effect of PFS treatment rate on the emissions of greenhouse gases; nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and methane (CH<sub>4</sub>), after PFS-treated effluent is applied to pasture soil and to compare these emissions to those from the application of untreated effluent.

## Chapter 3 Materials and methods

### 3.1 Field study

#### 3.1.1 Introduction

The field trial was conducted between April 2023 and March 2024 using a model field drainage measurement facility at the Lincoln University Research Centre lysimeter paddock, Canterbury, New Zealand (43° 38' 52''S, 172° 28' 07''E; 10 m a.s.l.). The area has an average annual temperature and rainfall of 11.3°C and 640 mm, respectively (ClimateData, n.d.). Each drainage model unit received two applications of effluent treatment, one in mid-autumn and one in early spring. A detailed description of the trial background, set-up, treatments, and collection of samples is given below.

The objective of the field study was: (i) to observe the effect of the poly-ferric sulphate (PFS) treatment rate on the reduction of phosphorus and *Escherichia coli* (*E. coli*) leaching through the soil; (ii) and to determine the effect of the rate application of PFS on greenhouse gas emissions from the soil.

#### 3.1.2 Trial background

This drainage model trial builds on a previous study where farm dairy effluent was treated with poly-ferric sulphate and applied onto land to determine the effect on phosphate leaching (Che et al., 2022). The trial by Che et al. (2022) used a single high rate of poly-ferric sulphate treatment, whilst in this new trial, two applications of treatments were carried out, one in mid-autumn and the other in early spring. In this new trial, there were 5 treatments which consisted of: (i) untreated farm dairy effluent (FDE), (ii) FDE with a full rate of PFS, as used in the EcoPond system (Cameron & Di, 2021) (250 mg Fe/L, termed 'PFS 250'), (iii) FDE with two thirds of the full rate (167 mg Fe/L, termed 'PFS 167'), (iv) FDE with one third of the full rate (83 mg Fe/L, termed PFS 83'), and (v) water (control, C).

#### 3.1.3 Soil properties and collection

A Templeton silt loam was collected from the Lincoln University Research Dairy Farm (LURDF), north of the university and 20 km south of Christchurch. The soil is classified as an Immature Pallic soil, formed from weakly weathered greywacke alluvium and described as moderately well drained (Soil Survey Staff, 1998; Hewitt, 2010). Soil chemical properties were analysed at Hill Laboratories, Christchurch, and shown in Table 3-1.

In February 2023, 25 undisturbed soil blocks were collected, which had previously been predominantly under undisturbed ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) pasture. Six months before the soil blocks were collected, the site was fenced off to prevent disturbance by cattle treading and grazing, and thus reduce the risk of compaction variation in the sampling area.

**Table 3-1.** Soil chemical analysis results.

Soil analysis	Value	Soil analysis	Value
pH	6.0	Exch-Na	0.27 cmol <sub>c</sub> /kg
Olsen-p	46 mg/kg	CEC	14.0 cmol <sub>c</sub> /kg
Exch-ca	8.1 cmol <sub>c</sub> /kg	Total N	4.0 g/kg
Exch-mg	1.29 cmol <sub>c</sub> /kg	Total C	36.5 g/kg
Exch-k	1.25 cmol <sub>c</sub> /kg	Organic-S	<4 mg/kg
<b>0 – 7.5 cm soil</b>			

### 3.1.4 Drainage unit model set-up

The cylindrical drainage model units were replicated from the study conducted by Che et al. (2022), using 50 cm by 70 cm metal cylinders. These model units were filled with 50 cm of gravel and a top layer of 20 cm layer of topsoil, as shown in Figure 3-1, to replicate artificial drainage systems on farms which have a gravel 'backfill' above drainage pipes (McLaren & Cameron, 1996).



**Figure 3-1.** Design of cylindrical drainage model used in study (Che et al., 2022).

The topsoil layers were collected by placing metal cylinders (50 cm diameter x 20 cm deep) on top of the pasture soil and pushed in using a heavy 1.5 m long metal bar to hammer the cylinders into the ground (Figure 3-2). Once each cylinder was fully inserted into the soil, the metal cylinder with the soil layer were removed using a metal bar to lever the bottom of the casing away from the subsoil. Any excess soil was scraped flush with the base of the metal cylinder using a spade. Once finished, each casing was placed on top of each drainage model units which had already been filled up with gravel to 50 cm height. A circular piece of wood matching the internal diameter of the cylinders was placed on top of the pasture in the metal cylinders and pushed in order to release the soil cores into the drainage model units (Cameron et al., 1992). The final drainage model unit is shown in Figure 3-3.



**Figure 3-2.** Metal cylinder used to obtain topsoil layer.



**Figure 3-3.** Final drainage model unit with gravel and topsoil layers before installing into the trench facility.

Each unit was placed in a pre-dug trench in the lysimeter research paddock, as shown in Figure 3-4. A drainage system was connected to each drainage model unit at the base, consisting of a plastic tube that connects to the nipple of the drainage model base and drains into a 10L plastic container below (Figure 3-5). Each container is housed in a metal box which prevents rainwater from seeping in. Aluminium water trough rings were then installed on top of each drainage model unit and sealed with silicone in order to sample gas emissions from each drainage unit.



**Figure 3-4.** Trench with the drainage model units installed.



**Figure 3-5.** Clean plastic tube and container attached to the drainage nipple at the base of each drainage unit and used to collect the drainage water samples.

Each drainage model received irrigation via a rain/irrigation simulation system (RISS). This system consists of a spray nozzle (Tee Jet FL-5VC) secured on a metal tripod placed on top of each drainage model unit (Figure 3-6). The system is controlled by a CR 1000 Campbell Scientific datalogger. This system operates using data collected by NIWA Broadfield weather station, Canterbury, New Zealand. These predefined daily climate parameters are used to simulate the daily average rainfall and evapotranspiration according to the 75<sup>th</sup> percentile of local rainfall records averaged in the period between 1975 and 1998. In the winter season (April - September), rain was supplemented randomly to simulate the 75<sup>th</sup> percentile. In the summer season (October – March), irrigation (between 10 mm and 15 mm every three days) was applied at regular intervals to balance the evapotranspiration and to match the irrigation practices of local dairy farms. This ensured that accurate and sufficient rainfall/irrigation was applied to obtain a phosphate breakthrough curve. The system was calibrated to apply water at a rate of 1 L per minute in 0.5 mm bursts.

Before treatments were applied, weeds were removed from the pasture of each drainage model unit using the herbicide Pasture-Kleen™. This killed most of the weeds which primarily consisted of dandelions (*Taraxacum officinale*) and plantain (*Plantago lanceolata*).

Prior to the treatments being applied, the pasture was cut to simulate normal grazing height (c. 25 cm).



**Figure 3-6.** Rain/irrigation simulation system placed on top of lysimeters.

### 3.1.5 Effluent collection and treatment

Fresh farm dairy effluent (FDE) was collected from the Lincoln University Demonstration Dairy Farm (LUDF) after the morning milking on the 18<sup>th</sup> of April 2023, as shown in Figure 3-7. This effluent comes from Friesian-Jersey dairy cows ('Kiwi-cross') which graze the perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) mixed pasture. After collection, the effluent was mixed and transferred into four containers, one for each treatment. Each container held 20 L of effluent. The required amounts of poly-ferric sulphate (PFS) were then added to each container, according to the required treatment rate shown in Table 3-2. The effluent was stirred for 2 minutes, following the protocols described in Cameron and Di (2019). Subsamples from each treatment container were collected and sent to Hill Laboratories for analysis, as described by Cameron and Di (2019). Results of these analyses are shown in Tables 3-3 and 3-4.



**Figure 3-7.** Farm dairy effluent was collected using a 15 L bucket from Lincoln University Demonstration Dairy Farm (LUDF).

**Table 3-2.** Amount of PFS added to each effluent treatment.

Treatment (mg Fe/L)	Amount added PFS/L (mL)	Amount added PFS/20L (mL)
250	1.56	31
167	1.04	20.8
83	0.52	10.4
0	0	0

**Table 3-3.** Chemical and Physical characteristics of the different treatments applied to the drainage model units at the first effluent application.

Treatment	E. coli (CFU/100mL)	TS (g/m <sup>3</sup> )	TSS (g/m <sup>3</sup> )	TVS (g/m <sup>3</sup> )	TN (g/m <sup>3</sup> )	NH4-N (g/m <sup>3</sup> )	TP (g/m <sup>3</sup> )	DRP (g/m <sup>3</sup> )	TC (g/m <sup>3</sup> )	pH	Eh (mV)
FDE	6.43 x 10 <sup>5</sup> a	2200.00 a	1160.00 a	1453.33 ab	114.00 a	43.67 ab	42.00 a	25.33 a	996.67 a	7.10 a	-252.67 a
250 mg Fe/L	0.00 b	3133.33 b	1963.33 b	1640.00 b	114.67 a	55.00 b	43.00 a	0.50 b	816.67 b	3.11 b	437.67 b
167 mg Fe/L	576.67 c	2900.00 ab	1863.33 ab	1590.00 b	118.67 a	52.33 b	49.67 a	0.00 c	933.33 ab	4.08 ab	311.00 ab
83 mg Fe/L	1.02 x 10 <sup>6</sup> d	2300.00 ab	1670.00 ab	1326.67 a	114.67 a	34.33 a	43.00 a	0.63 d	866.67 ab	6.11 ab	-46.33 ab

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus; TC, total carbon.

**Table 3-4.** Chemical and physical characteristics of the different treatments applied to the drainage model units at the second effluent application.

Treatment	E. coli (CFU/100mL)	TS (g/m <sup>3</sup> )	TSS (g/m <sup>3</sup> )	TVS (g/m <sup>3</sup> )	TN (g/m <sup>3</sup> )	NH4-N (g/m <sup>3</sup> )	TP (g/m <sup>3</sup> )	DRP (g/m <sup>3</sup> )	TC (g/m <sup>3</sup> )	pH	Eh (mV)
FDE	1.87 x 10 <sup>5</sup> a	2633.33 a	1613.33 a	1756.67 a	104.00 a	37.00 b	20.30 a	9.83 a	713.33 a	6.48 a	-278.33 a
250 mg Fe/L	0.67 b	3466.67 c	2266.67 b	1833.33 a	97.67 a	34.67 ab	18.30 a	0.10 b	523.00 a	3.00 b	454.00 b
167 mg Fe/L	37.33 c	3366.67 c	2366.67 b	1843.33 a	99.00 a	32.33 a	20.77 a	0.00 b	580.00 a	3.80 ab	319.00 ab
83 mg Fe/L	2.04 x 10 <sup>4</sup> d	3066.67 b	2133.33 b	1826.67 a	109.00 a	32.67 a	19.03 a	0.00 b	773.33 a	5.55 ab	-73.67 ab

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus; TC, total carbon.

### 3.1.6 Treatments

The experimental protocol consisted of five treatments, with five replicates, resulting in 25 separate cylindrical drainage model units. The five treatments were: (i) untreated farm dairy effluent (FDE), (ii) FDE with a full rate of PFS, as used in the EcoPond system (Cameron & Di, 2021) (250 mg Fe/L, termed 'PFS 250'), (iii) FDE with two thirds of the full rate (167 mg Fe/L, termed 'PFS 167'), (iv) FDE with one third of the full rate (83 mg Fe/L, termed 'PFS 83'), and (v) water (control, C). The treatments were allocated to the cylindrical drainage model units using a randomised block statistical design.

Each drainage model unit received a 2 L application of each treatment on the 19<sup>th</sup> of April 2023 and the 28<sup>th</sup> of August 2023. This applied the equivalent of a 10 mm per application which would be a typical effluent application rate on a farm where subsurface drains have been installed.

### 3.1.7 Sample collection

#### 3.1.7.1 Drainage water collection, sampling, and analysis

Throughout the autumn and winter months, drainage water was collected at least once a week, and more often when irrigation and/or rainfall caused the drainage levels to reach 200 mL or greater per model unit. In the spring and summer, drainage decreased, and drainage collections occurred less frequently. Following the first treatment application, there were 22 drainage collections, and 12 following the second treatment application. During each collection event, the volume of drainage water collected was measured using a plastic measuring jug and recorded. Subsamples were then taken in 100 mL bottles for the immediate analysis of total phosphorus (TP), dissolved reactive phosphorus (DRP), and total dissolved phosphorus (TDP) concentrations.

For the first two collections after each treatment application sterile plastic bags were used to collect the drainage water. This was done to reduce the risk of cross contamination between drainage water collections and to enable determination of *E. coli* content as well as TP, DRP, and TDP. The plastic bags were used once, then exchanged with new bags for the next drainage water collection (Figure 3-9). After the initial two collections, *E. coli* concentrations decreased to near zero, therefore, the bags were replaced with clean plastic containers.

The DRP, TDP, and TP concentrations were measured at Lincoln University, Lincoln. The DRP concentration was determined by filtering the samples through a 0.45 µm filter and 3 mL of the filtrate was analysed following the Murphy and Riley (1962) colourimetric method. The samples for TDP analysis were also filtered and 8 mL of the filtrate was digested with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> (EPA, 1978; Ohno & Zibilske, 1991), in an autoclave, followed by the Murphy and Riley colourimetric method to determine the concentration. The TP concentrations were determined using unfiltered samples, which were digested and analysed in the same way as TDP.

The concentration of *E. coli* in 100 mL aliquots was measured using a Colilert test (incubated at 35°C for 24 h), or 1-20 Colilert 18 test (incubated at 35°C for 18 h) to give an MPN count, as described in Cameron and Di (2019). Total DRP, TDP, and TP losses in drainage from each treatment were determined by multiplying the concentration at each sampling event by the volume of leachate collected. These values were then converted to losses on a per hectare basis by dividing the treatment average loss by the area of the lysimeter (0.196 m<sup>2</sup>) then dividing by 10,000 to obtain the loss in kg P/ha.

To determine the effect of the PFS treatment rates on P drainage concentrations compared to the untreated FDE and relative to background leaching levels from the control, the P leaching loss factor percentage was calculated for each treatment according to equation 3-1.

$$\text{P leaching loss factor (\%)} = (\text{Treatment cumulative loss} - \text{Control cumulative loss}) / (\text{TP in effluent first application} + \text{TP in effluent second application}) \times 100. \text{ Equation 3-1.}$$

The P leaching loss factor percentages of each PFS treatments were then compared that of the untreated FDE treatment, as shown in Equation 3-2.

$$\text{Reduction in P leaching loss factor (\%)} = (\text{FDE P leaching loss factor} - \text{PFS treatment P leaching loss factor}) / \text{FDE P leaching loss factor} \times 100. \text{ Equation 3-2.}$$



**Figure 3-9.** Sterile bags were used to collect the first two drainage samples.

#### 3.1.7.2 Gas sampling and analysis

Gas sampling was conducted using a closed chamber method, as described by Di et al. (2007). This procedure was used to determine the concentration and flux of the greenhouse gases methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), and carbon dioxide ( $\text{CO}_2$ ). The gas chambers consisted of a metal cylinder insulated with 2.5 cm thick polystyrene foam which prevent the chambers from experiencing significant temperature changes when in use. During the gas sampling process, the chambers are placed on top of the aluminium water trough rings on the drainage model units. The water troughs were filled with water to stop any gas exchange between the atmosphere and the chamber. Gas samples were taken from each chamber three times, at 20 minutes intervals, using a syringe needle through a rubber septum located on top of the gas chamber (Figure 3-10). The 20 mL gas sample was pulled from the chamber using the syringe. The gas sample was then transferred to a 5 mL vial. The temperature at the soil surface was recorded three times, every 20 minutes, throughout the sampling process.

Gas sampling was conducted on the day prior to and the day after the first treatment application. For the second treatment application, gas sampling was conducted on the day following the application. After both treatment applications, sampling occurred twice weekly for the first month, then once weekly for the remainder of the time. The last sample was taken on the 4<sup>th</sup> of March 2024.

To conduct GHG concentration analyses, a gas chromatograph (GC – Model 8610, SRI instruments, CA, USA) with an automated Gilson GX-271 auto sampler (Gilson Inc., MI, USA) was used coupled to an electron capture detector (ECD) and flame ionised detector (FID). The ECD was used to measure  $\text{N}_2\text{O}$  concentrations while  $\text{CH}_4$  and  $\text{CO}_2$  were measured using the FID. Three Haysep D packed columns are used as the precolumn and two Haysep D as the analytical column within the GC. The GC uses oxygen free nitrogen in argon (Ar) as the carrier gas and 10% methane in Ar as the ECD make-up gas, while hydrogen and air are used for the FID flame. Detector temperature settings were at 31°C for the ECD and 37°C for the FID.

Calculations for hourly GHG emissions were performed using the ideal gas law and based on the increase in GHG concentration within the chamber from 0 to 40 minutes. This calculation was corrected for temperature and the ratio of surface area to chamber volume. Daily emissions were then calculated using the hourly flux and converted from  $\text{mg}/\text{m}^2$  to  $\text{g}/\text{ha}$  as shown in Hutchinson and Mosier (1981). Cumulative emissions were calculated by integrating the daily GHG fluxes calculated

using linear interpolation between measurement points. Calculations were then carried out to convert the results into CO<sub>2</sub> equivalents.



**Figure 3-10.** Gas chamber atop drainage model unit with syringe and 5 mL vial.

#### 3.1.7.3 Herbage sampling and analysis

The pasture on the drainage model units was harvested approximately every three weeks or once it had reached 200 mm in height, using mechanical shears. The pasture was cut to about 30 mm in height, to simulate grazing conditions on a farm. The harvested herbage was then dried at 70°C for 72 hours to obtain the dry matter yield. Dried herbage was ground and analysed for total P concentration using an inductive coupling plasma emission spectrometer (Agilent 5110, ICP-OES Analyser, American) and total N concentration using an Elementar Vario-Max CN Elemental Analyser (Elementar GmbH, Hanau, Germany). The dry matter yield values were then calculated on a per hectare basis.

#### 3.1.8 Statistical analysis

The leaching losses of TP, DRP, and TDP, as well as the GHG emissions, and the P and N content of the herbage from each drainage model unit were statistically analysed using a one-way analysis of variance (ANOVA) in GenStat (22nd edition, Lawes Agricultural Trust) to test for treatment effect significance. The significant differences between treatments were determined using Tukey's test ( $P < 0.05$ ). Where necessary, the data was transformed to log<sub>10</sub> in order to meet the assumptions of ANOVA. A Kruskal Wallis test followed by a Dunn's test was used to determine the significant difference between the physicochemical properties of the four effluent treatments (Tables 3-3 & 3-4). This was conducted in RStudio (RStudio Team, 2020) using the "FSA" package (Ogle et al., 2023).

To allow for fair comparisons, equal drainage losses were presented for the total losses of P in drainage (equal drainage 420 mm).

# Chapter 4 Effect of treating effluent with different rates of PFS of phosphate leaching

## 4.1 Introduction

The loss of phosphate (P) to surface and ground waters has significant environmental and ecological consequences. In waterways that are phosphorus-limited, a small increase in phosphate levels can significantly disrupt the ecosystem's balance, potentially leading to eutrophication (Smith and Schindler, 2009; Abell et al., 2010). This is a significant environmental issue worldwide, resulting in de-oxygenation of the waterway, increased toxicity, loss of species diversity, and reduced aesthetics (Dorgham, 2014; Rodgers, 2021). One of the principal P contributors to waterways is the agricultural sector, especially via the additions of P-fertilisers and manure to land (Drewry et al., 2006).

Iron based coagulants are commonly used in the treatment of wastewater and surface waters for the removal of contaminants and particles (Lal & Garg, 2019; Mohamad et al., 2023). Poly-ferric sulphate (PFS) is a polymerised form of ferric sulphate, and a coagulating agent widely used in wastewater treatment plants (Zouboulis et al., 2008; Wang et al., 2010; Tzoupanos & Zouboulis, 2011). When farm dairy effluent (FDE) is treated with PFS, ferric-phosphate precipitates form, decreasing the phosphorus solubility and mobility in the effluent (Cameron & Di, 2019). Hence, when PFS-treated FDE is applied to land, more phosphate is retained in the soil compared to untreated FDE.

Previous work has already been carried out to investigate the effect of treating FDE with PFS on phosphate concentrations in drainage (Wang et al., 2019; Chisholm et al., 2020; Che et al., 2022). Che et al. (2022) used drainage model units that replicated soil with an artificial subsurface drainage system to demonstrate the P-leaching rate, and how effective treating effluent with PFS is at reducing P leaching under those conditions. However, Che et al. (2022) only used the maximum PFS rate to achieve clarification (250 mg Fe/L as described in Cameron and Di, 2019) and did not investigate the effectiveness of lower rates of PFS.

Cameron and Di (2019) clearly showed that effluent treated with 250 mg Fe/L was effective at reducing P loss in drainage. However, it is unknown whether a lower dose would be as efficient. This information is important because it could lower the cost of this treatment technology for farmers.

The aims of this trial were to:

- (1) Quantify the phosphate concentrations in drainage water and the cumulative losses of P from lysimeters that received farm dairy effluent treated with different rates of poly-ferric sulphate.
- (2) Identify the rate of PFS that would be most cost-effective for farmers applying effluent to land and beneficial to waterways by reducing the risk of P leaching from effluent areas.
- (3) Quantify N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> emissions from the soil lysimeters that received farm dairy effluent treated with different rates of poly-ferric sulphate.

## 4.2 Materials and methods

Materials and methods have been described in more detail in Chapter 3 and only a summary is given here to introduce this chapter.

### 4.2.1 Lysimeter study

#### 4.2.1.1 Design of lysimeter study

A lysimeter study was established, using 25 undisturbed soil blocks of Templeton silt loam collected in February 2023 from the Lincoln University Research Dairy Farm (LURDF), north of the university campus and 20 km south of Christchurch. This soil had previously been predominantly under undisturbed ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) pasture. Six months

before the soil blocks were collected, the site was fenced off to prevent disturbance by cattle treading and grazing, hence reducing the risk of compaction variation in the sampling area.

Cylindrical drainage model units (50 cm by 70 cm) were used, similar to those used in the study conducted by Che et al. (2022). These were filled with gravel and a top layer of 20 cm of topsoil, as shown in Figure 4-1, to replicate artificial drainage systems on farms which have a gravel ‘backfill’ above drainage pipes (McLaren & Cameron, 1996).



**Figure 4-1.** Design of cylindrical drainage model used in study (Che et al., 2022).

The units were placed in a pre-dug trench in the lysimeter research paddock at the University and a drainage system was connected to each drainage model unit at the base. Each drainage model received irrigation via a rain/irrigation simulation system.

#### 4.2.1.2 Treatment application

Fresh farm dairy effluent (FDE) was collected from the Lincoln University Demonstration Dairy Farm (LUDF) after the morning milking on the 18<sup>th</sup> of April 2023. This effluent comes from Friesian-Jersey dairy cows (‘Kiwi-cross’) which graze the perennial ryegrass (*Lolium perenne L.*) and white clover (*Trifolium repens L.*) mixed pasture. The FDE was separated into four containers and treated with three PFS rates (250, 167, and 83 mg Fe/L FDE) plus another treatment ‘FDE’ with no PFS added.

Then the effluent plus PFS mixtures were stirred for 2 minutes, following protocols described in Cameron and Di (2019).

Subsamples of each treatment container were collected and sent to Hill Laboratories for analysis, as described by Cameron and Di (2019). Results of these analyses are shown in Tables 4-1 and 4-2.

**Table 4-1.** Chemical and Physical characteristics of the different treatments applied to the drainage model units at the first effluent application.

Treatment	E. coli (CFU/100mL)	TS (g/m <sup>3</sup> )	TSS (g/m <sup>3</sup> )	TVS (g/m <sup>3</sup> )	TN (g/m <sup>3</sup> )	NH4-N (g/m <sup>3</sup> )	TP (g/m <sup>3</sup> )	DRP (g/m <sup>3</sup> )	TC (g/m <sup>3</sup> )	pH	Eh (mV)
FDE	6.43 x 10 <sup>5</sup> a	2200.00 a	1160.00 a	1453.33 ab	114.00 a	43.67 ab	42.00 a	25.33 a	996.67 a	7.10 a	-252.67 a
250 mg Fe/L	0.00 b	3133.33 b	1963.33 b	1640.00 b	114.67 a	55.00 b	43.00 a	0.50 b	816.67 b	3.11 b	437.67 b
167 mg Fe/L	576.67 c	2900.00 ab	1863.33 ab	1590.00 b	118.67 a	52.33 b	49.67 a	0.00 c	933.33 ab	4.08 ab	311.00 ab

<b>83 mg Fe/L</b>	1.02 x 10 <sup>6</sup> d	2300.00 ab	1670.00 ab	1326.67 a	114.67 a	34.33 a	43.00 a	0.63 d	866.67 ab	6.11 ab	-46.33 ab
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Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus; TC, total carbon.

**Table 4-2.** Chemical and physical characteristics of the different treatments applied to the drainage model units at the second effluent application.

Treatment	E. coli (CFU/100mL)	TS (g/m <sup>3</sup> )	TSS (g/m <sup>3</sup> )	TVS (g/m <sup>3</sup> )	TN (g/m <sup>3</sup> )	NH4-N (g/m <sup>3</sup> )	TP (g/m <sup>3</sup> )	DRP (g/m <sup>3</sup> )	TC (g/m <sup>3</sup> )	pH	Eh (mV)
<b>FDE</b>	1.87 x 10 <sup>5</sup> a	2633.33 a	1613.33 a	1756.67 a	104.00 a	37.00 b	20.30 a	9.83 a	713.33 a	6.48 a	-278.33 a
<b>250 mg Fe/L</b>	0.67 b	3466.67 c	2266.67 b	1833.33 a	97.67 a	34.67 ab	18.30 a	0.10 b	523.00 a	3.00 b	454.00 b
<b>167 mg Fe/L</b>	37.33 c	3366.67 c	2366.67 b	1843.33 a	99.00 a	32.33 a	20.77 a	0.00 b	580.00 a	3.80 ab	319.00 ab
<b>83 mg Fe/L</b>	2.04 x 10 <sup>4</sup> d	3066.67 b	2133.33 b	1826.67 a	109.00 a	32.67 a	19.03 a	0.00 b	773.33 a	5.55 ab	-73.67 ab

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus; TC, total carbon.

The five treatments were: (i) untreated farm dairy effluent (FDE), (ii) FDE with a full rate of PFS, as used in the EcoPond system (Cameron & Di, 2021) (25 0mg Fe/L, termed 'PFS 250'), (iii) FDE with two thirds of the full rate (167 mg Fe/L, termed 'PFS 167'), (iv) FDE with one third of the full rate (83 mg Fe/L, termed 'PFS 83'), and (v) water (control, C). The treatments were allocated to the cylindrical drainage model units using a randomised block statistical design.

On the 19<sup>th</sup> of April 2023 and the 28<sup>th</sup> of August 2023 each drainage model unit received a 2 L application of treatment. This applied the equivalent of a 10 mm per application which would be a typical effluent application rate on a farm where subsurface drains have been installed.

#### 4.2.1.3 Drainage water collection, sampling, and analysis

Drainage water was collected at least once a week throughout the autumn and winter months, and more often when irrigation and/or rainfall caused the amount of drainage to reach 200 mL or greater per model unit. During the spring and summer, drainage volumes decreased due to evapotranspiration and collections therefore occurred less frequently. During each collection event, the volume of drainage water collected was recorded. Subsamples were then taken in 100 mL bottles for the immediate analysis of total phosphorus (TP), dissolved reactive phosphorus (DRP), and total dissolved phosphorus (TDP) concentrations.

The DRP concentration was determined by filtering the samples through a 0.45 um filter and 3 mL of the filtrate was analysed following the Murphy and Riley (1962) colourimetric method. The samples for TDP analysis were also filtered and 8 mL of the filtrate was digested with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>SO<sub>4</sub> (EPA, 1978; Ohno & Zibilske, 1991), in an autoclave, followed by the Murphy and Riley colourimetric method to determine the concentration. The TP concentrations were determined using unfiltered samples, which were digested and analysed in the same way as TDP.

The concentration of *E. coli* in 100ml aliquots was measured using a Colilert test (incubated at 35°C for 24 h), or 1-20 Colilert 18 test (incubated at 35°C for 18 h) to give an MPN count, as described in Cameron and Di (2019). Total DRP, TDP, and TP losses in drainage from each treatment were determined by multiplying the concentration at each sampling event by the volume of leachate collected. These values were then converted to losses on a per hectare basis by dividing the treatment average loss by the area of the lysimeter (0.196 m<sup>2</sup>) then dividing by 10,000 to obtain the concentration loss in kg P/ha.

To determine the effect of the PFS treatment rates on P drainage concentrations compared to the untreated FDE and relative to background leaching levels from the control, the P leaching loss factor percentage was calculated for each treatment according to equation 4-1.

$$\text{P leaching loss factor (\%)} = (\text{Treatment cumulative loss} - \text{Control cumulative loss}) / (\text{TP in effluent first application} + \text{TP in effluent second application}) \times 100. \text{ Equation 4-1.}$$

The P leaching loss factor percentages of each PFS treatments were then compared that of the untreated FDE treatment, as shown in Equation 4-2.

$$\text{Reduction in P leaching loss factor (\%)} = (\text{FDE P leaching loss factor} - \text{PFS treatment P leaching loss factor}) / \text{FDE P leaching loss factor} \times 100. \text{ Equation 4-2.}$$

#### 4.2.1.4 Gas sampling and analysis

Gas sampling was carried out using a closed chamber method, as described by Di et al. (2007). This procedure was used to determine the concentration and flux of the greenhouse gases methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>).

Gas samples were taken twice weekly for a month following the treatment applications, then once a week for the remainder of the time. To conduct GHG concentration analyses, a gas chromatograph (GC – Model 8610, SRI instruments, CA, USA) with an automated Gilson GX-271 auto sampler (Gilson Inc., MI, USA) was used coupled to an electron capture detector (ECD) and flame ionised detector (FID). The ECD was used to measure N<sub>2</sub>O concentrations while CH<sub>4</sub> and CO<sub>2</sub> were measured using the FID.

Calculations for hourly GHG emissions were performed using the ideal gas law and based on the increase in GHG concentration rate within the chamber from 0 to 40 minutes. This calculation was corrected for temperature and the ratio of surface area to chamber volume. Daily emissions were then calculated using the hourly flux and converted from mg/m<sup>2</sup> to g/ha as shown in Hutchinson & Mosier (1981). Cumulative emissions were calculated by integrating the daily GHG fluxes calculated using linear interpolation between measurement points. Calculations were then carried out to convert results into CO<sub>2</sub> equivalents.

#### 4.2.1.5 Herbage sampling and analysis

The pasture from the drainage model units was harvested approximately every three weeks or once it had reached 200 mm in height, using mechanical shears. The pasture was cut to about 30 mm in height, to simulate grazing conditions on a farm. The harvested herbage was then dried at 70°C for 72 hours to obtain the dry matter yield. Dried herbage was ground and analysed for total P concentration using an inductive coupling plasma emission spectrometer (Agilent 5110, ICP-OES Analyser, American) and total N concentration using an Elementar Vario-Max CN Elemental Analyser (Elementar GmbH, Hanau, Germany). The dry matter yield values were then calculated on a per hectare basis.

#### 4.2.2 Statistical analysis

Results for the leaching losses of TP, DRP, and TDP, as well as the GHG emissions, and the P and N content of the herbage from each drainage model unit were statistically analysed using a one-way analysis of variance (ANOVA) in GenStat (22nd edition, Lawes Agricultural Trust) to test for treatment effect significance. The significant differences between treatments were determined using Tukey's test. Where necessary, the data was transformed to logbase10 in order to meet the assumptions of ANOVA. A Kruskal Wallis test followed by a Dunn's test was used to determine the significant difference between the physicochemical properties of the four effluent treatments (Tables 4-1 & 4-2). This was conducted in RStudio (RStudio Team, 2020) using the "FSA" package (Ogle et al., 2023).

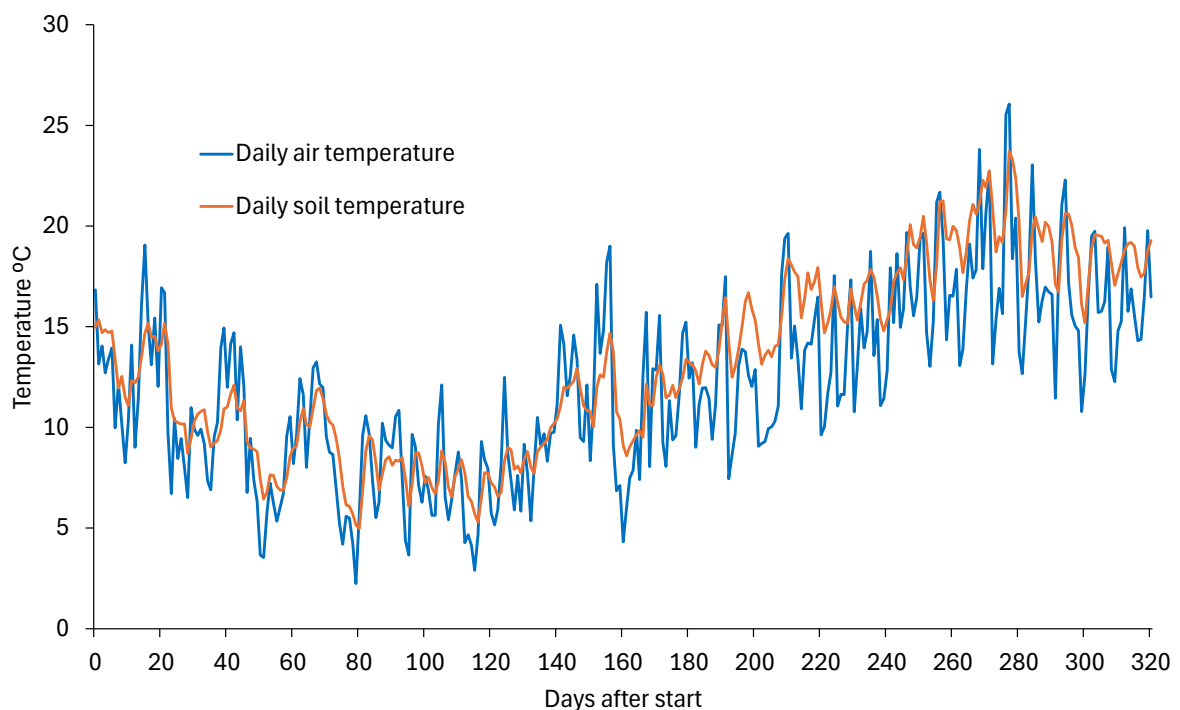
#### 4.3 Results

##### 4.3.1 Climate conditions and drainage data

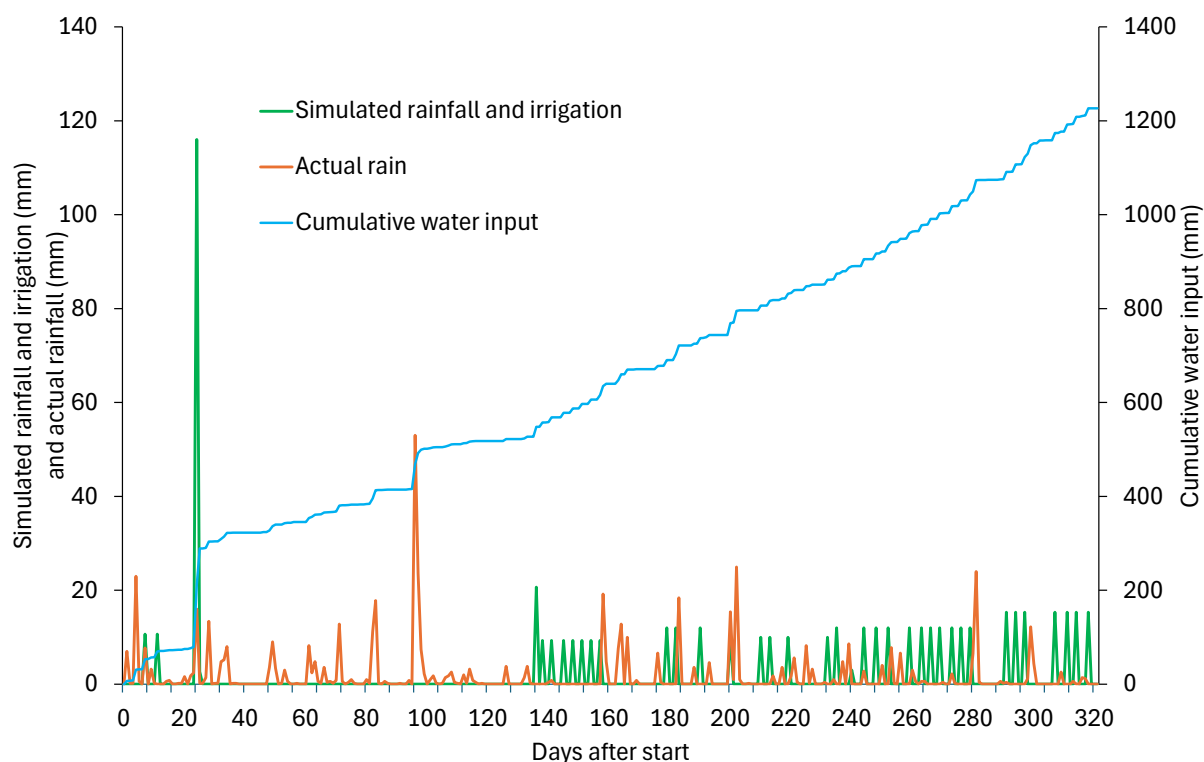
Over the experiment period, the average daily air and soil temperatures were 12.1°C and 13.2°C, respectively (18<sup>th</sup> of April 2023 – 4<sup>th</sup> of March 2024) (Figure 4-2). The cumulative water input was 1226.8 mm, of which 554.3 mm was from simulated rainfall and irrigation and 672.5 mm from actual rainfall (Figure 4-3). Simulated rainfall/irrigation was applied frequently from September to March. The cumulative drainage of the different treatments ranged from 554.1 mm to 643.7 mm, accounting for 45-52% of the total water inputs.

There was no significant difference in the average cumulative drainage volumes between all five treatments.

On the 12<sup>th</sup> of May 2023, the RISS system encountered an error and applied 116 mm of irrigation onto each drainage unit. This caused a great amount of drainage and was kept in as a simulation of what could happen if an extreme rainfall event occurred or if irrigators malfunctioned.



**Figure 4-2.** Average daily air temperature and daily soil temperature (10 cm depth) during the experimental period.



**Figure 4-3.** Daily actual rainfall and simulated rainfall and irrigation, and cumulative water input for the experimental period.

#### 4.3.2 Pre-application effluent composition

Treating FDE with 250 mg Fe/L, 167 mg Fe/L, and 83 mg Fe/L PFS before the first application resulted in a 98%, 100%, and 97.5% reduction in DRP concentration in the treated effluent, respectively (Table 4-1). Treating FDE with the same rate of PFS before the second application resulted in a 99%, 100% and 100% reduction in the treated effluent, respectively (Table 4-2). There was no significant difference between the treatments for total P, or total N in the effluent.

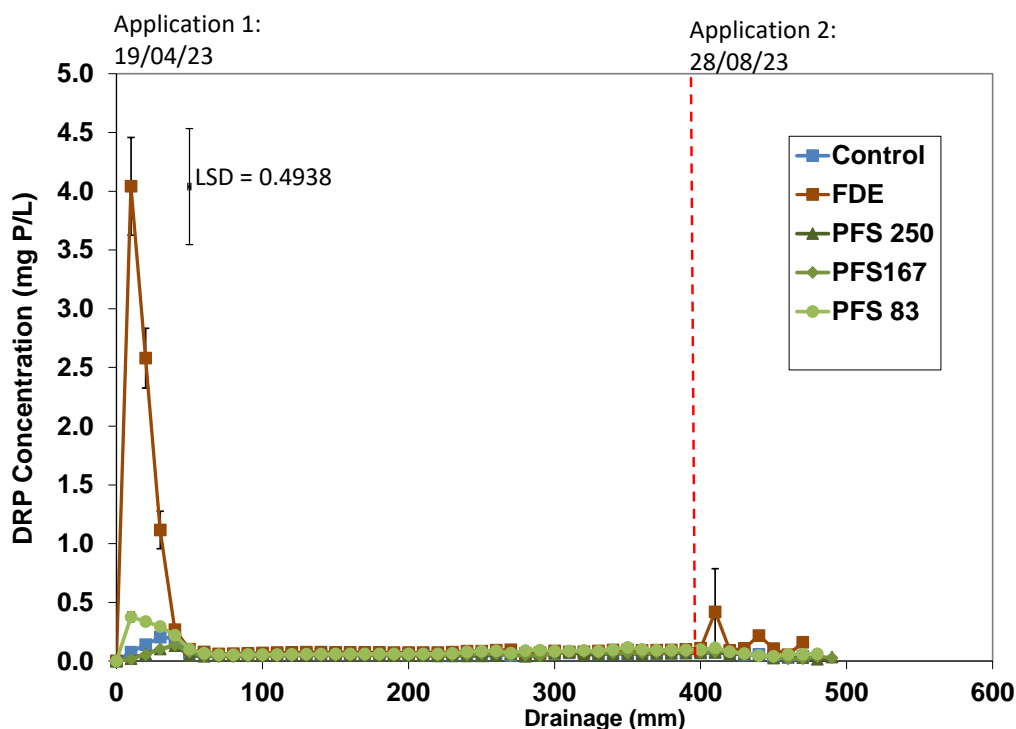
Treating the first batch of effluent at the PFS 250 and PFS 167 rates significantly reduced effluent *E. Coli* concentrations by 100% and 99%, respectively, compared to untreated FDE ( $P < 0.05$ ) (Table 4-1). Treating the second batch of effluent at the PFS 250, PFS 167, and PFS 83 rates resulted in a 100%, 99%, and 89% significant reduction, compared to the untreated FDE, respectively (Tables 4-2).

#### 4.3.3 Peak phosphate concentrations in drainage water

After the first treatment application to the lysimeters, the PFS 250 and PFS 167 treatment rates resulted in significant reductions in the DRP peak drainage concentrations of 96.7% (0.13 mg P/L) and 96.5% (0.14 mg P/L), relative to the untreated FDE peak concentration (4.04 mg P/L), respectively. These PFS 250 and PFS 167 treatment rate concentrations were not significantly different from each other and were significantly lower than that of the control (water only) ( $P < 0.05$ ). The PFS 83 treatment resulted in a significant reduction in DRP of 90.5% (0.38 mg P/L) in peak drainage concentration compared to the untreated FDE, but the peak concentration was significantly higher than the concentration of the PFS 250, PFS 167, and the control treatments (Figure 4-4).

The DRP concentrations in each treatment declined rapidly and there was no significant difference between the control and the four treatments after 50mm of drainage (first application).

Following the second treatment application there was no significant difference between the peak DRP drainage concentrations of all five treatments (Table 4-3).



**Figure 4-4.** Average concentration of dissolved reactive phosphorus (DRP) drainage water collected from the model drainage units.

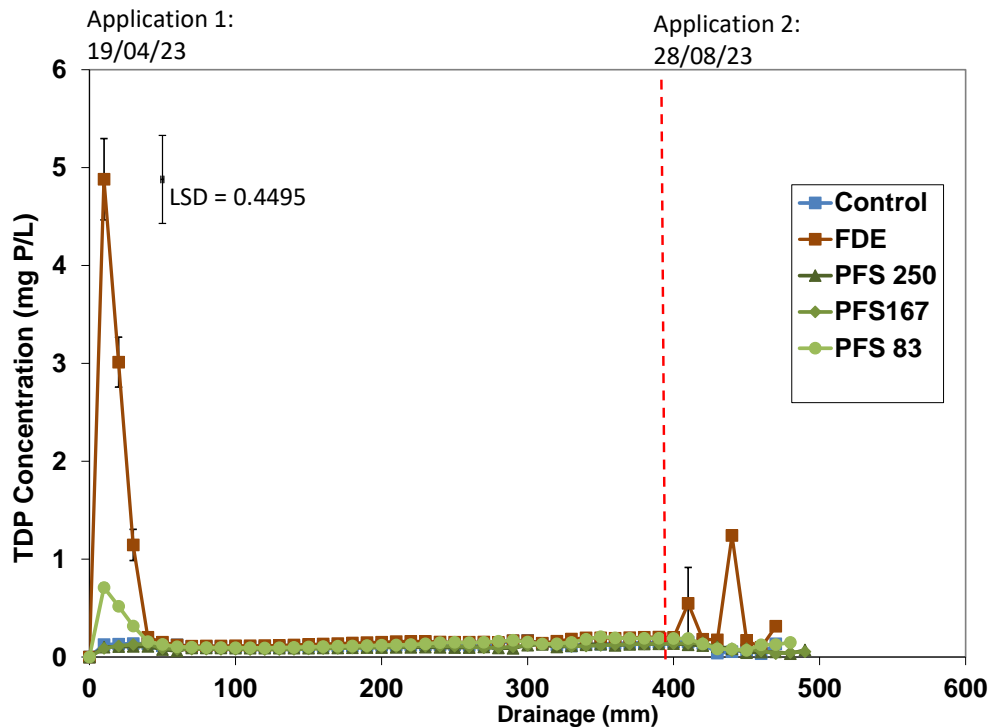
*Note:* Error bars represent standard error of the mean. Dashed red line = second treatment application. Application 1: 19/04/23; application 2: 28/08/23.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

After the first treatment application to the lysimeters, TDP peak drainage concentrations from the PFS 250 and PFS 167 treatments resulted in significant reductions of 97.7% (0.11 mg P/L) and 97.3% (0.13 mg P/L), respectively, when compared to FDE (4.88 mg P/L) (Figure 4-5). These PFS 250 and PFS 167 treatment rate concentrations were not significantly different to each other or to the TDP concentration of the control. The PFS 83 treatment resulted in a significant reduction in TDP peak drainage concentration of 85.5% (0.71 mg P/L) but this concentration was significantly higher than the concentrations of the PFS 250, PFS 167, and the control ( $P < 0.05$ ).

TDP concentrations in each treatment declined rapidly and there was no significant difference between control and the four treatments after 40 mm of drainage (first application).

Following the second treatment application there was no significant difference between the peak TDP drainage concentrations of all five treatments (Table 4-3).



**Figure 4-5.** Average concentration of total dissolved phosphorus (TDP) drainage water collected from the model drainage units.

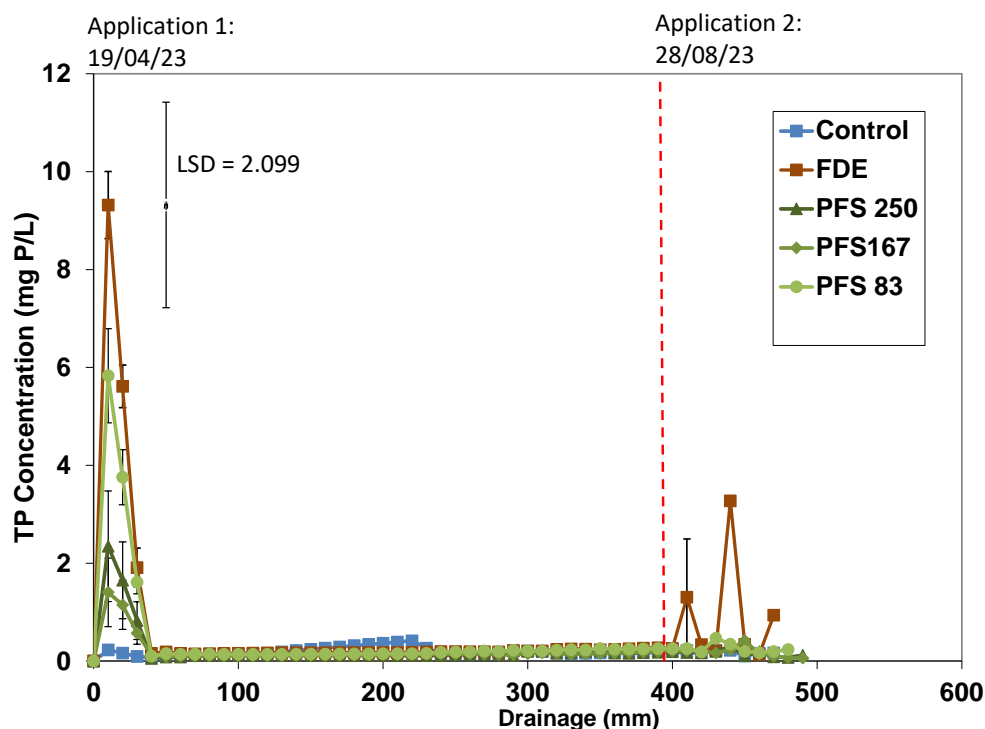
*Note:* Error bars represent standard error of the mean. Dashed red line = second treatment application. Application 1: 19/04/23; application 2: 28/08/23.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

After the first treatment application to the lysimeters, relative to the untreated FDE peak TP drainage concentration (9.32 mg P/L), the PFS 250 and PFS 167 treatments resulted in significant reductions in peak TP drainage concentrations of 74.7% (2.35 mg P/L) and 85.0% (1.40 mg P/L), respectively ( $P < 0.05$ ) (Figure 4-6). These PFS 250 and PFS 167 treatment rate concentrations were not significantly different from each other or the control. In comparison, the PFS 83 treatments resulted in a peak TP drainage concentration of 5.83 mg P/L which was significantly higher than the PFS 250, PFS 167, and the control, but not significantly different to the untreated FDE.

TP concentrations in each treatment declined rapidly and there was no significant difference between the control and the four treatments after 40 mm of drainage (first application).

Following the second treatment application the only significant reduction in TP peak drainage concentrations was between the untreated FDE (3.27 mg P/L) and the PFS 250 treatment (0.3 mg P/L) ( $P < 0.05$ ) which represented a 90.8% reduction (Table 4-3).



**Figure 4-6.** Average concentration of total phosphorus (TP) drainage water collected from the model drainage units.

*Note:* Error bars represent standard error of the mean. Dashed red line = second treatment application. Application 1: 19/04/23; application 2: 28/08/23.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

**Table 4-3.** DRP, TDP, and TP peak concentrations in drainage following both treatment applications.

Treatment	DRP (mg P/L)		TDP (mg P/L)		TP (mg P/L)	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
Control	0.20 a	0.07 a	0.13 a	0.16 a	0.23 a	0.22 ab
FDE	4.04 b	0.42 a	4.88 b	1.24 a	9.32 b	3.27 b
PFS 250	0.13 c	0.07 a	0.11 a	0.13 a	2.35 a	0.30 a
PFS 167	0.14 c	0.09 a	0.13 a	0.15 a	1.40 a	0.42 ab
PFS 83	0.38 d	0.11 a	0.71 c	0.19 a	5.83 b	0.47 ab

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

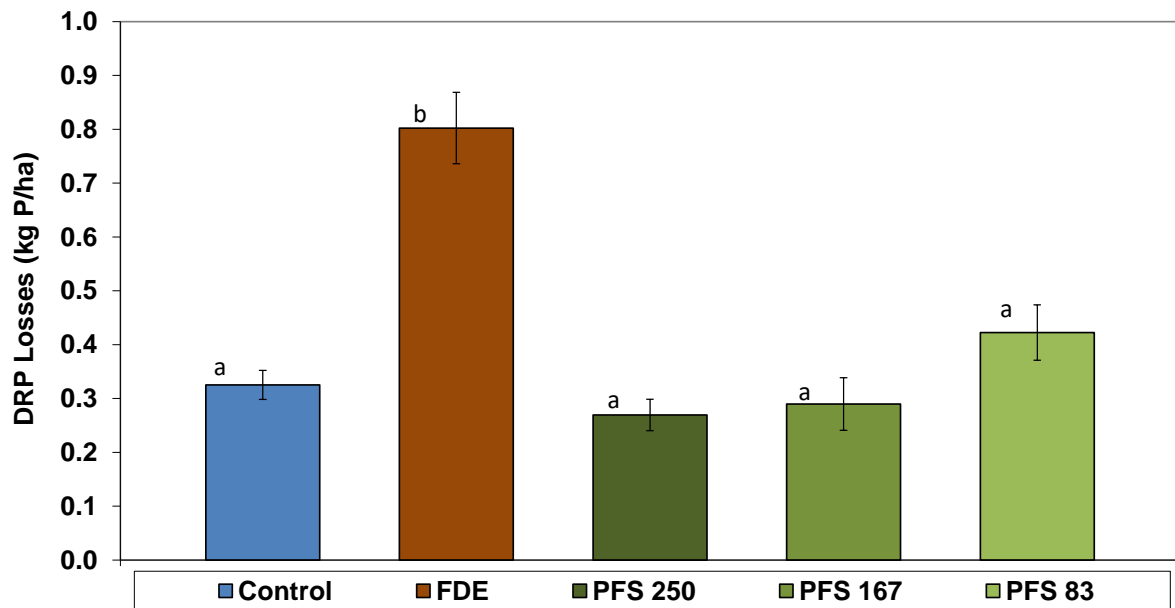
Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus.

Peak 1 following application 1 (19/03/23); peak 2 following application 2 (28/08/23).

#### 4.3.4 Total amount of DRP, TDP, and TP detected in drainage water

The total amount of DRP leached from the untreated FDE treatment was 0.80 kg P/ha (Table 4-4). All rates of PFS treatment of FDE (PFS 250, PFS 167, and PFS 83) resulted in significant reductions in the leaching loss factors from the total amount of DRP leached; 111.13%, 107.77%, and 80.56%, respectively, ( $P < 0.05$ ) (Table 4-4 & 4-6; Figure 4-7). Reductions exceeding 100% indicate that these treatments reduced leaching losses to levels below those of the control. The total amount of DRP

leached from the PFS 250, PFS 167, and PFS 83 treatments were not significantly different to the control.

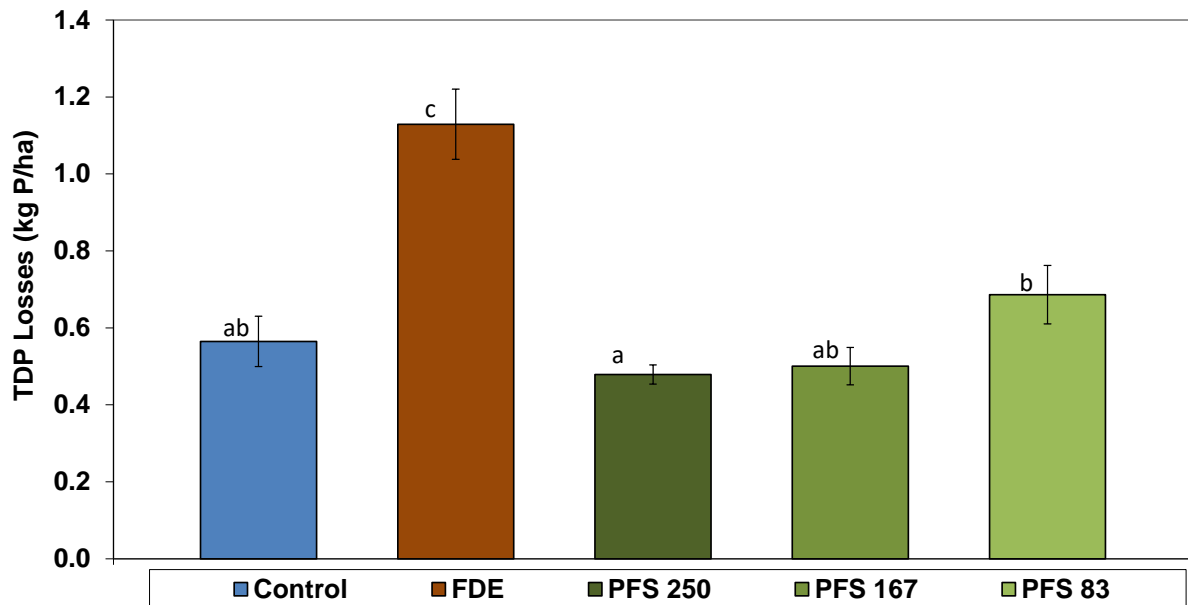


**Figure 4-7.** Total amount of dissolved reactive phosphorus (DRP) in kg P/ha in cumulative drainage collected over the duration of the trial. Equal drainage across the data was used to allow for fair comparison (420 mm).

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

The total amount of TDP in drainage water collected from the untreated FDE treatment was 1.13 kg P/ha (Table 4-4). All rates of PFS treatment of FDE resulted in significant ( $P < 0.05$ ) reductions in the leaching loss factors from the total amount of TDP leached compared to that from the untreated FDE (Table 4-6 & Figure 4-8). These reductions were of 115.47%, 112.85%, and 80.17%, from the PFS 250, PFS 167, and PFS 83, respectively. Reductions exceeding 100% indicate that these treatments reduced leaching losses to levels below those of the control. The total amount of TDP in drainage from the PFS 250, PFS 167, and PFS 83 treatments were not significantly different from the control.

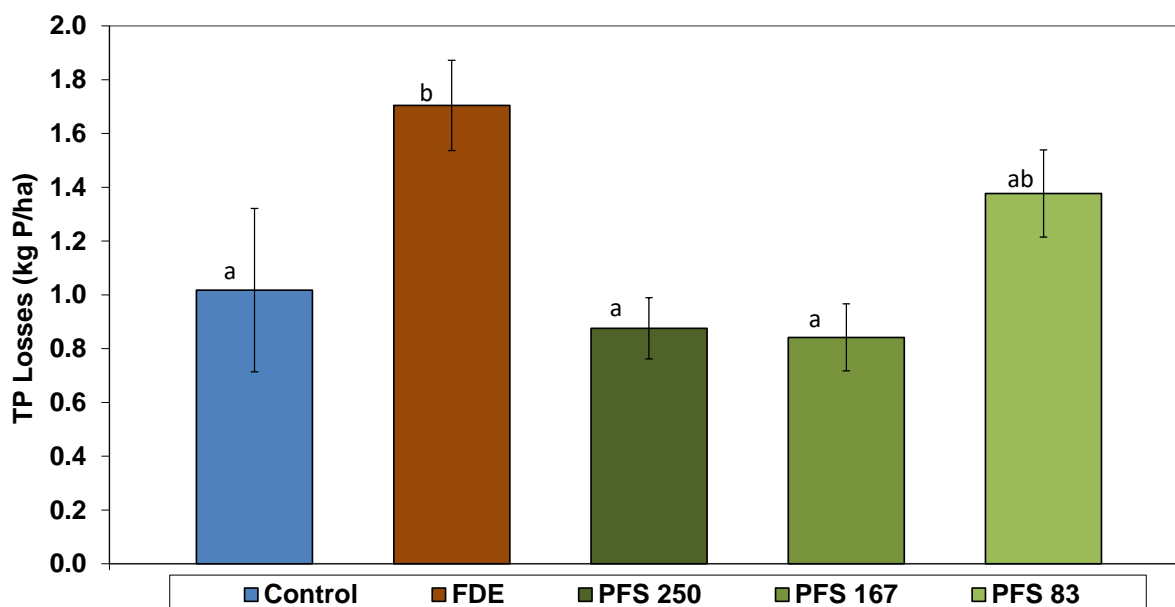


**Figure 4-8.** Total amount of total dissolved phosphorus (TDP) in kg P/ha in cumulative drainage collected over the duration of the trial. Equal drainage across the data was used to allow for fair comparison (420 mm).

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

The total amount of TP in drainage water collected from the untreated FDE treatment was 1.70 kg P/ha. The PFS 250 and PFS 167 treatments significantly reduced the leaching loss factor by 85.02% and 90.72% (Table 4-6), respectively, and were not significantly different to the control ( $P < 0.05$ ). The PFS 83 treatment was not significantly different to the untreated FDE, the control, or the PFS 250 and PFS 167 (Table 4-4 & Figure 4-9).



**Figure 4-9.** Total amount of total phosphorus (TP) in kg P/ha in cumulative drainage collected over the duration of the trial. Equal drainage across the data was used to allow for fair comparison (420 mm).

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

**Table 4-4.** DRP, TP, and TDP total cumulative leaching losses over the experimental period.

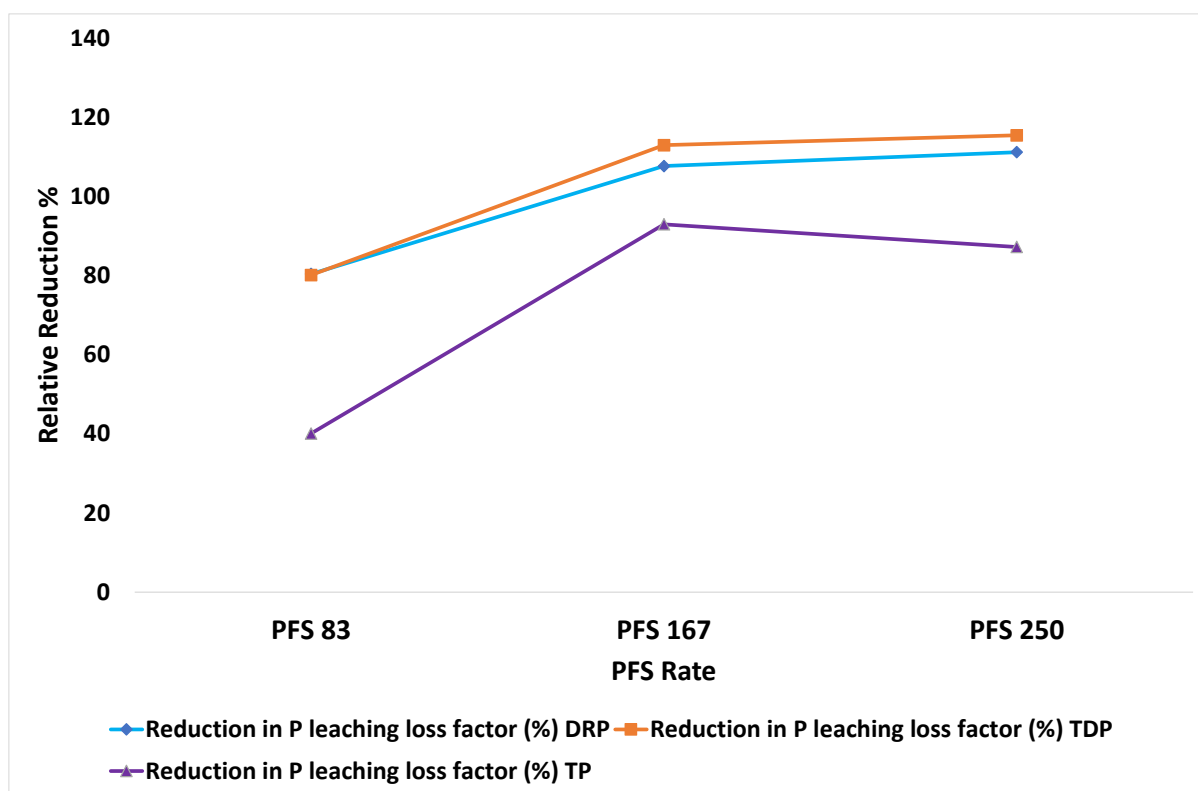
Treatments	P losses (kg P/ha)		
	DRP	TDP	TP
<b>Control</b>	0.31 a	0.54 ab	0.96 a
<b>FDE</b>	0.80 b	1.13 c	1.70 b
<b>PFS 250</b>	0.25 a	0.45 a	0.82 a
<b>PFS 167</b>	0.27 a	0.47 ab	0.77 a
<b>PFS 83</b>	0.41 a	0.66 b	1.30 ab

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; TS, total solids; TSS, total suspended solids; TN, total nitrogen; TP, total phosphorus; DRP, dissolved reactive phosphorus; TC, total carbon.

The DRP and TDP leaching loss factors of the PFS 250, PFS 167 and PFS 83 treatments were significantly lower ( $P < 0.05$ ) than those of the untreated FDE. The TP leaching loss factor of the PFS 250 and PFS 167 were significantly lower than that of the untreated FDE, while the PFS 83 was not significantly different (Table 4-5).

These data demonstrate that there was a material reduction in all three forms of P leaching losses under the top two rates of PFS treatment (PFS 250 and PFS 167) whilst the lowest rate of treatment (PFS 83) produced a material reduction in DRP and TDP but not in TP leaching losses (Figure 4-10).



**Figure 4-10.** Comparison of the relative reduction (%) in P leaching loss factor of DRP, TDP, and TP from the PFS 83, PFS 167, and PFS 250.

Abbreviations: PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

**Table 4-5.** P leaching loss factor as a percentage of P applied for DRP, TP and TDP when background concentrations are removed.

Treatments	P leaching loss factor (% of P applied)		
	DRP	TDP	TP
FDE	0.772 a	0.918 a	1.616 a
PFS 250	-0.086 b	-0.142 b	0.242 b
PFS 167	-0.06 b	-0.118 b	0.15 b
PFS 83	0.15 b	0.182 b	0.998 a

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ) and are for within-column contrasts.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

**Table 4-6.** Reduction in P leaching loss factor as a percentage for all three PFS rates as compared to the untreated FDE.

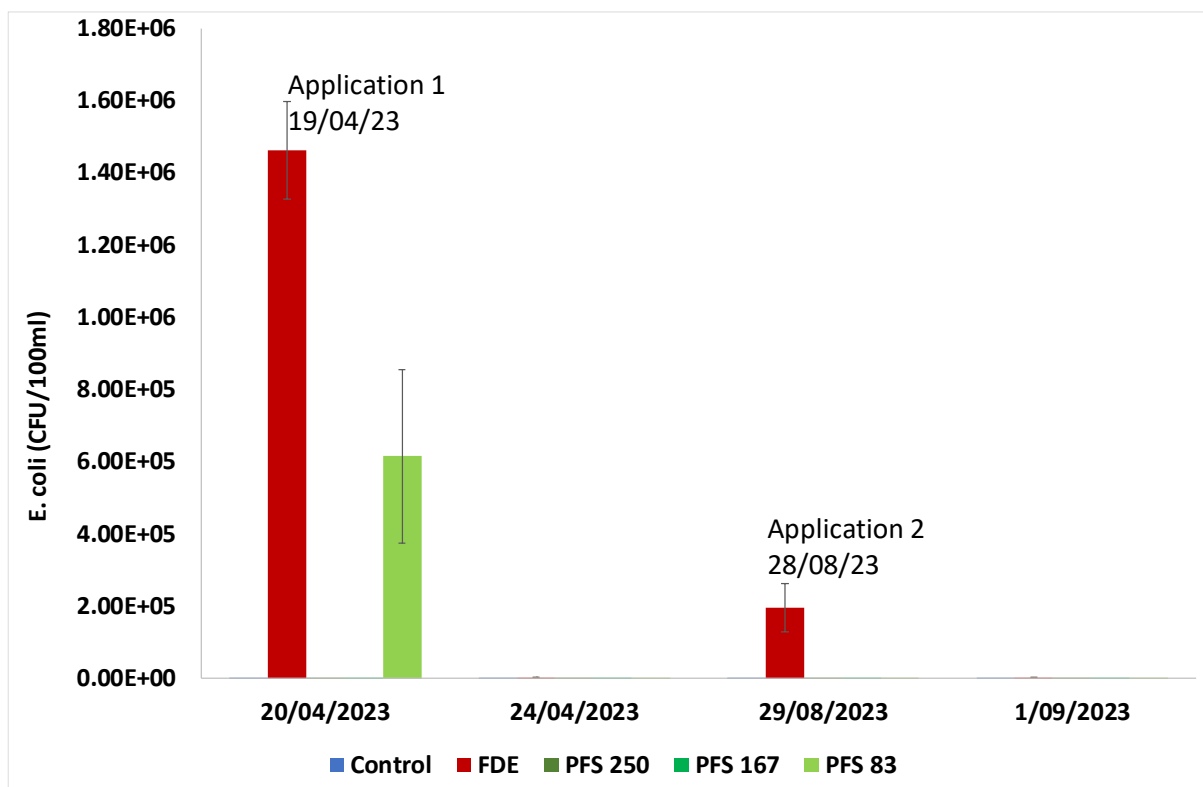
Treatments	Reduction in P leaching loss factor (%)		
	DRP	TDP	TP
PFS 250	111.13	115.47	85.02
PFS 167	107.77	112.85	90.72
PFS 83	80.56	80.17	-

Abbreviations: PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

#### 4.3.5 *E. coli* concentrations in drainage water

Compared to the untreated FDE, the *E. coli* concentrations in the drainage water from the PFS 250, PFS 167, and PFS 83 treatments were significantly lower ( $P < 0.05$ ) which represented a 99.9%, 99.9%, and 57.9% reduction after the first application and a 99.9%, 99.9%, and 99.4% reduction after the second application, respectively (Figure 4-11).

There was no significant difference detected in *E. Coli* drainage concentrations between the control, the 250 mg Fe/L, and the 167 mg Fe/L treatments following the first application and second applications. The *E. Coli* concentrations from the PFS 83 treatment were significantly higher than the control following the first application and not significantly different to the control following the second application.



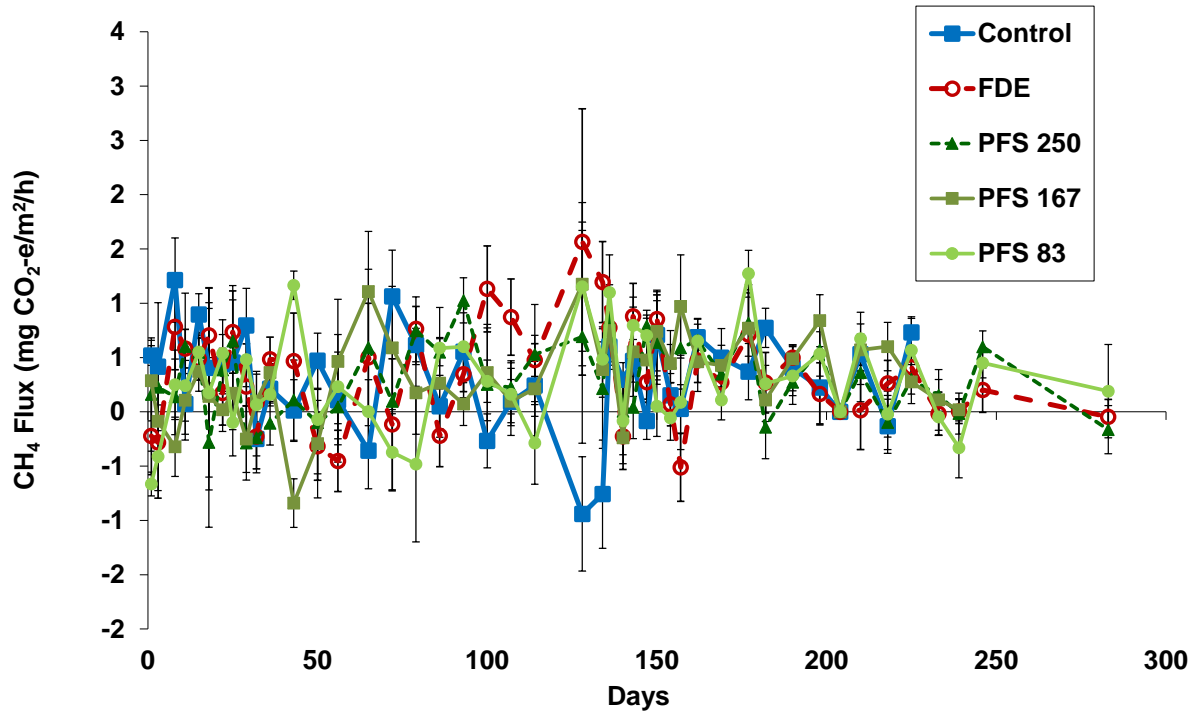
**Figure 4-11.** Average concentration of *E. coli* in drainage water collected from the model drainage units.

*Note:* Error bars represent standard error of the mean.

Abbreviations: FDE – farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L. Error bars represent standard error of the mean.

#### 4.3.6 Greenhouse gas emissions

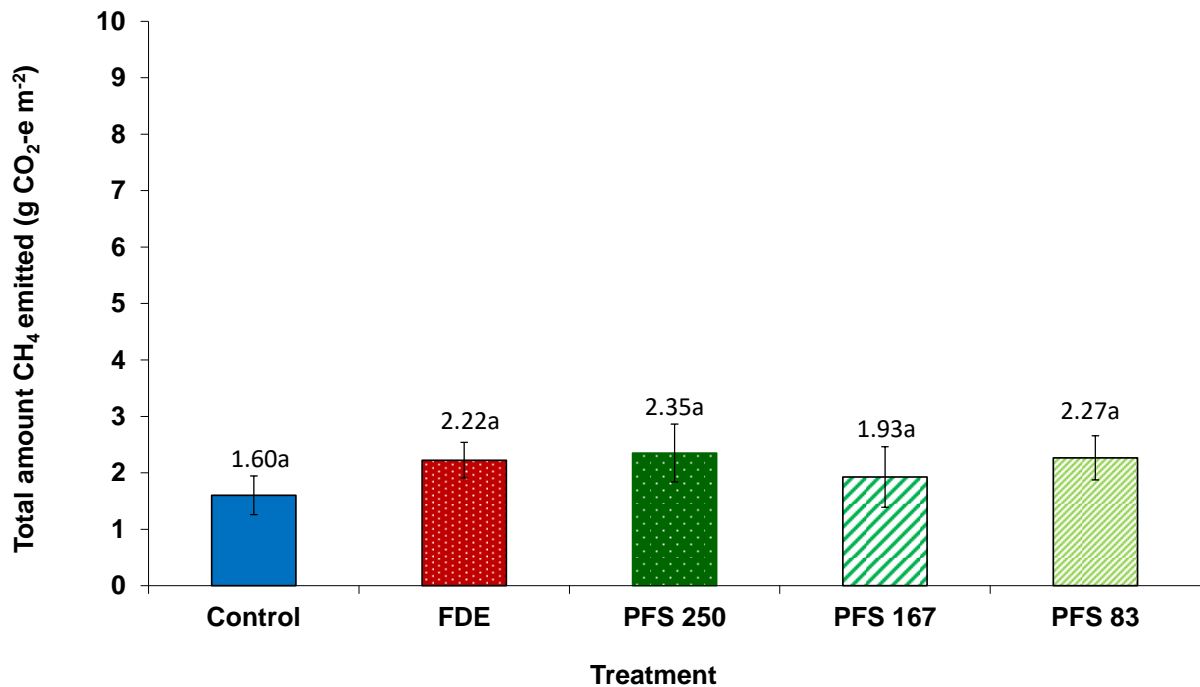
Over the trial period, daily emissions of CH<sub>4</sub> gas ranged from -0.8409 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (PFS 167) to 1.5650 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (FDE) (Figure 4-12). Daily emissions and total cumulative emissions did not differ significantly between treatments (Figure 4-13).



**Figure 4-12.** Daily CH<sub>4</sub> emissions per treatment (mg CO<sub>2</sub>-e/m<sup>2</sup>/h) over the trial period.

Note: Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

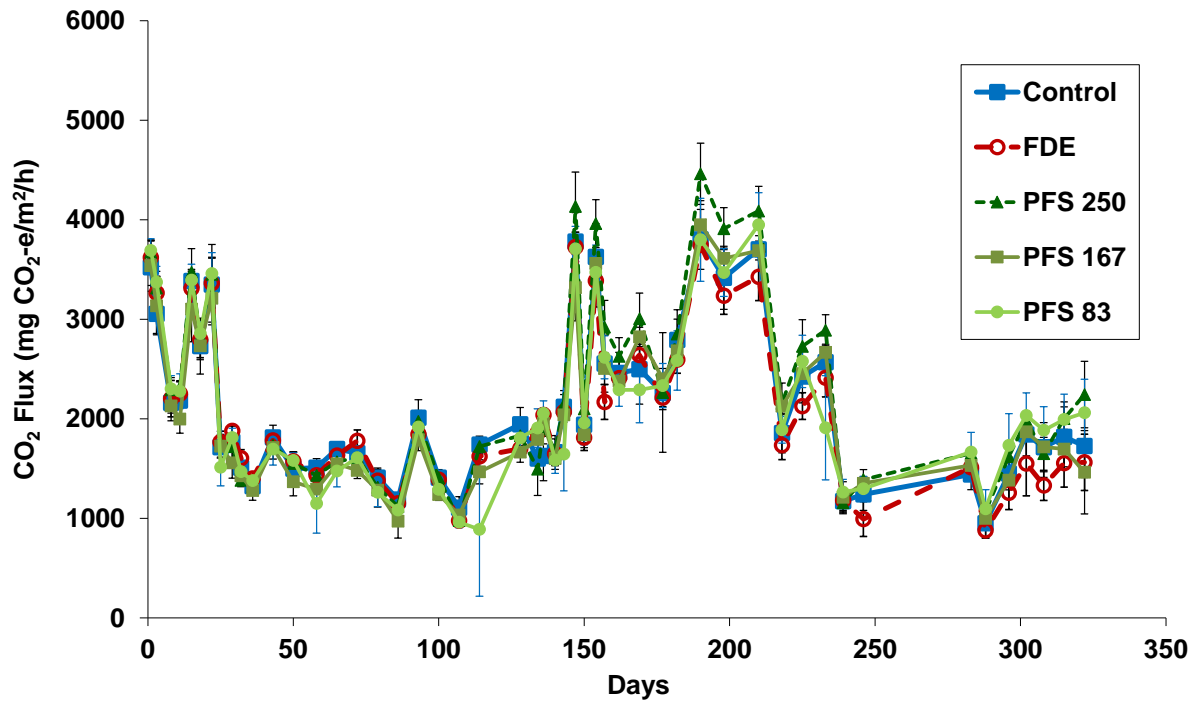


**Figure 4-13.** Cumulative CH<sub>4</sub> emissions per treatment (g CO<sub>2</sub>-e/m<sup>2</sup>/h).

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

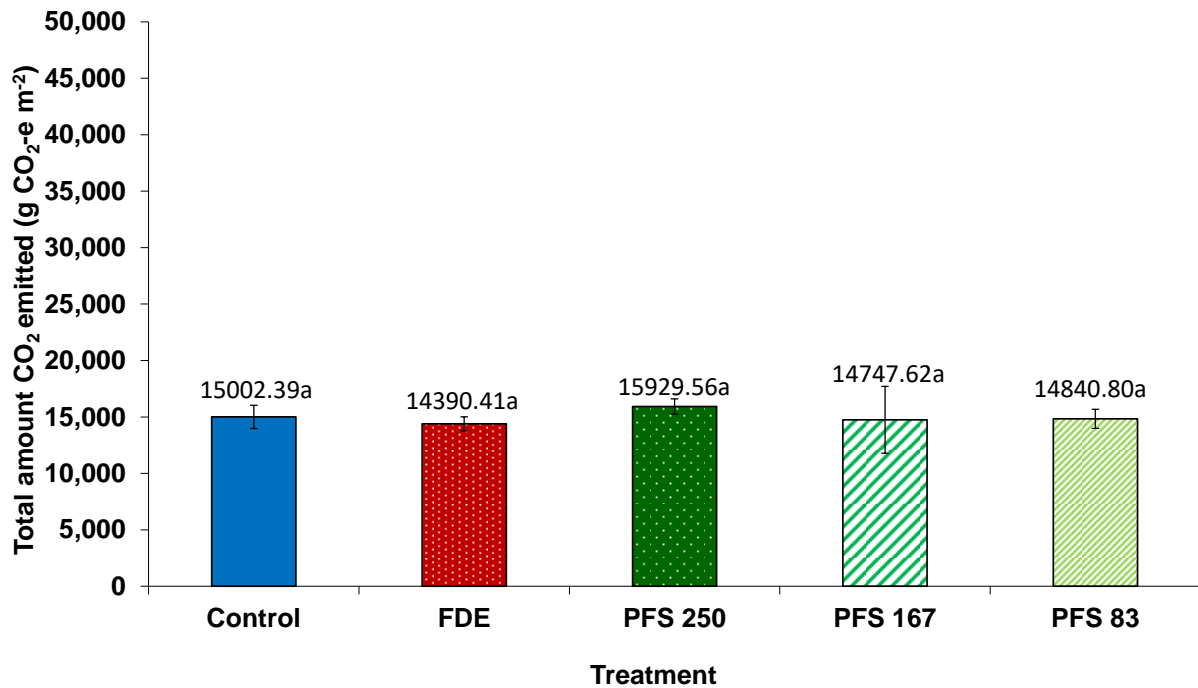
The daily CO<sub>2</sub> emissions ranged from 890.3730 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (PFS 250) to 4133.8999 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (PFS 83) (Figure 4-14). There were no significant differences in daily emissions between treatments or in total cumulative CO<sub>2</sub> emissions (Figure 4-15).



**Figure 4-14.** Daily CO<sub>2</sub> emissions per treatment (mg CO<sub>2</sub>-e/m<sup>2</sup>/h) over the trial period.

*Note:* Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

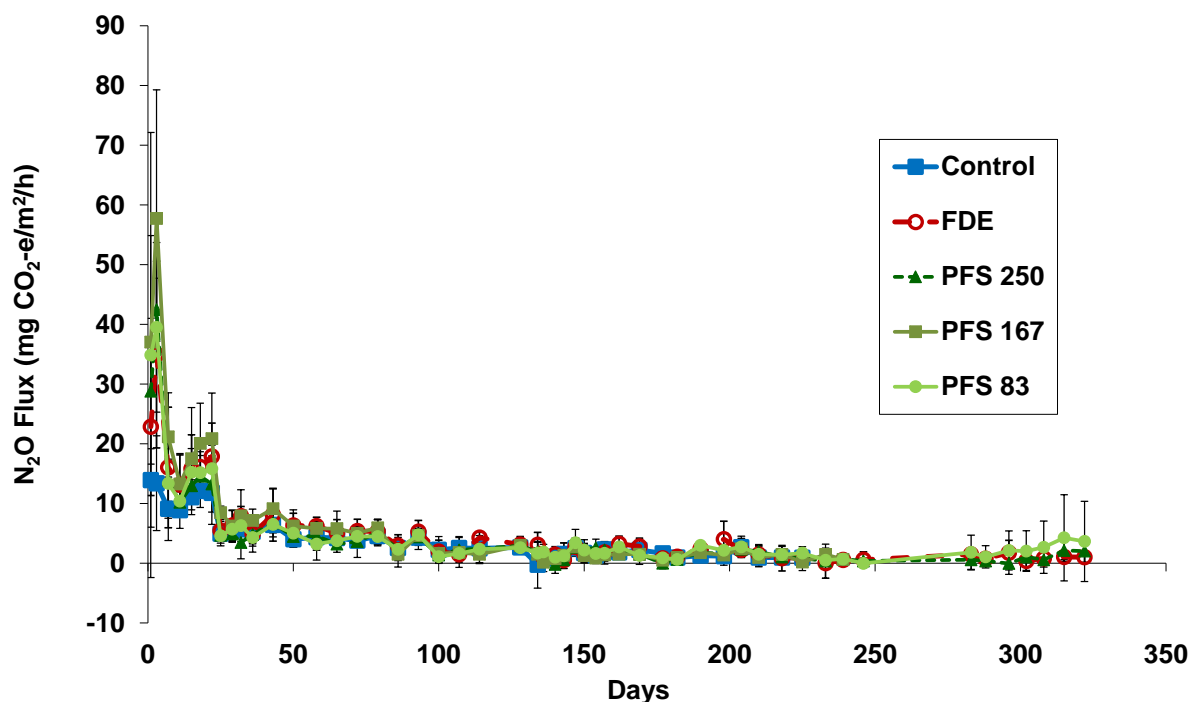


**Figure 4-15.** Cumulative CO<sub>2</sub> emissions per treatment (mg CO<sub>2</sub>-e/m<sup>2</sup>/h).

*Note:* values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

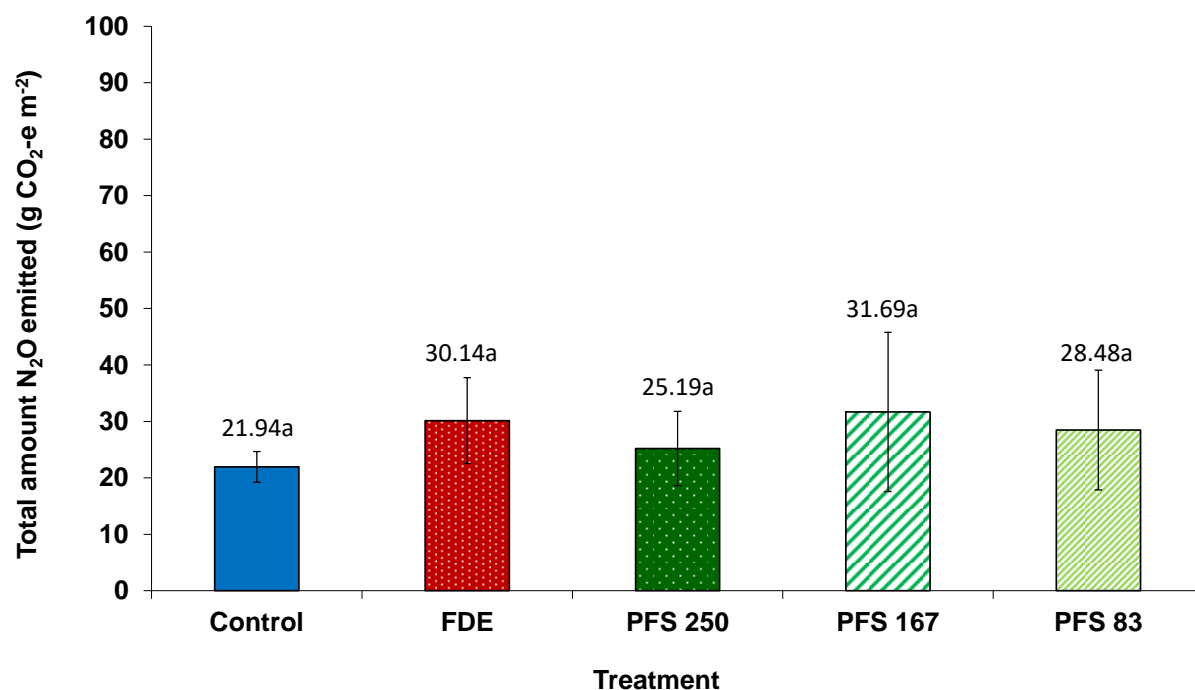
The daily N<sub>2</sub>O emissions decreased over time and ranged between 0.0016 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (PFS 250) and 57.7353 mg CO<sub>2</sub>-e/m<sup>2</sup>/h (PFS 167) (Figure 4-16). Immediately following the first treatment application there was a significant difference in N<sub>2</sub>O emissions whereby the three PFS-treated effluents and the untreated effluent produced greater average N<sub>2</sub>O emissions than the control ( $P < 0.05$ ). However, for the remainder of the trial, daily emissions and total cumulative emissions showed no significant difference between treatments (Figure 4-17).



**Figure 4-16.** Daily N<sub>2</sub>O emissions per treatment (mg CO<sub>2</sub>-e/m<sup>2</sup>/h) over the trial period.

Note: Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.



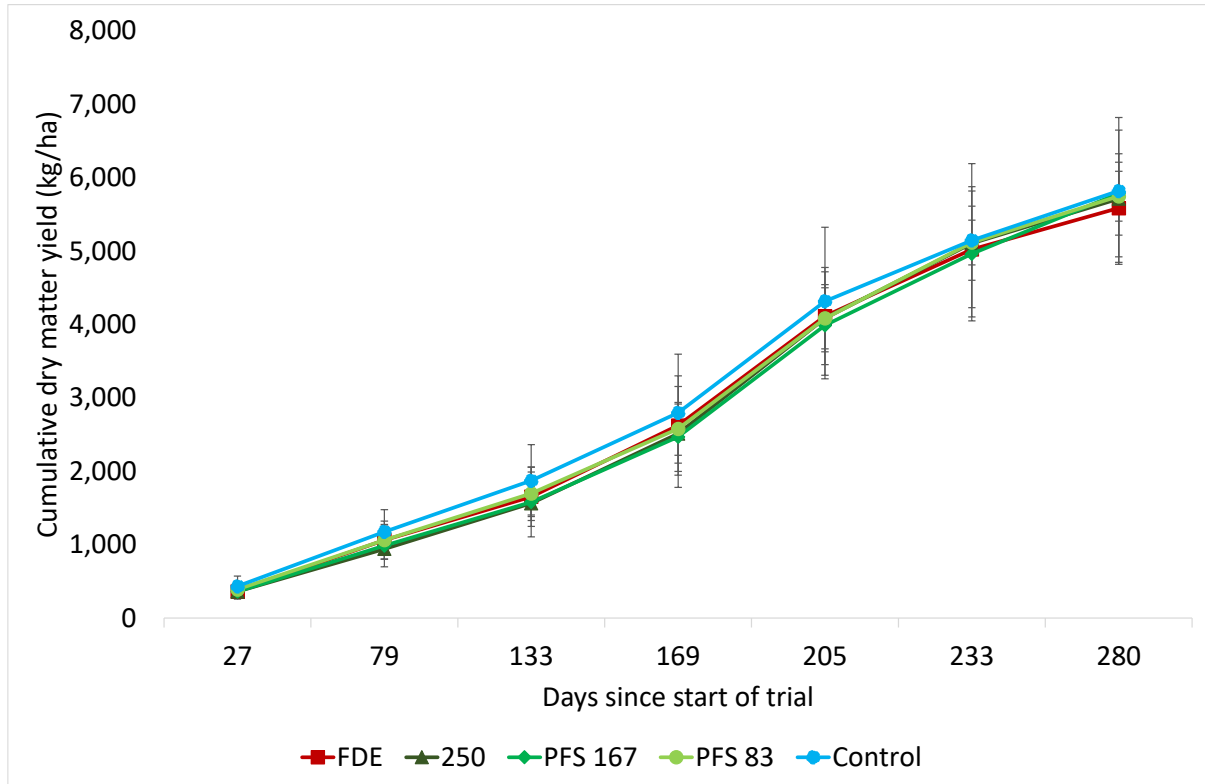
**Figure 4-17.** Cumulative N<sub>2</sub>O emissions per treatment (mg CO<sub>2</sub>-e/m<sup>2</sup>/h).

Note: values with a letter in common are not statistically significantly different ( $P < 0.05$ ). Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

#### 4.3.7 Herbage yield and P and N uptake

The cumulative herbage yield increased over time for all five of the treatments, reaching a maximum total of 5819.21 kg DM/ha (control) and a minimum total of 5584.94 kg DM/ha (FDE) over the duration of the field trial (Figure 4-18). There were no significant differences in cumulative herbage yields between the treatments.

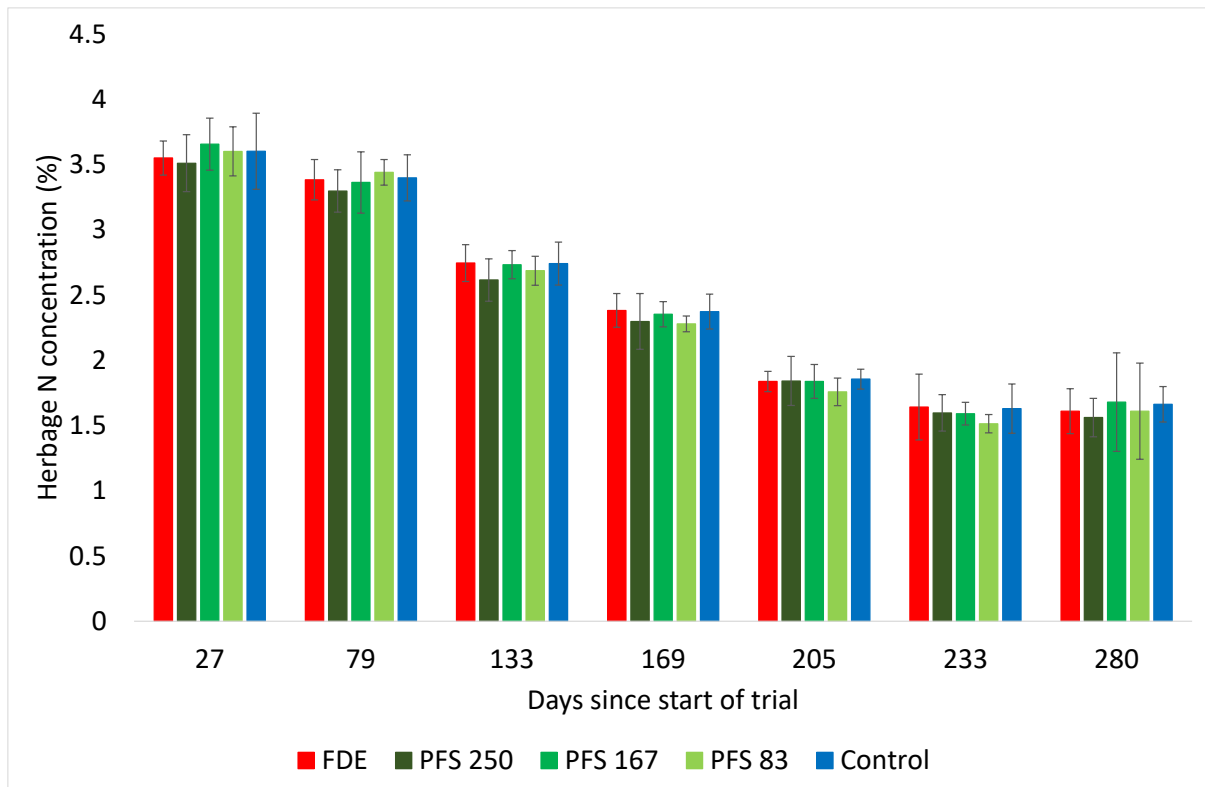


**Figure 4-18.** Cumulative dry matter yields per treatment over the duration of the trial (kg DM/ha).

*Note:* Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

Herbage nitrogen concentrations are shown in Figure 4-19. The concentrations were analysed seven times during the duration of the trial and decreased over time. There were no significant differences in herbage nitrogen concentrations at each sampling date between treatments.

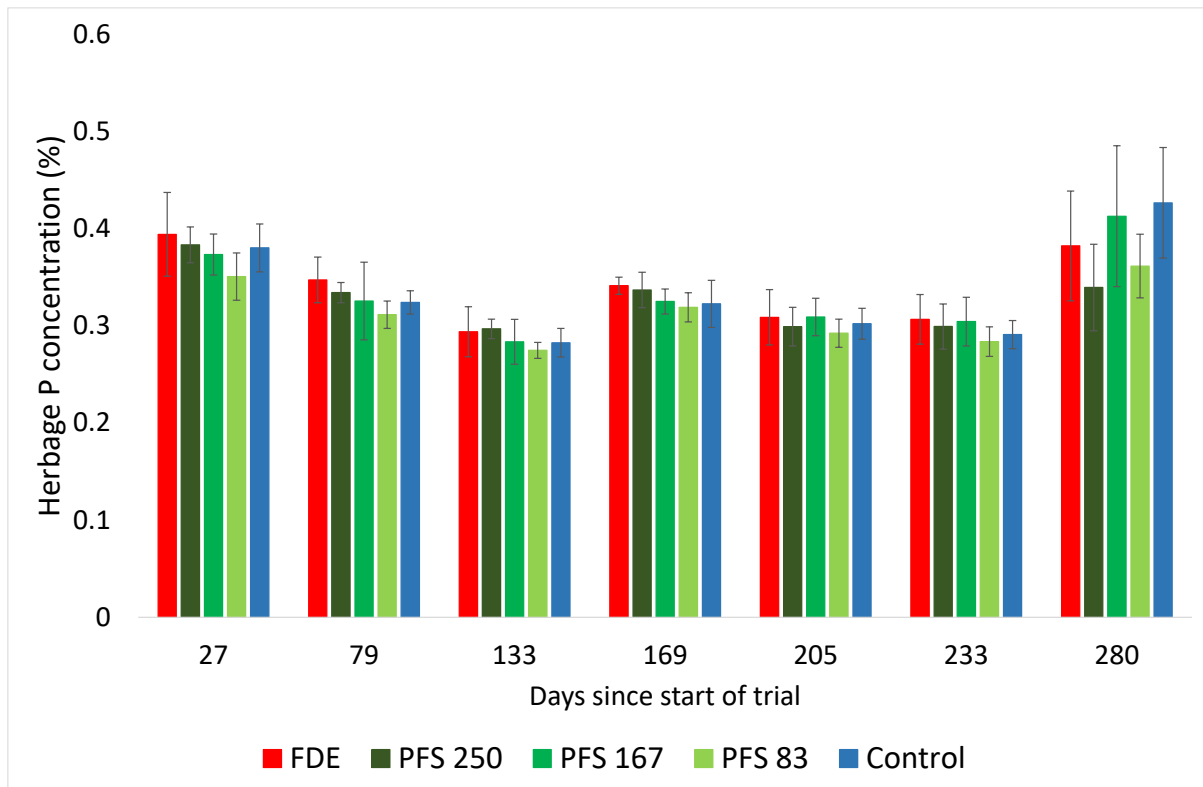


**Figure 4-19.** Herbage N (nitrogen) concentrations (%) per treatment over seven sampling periods during the duration of the trial.

*Note:* Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

Herbage phosphate concentrations were analysed seven times during the duration of the trial and remained fairly consistent with time. There were no significant differences in herbage phosphate concentrations at each sampling date between treatments (Figure 4-20).



**Figure 4-20.** Herbage P (phosphorus) concentrations (%) per treatment over seven sampling periods during the duration of the trial.

*Note:* Error bars represent standard error of the mean.

Abbreviations: FDE, farm dairy effluent; PFS 250, PFS rate of 250 mg Fe/L; PFS 167, 167 mg Fe/L; PFS 83, 83 mg Fe/L.

#### 4.4 Discussion

The consistent and significant effect of the PFS treated effluent on phosphate and *E. coli* leaching losses has demonstrated that PFS treatment is highly effective at mitigating key environmental impacts of dairy farm effluent management on water quality. However, incorporating and running an EcoPond system on-farm to treat the effluent increases management costs. Therefore, the results from this trial are important because they provide a better understanding of the efficacy of different rates of PFS treatment in mitigating phosphate and *E. coli* leaching losses from effluent. The data from the drainage model unit study demonstrates that lower rates of PFS treatment of effluent than previously published could achieve similar reductions in phosphate and *E. coli* leaching losses.

##### 4.4.1 Phosphate leaching losses

###### 4.4.1.1 Poly-ferric sulphate as a chemical coagulant

The results of the trial showed that significant reductions in phosphate leaching could be achieved at lower rates of PFS treatment than reported previously (Che et al., 2022).

The chemical removal of P is a common process in wastewater treatment plants (WWTP) and relies on the precipitation of phosphate via the addition of metal salts (Carliell-Marquet et al., 2010; Wu et al., 2019). Generally, iron (Fe) salt is used in these processes, whereby it hydrolyses and precipitates with phosphate and hydroxyl ions (Flynn, 1984; Cornell et al., 1989). Poly-ferric sulphate (PFS) is a coagulation reagent used for the removal of P in wastewater (Zouboulis et al., 2008). This coagulant is pre-hydrolysed and prepared by partial neutralisation of iron salts, during which several polymerisation reactions occur. This results in PFS containing polynuclear complexes including

$\text{Fe}_2(\text{OH})_2^{4+}$  and  $\text{Fe}_3(\text{OH})_4^{5+}$  (Chang & Wang, 2002). These polymeric species give PFS a high cationic charge, improving its charge neutralisation capacity and its effectiveness at a lower dose, compared to other commonly used coagulants (Jian & Graham, 1996). The iron polymeric cations have been shown to form ferric (Fe(III)) hydroxides which bind rapidly to phosphate and colloidal particles via electro neutralisation, adsorption, and sweep-flocculation (Carliell-Marquet et al., 2010; Li et al., 2018; Ping et al., 2023). Liu and Zhou (2022) found many complex ions formed during the hydrolysis process of PFS such as  $\text{Fe}_2(\text{OH})_3^{3+}$ ;  $\text{Fe}_2(\text{OH})_2^{4+}$ , and  $\text{Fe}_3(\text{OH})_4^{5+}$ . Ping et al. (2023) describes three methods for the binding of iron and phosphate: (1) Fe and  $\text{PO}_4^{3-}$  react to form insoluble phosphate precipitates; (2) co-precipitation of  $\text{PO}_4^{3-}$  and Fe occurs during Fe hydrolysis forming iron hydroxyphosphate complexes (general formula  $\text{Fe}_r\text{PO}_4(\text{OH})_{3-r-3}$ ); (3)  $\text{PO}_4^{3-}$  is adsorbed onto iron hydroxides and other precipitates.

Similarly, Zouboulis et al. (2008) showed that P removal from wastewater was achieved at a greater percentage when using PFS compared to using ferric sulphate (FS), and that the greater the dosage was, the higher the removal percentage. They further showed that a dose over two times lower of PFS than ferric sulphate could be used to obtain the same amount of P removal in wastewater. The results were attributed to the fact that the primary mechanism at work when using FS was the hydrolysis of  $\text{Fe}^{3+}$  to ferric hydroxide which adsorbs  $\text{PO}_4^{3-}$  ions, while PFS does both this and uses other polymeric species which provide a surface for adsorption and can form Fe-hydroxo-phosphate complexes (Jian & Graham, 1998). Therefore, for the removal of P, PFS is a better coagulating agent than FS. Ping et al. (2023) showed that P removal efficiency using PFS (99.4%) was significantly higher than when using polymeric aluminium ferric chloride (PAFC) (53.0%) from wastewater.

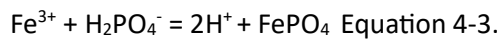
#### *4.4.1.2 Forms of P in drainage water after applying PFS-treated effluent to soils with artificial subsurface drains*

The results showed that both the PFS 250 and PFS 167 treatments led to similar significant reductions and were determined to be equally effective. Specifically, these treatments resulted in reductions of 111.13% and 107.77%, respectively, of the dissolved reactive phosphate (DRP) leaching loss factor. For total dissolved phosphate (TDP), the reductions were 115.47% from the PFS 250 and 112.85% from the PFS 167, while total phosphate (TP) leaching loss factors were reduced by 85.02% and 90.72%, respectively. Reductions exceeding 100% indicate that these treatments reduced leaching losses to levels below those of the control. The PFS 83 treatment reduced the DRP and TDP leaching loss factors by 80.56% and 80.17%, respectively, but did not reduce the TP leaching loss factor. Consequently, the PFS 83 rate was deemed inadequate for effectively reducing leaching losses and would therefore not be recommended for further use on-farm.

When Equation 4-1 was used to calculate the P leaching loss factor the results showed that treating FDE with the PFS 250 and PFS 167 rates significantly reduced all forms of P leaching losses (i.e. DRP, TDP, and TP). The negative values under the PFS 250 and PFS 167 in Table 4-5 show that less P leaching occurred when PFS-treated FDE was applied to land than that which would occur in this soil (i.e. loss from the control). This is caused by the PFS in the treated FDE reducing the mobility of both the P in the effluent and the P already present in the soil at background concentrations. The P already in the soil binds to the ferric iron in the PFS in the same reactions which occur between the ferric iron and the P in the effluent. This reacted ferric-P is then bound in the soil and will be slowly released with time as per the reactions described in section 2.2.2.

The reductions in DRP and TDP in the drainage water collected under the treated-effluent applications compared with the untreated effluent showed similar results to those of Che et al. (2022) who showed a reduction in TDP, DRP, and TP in drainage under the PFS-treated effluent applications compared to the untreated effluent. Chisholm et al. (2020) and Wang et al. (2019) also

showed reductions in phosphate leaching under applications of PFS-treated effluent, but these studies used greater depths of soil compared to the shallow depth of soil (20 cm) used in this study. When the depth of soil is greater, there is more interaction which can occur between the effluent applied and soil particles, hence more reactions taking place which remove P from the soil solution and a lower P concentration is found in drainage (McLaren & Cameron, 1990). As Ping et al. (2023) describe the water-soluble P in the FDE combines with Fe to form iron phosphates which precipitate as solids (Equation 4-3) (Cameron & Di, 2019). These solid forms are less mobile in the soil matrix and, hence, are less likely to leach from the soil.



The TP leaching loss was reduced under the PFS 250 and PFS 167 treatments compared to the untreated FDE. This is in part as a result of the TDP leaching reduction, but also due to a reduction in total particulate phosphorus (TPP) leaching. This reduction is most likely to be due to the formation of amorphous ferric hydroxide when PFS is added to effluent (Ping et al., 2023). Amorphous ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) has been shown to be a highly effective adsorbent and to enhance aggregation of colloidal particles in solution (Simon et al., 1974; Shigematsu et al., 1975; Esmadi & Simm, 1995; Bronick & Lal, 2005; Chitrakar et al., 2006; Quinn et al., 2007; Guan et al., 2008; Bei et al., 2015). When effluent is treated with PFS and applied to land, the  $\text{Fe}(\text{OH})_3$  complexes bind to particulate phosphate, forming larger flocs which 'stick' to the soil, decreasing the loss of particulate phosphate via preferential flow (Bronick & Lal, 2005).

This hypothesis is further supported by the effluent analysis results which showed that all three rates of PFS-treated effluent had reduced concentrations of DRP, and increased levels of total suspended solids (TSS) and total solids (TS) compared to the untreated effluent. Meanwhile, the TP concentrations remained consistent across both the treated and untreated effluents. This suggests that treating FDE with PFS leads to reactions that precipitate phosphate, thereby reducing the DRP concentrations in the effluent. As a result, a larger fraction of the TP in the effluent is present as particulate phosphorus, which explains the observed increase in TSS and TS concentrations in the treated effluent. Che et al. (2022) measured the concentration of TSS in drainage water after the application of PFS-treated FDE and untreated FDE. Their results showed that there was no significant difference in TSS concentrations within drainage between treatments, despite the higher concentrations of TSS within the treated effluent compared to the untreated. Hence, TPP leaching was reduced by treating FDE with PFS.

Additionally, the pH of the environment influences the capacity for phosphorus removal. Generally, iron (Fe) is most effective at binding phosphorus in solution under acidic conditions (McBride, 1994; Penn et al., 2007). Ping et al., (2023) found that the optimal phosphorus removal occurred at a pH of 4.7 when using Fe salts to treat wastewater. Similarly, Fytianos et al. (1998) identified a pH of 4.5 as optimal for phosphorus removal in wastewater using ferric iron. Ping et al. (2023) also observed that as pH decreases, the efficiency of phosphorus removal improves, due to the conversion of Fe(III) into oxides and hydroxides occurring at pH levels below 6.5. Zhang et al. (2010) demonstrated that as pH increases, hydroxide ions ( $\text{OH}^-$ ) compete with phosphate ions ( $\text{PO}_4^{3-}$ ) for Fe(III), therefore ferric phosphate formation is favoured at lower pH levels (Irdemez et al., 2006). In this study, the addition of PFS to FDE lowered the pH from 7.10 in the untreated effluent to 3.11, 4.08, and 6.11 in the PFS 250, PFS 167, and PFS 83 treatments, respectively (first application). This reduction in pH would thereby create conditions more conducive to phosphorus removal in the effluent.

The rapid breakthrough curve for P and *E. coli* immediately after the effluent was applied in this study is likely to have occurred via preferential flow through soil 'macropores' into the underlying

gravel that was installed as part of the simulated agricultural drainage system. Shallow soils with gravel layers such as this are common when subsurface drains are installed and have greater amounts of preferential flow compared to deeper soils which are generally dominated by matrix flow, as described in section 2.5.1.2.

The hypothesis was therefore accepted that P leaching reduction is affected by the rate of PFS used to treat effluent, and that a rate lower than 250 mg Fe/L PFS can achieve similar effects.

#### 4.4.2 *E. coli* concentrations in drainage

A reduction in *E. Coli* concentrations in drainage was observed under the PFS 250, PFS 167, and PFS 83 treatments compared to the untreated effluent, following both treatment applications. Similar results were reported by Chisholm et al. (2020) and Che et al. (2022), who observed significant reductions in *E. coli* leaching losses when PFS-treated FDE was applied to soil drainage models. Initial *E. coli* concentrations in the PFS-treated effluents decreased substantially (Tables 4-1 & 4-2) compared to the untreated FDE. Most *E. coli* strains in effluent are neutrophilic and cannot thrive in low pH environments, which occur when FDE is treated with PFS. Furthermore, the coagulation of particles in the effluent led to *E. coli* being trapped within flocs, effectively suffocating the bacteria (Cameron & Di, 2019). As a result, the acidic nature of the PFS solution and the encapsulation within flocs led to the death of most of the of the *E. coli*, thereby reducing the amount of bacteria that could be leached out with drainage water.

This is a notable finding, as *E. coli* concentrations were almost eliminated by the two higher treatment rates, PFS 250 and PFS 167. In New Zealand, many surface waters have *E. coli* concentrations that exceed those expected under natural conditions (MfE, 2020b), posing a health risk to both humans and animals. The results from this study indicate that FDE can be effectively treated with a lower rate of PFS than previously used while still achieving the same environmental benefit of reducing *E. coli* leaching.

#### 4.4.3 Timing of application

The environmental conditions during the first and second applications were substantially different due to seasonal effects. The first application occurred in autumn following a precipitation event (7 mm), with another precipitation event (23 mm) occurring two days following the application. This represented a simulation of poor management of application of effluent to land but one that could occur on farm. Following the first application, the results showed that treating FDE with PFS 250 and PFS 167 eliminated leaching losses of DRP, TDP, and TP (Figure 7) despite the poor timing of the application.

Following the second application, which took place in late winter and when no rain was forecasted, all three PFS rates achieved similar breakthrough curves to the untreated FDE. This can primarily be explained by the fact that there were lower TP and *E. coli* concentrations within the effluent used in the second application compared to the first, reducing the amount that could be leached.

As discussed in Chapter 2, section 2.6.3.2, Houlbrooke et al. (2008) investigated nitrogen and phosphorus losses in subsurface drains after a poorly timed application of 25 mm of FDE at a soil moisture deficit of 7 mm in mid-September. The following day, 12 mm of rainfall caused additional nutrient loss through preferential flow. Their findings indicated that improperly timing an application of FDE to land could lead to nutrient concentrations in drainage that are 6 to 10 times higher than those expected under best management practices, something which can severely impact waterway health. In comparison, the study presented in this paper demonstrated that even under a poorly

timed FDE application such as the first treatment application in this experiment, treating FDE with PFS significantly reduced phosphorus concentrations in drainage.

A malfunction occurred with the data logger system controlling the RISS on top of the drainage model units, leading to multiple unintended irrigation events of 10 mm each during the night of May 12<sup>th</sup> 2023, approximately a month after the treatment application. This resulted in a total application of 116 mm irrigation. The experiment continued, with the decision made to consider this error as a simulation of an extreme rainfall event or a farm irrigator malfunctioned. Due to this malfunction, about 100 mm of drainage was collected. However, there was no significant increase in P concentrations in the drainage, likely because most of the mobile P in the soil had already been leached out. Therefore, the results were not affected by this incident.

#### 4.4.4 Greenhouse gas emissions from land after effluent application

There were no significant differences in the cumulative CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> gas emissions between all three rates of PFS-treated effluent, the untreated effluent, and the control. This demonstrates that FDE can be treated with PFS before being applied to land without causing an increase in GHG emissions. Similar results have been obtained by Wang et al. (2019) and Chisholm et al. (2020).

The N<sub>2</sub>O emissions under the untreated FDE and PFS-treated effluents immediately after treatment application were similar to those reported in previous studies. These studies showed that nitrous oxide emissions increase immediately following the application of animal urine and/or FDE application to land, then decrease to levels similar to the control after about 24 hours (Barton & Schipper, 2001; Bhandral et al., 2007; Li et al., 2015). The total amount of N<sub>2</sub>O emitted was however not significantly different between the treated and untreated FDE treatments.

The CH<sub>4</sub> emissions and uptakes were similar across all treatments. Studies have shown that soils can uptake methane from the atmosphere, with the CH<sub>4</sub> uptake rate largely depending on soil properties such as soil texture, bulk density, and water content, and on climate (Wang et al., 2014; Hansen et al., 2024).

The data from this study shows that PFS rates of 250 mg Fe/L, 167 mg Fe/L, and 83 mg Fe/L would not increase GHG emissions after application of PFS-treated effluent to land compared to the application of untreated FDE. Therefore, the hypothesis that the treatment of FDE with varying rates of PFS would have no effect on GHG emissions can be accepted, demonstrating that all three rates can be used without adverse environmental effects.

#### 4.4.5 Herbage yield

There were no significant differences in herbage dry matter yield and N and P herbage uptake between all five treatments. This shows that the rate of PFS used to treat effluent applied to land does not compromise pasture production or typical plant mechanisms of nutrient uptake. These results agree with previous studies which came to the same conclusion (Cameron & Di, 2019; Chisholm et al., 2020; Che et al., 2022).

The N concentrations in herbage declined across all five of the treatments as the trial progressed. Initially, during the autumn, the perennial ryegrass pasture required more nitrogen to support its active vegetative growth. As the trial went on, nitrogen uptake decreased as the pasture transitioned into its reproductive phase, where energy was redirected from leaf production to seed development (Gislum et al., 2007).

#### 4.5 Conclusions

Results from this study show that farm dairy effluent can be treated with a reduced rate of poly-ferric sulphate than has been previously used to reduce phosphate and *E. coli* leaching losses from treated effluent applied to land. The hypothesis that treating FDE with a lower rate of PFS than 250 mg Fe/L can achieve significant reductions in phosphate leaching is therefore supported by this study.

Although the PFS 83 treatment rate also showed some significant reductions, it was not as effective as the higher rates and would not be a suitable rate to achieve sufficient reductions in P and *E. coli* leaching losses. This was most likely because the concentration of ferric hydroxides produced in the effluent was not sufficient to bind phosphate.

The reductions in phosphate concentrations in drainage under the PFS-treated effluents were attributed to ferric hydroxides within the PFS reacting with phosphate ions in the effluent to reduce their mobility in the soil. Additionally, the ferric hydroxides bind with particulate phosphate to form flocs, encapsulating the *E. coli* in the process. This, along with the acidification of the effluent caused by the acidic nature of PFS caused the majority of the *E. coli* to be killed.

Furthermore, the hypothesis that greenhouse gas emissions are not affected by the rate of PFS used to treat the effluent was also accepted as there were no significant differences between the CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> gas emissions from the PFS-treated effluents and the untreated FDE.

These results were in accordance with studies by Cameron and Di (2019), Wang et al. (2019), Chisholm et al. (2020), Cameron and Di (2021), and Che et al. (2022).

## Chapter 5 General conclusions and recommendations for future research

### 5.1 General conclusions

A review of the literature identified gaps in knowledge around the effect of treating farm dairy effluent with poly-ferric sulphate at rates lower than 250 mg Fe/L. The research described in this thesis has addressed these knowledge gaps through a field trial experiment.

#### 5.1.1 Effect of different rates of PFS on phosphorus leaching losses

In the field trial (Chapter 4) it was found that the peak DRP, TDP, and TP concentrations in the drainage water following the first effluent application of FDE reached 4.04 mg P/L, 4.88 mg P/L, and 9.32 mg P/L, respectively. Treating FDE with the two higher rates of PFS (250 mg Fe/L and 167 mg Fe/L) resulted in reduced peak concentrations of DRP, TDP, and TP compared to untreated FDE, following the first effluent application. Following the second effluent application there was no significant difference between the peak DRP and TDP drainage water concentrations of all five treatments. For the peak TP drainage concentrations, the PFS 250 (0.3 mg P/L) resulted in a significant reduction of 90.8% compared to the untreated FDE (3.27 mg P/L).

The PFS 250 showed reduced peak concentrations of DRP, TDP, and TP by 96.7% (0.13 mg P/L), 97.7% (0.11 mg P/L), and 74.7% (2.35 mg P/L), respectively, compared with the untreated FDE treatment. The PFS 167 resulted in reduced peak concentrations of DRP, TDP, and TP by 96.5% (0.14 mg P/L), 97.3% (0.13 mg P/L), and 85.0% (1.40 mg P/L), respectively, compared with the untreated FDE treatment. The reductions in peak concentrations from the PFS 250 and PFS 167 were not significantly different from each other, or to those of the control for TDP and TP. For DRP peak concentrations, the PFS 250 and PFS 167 results were not significantly different from each other and were significantly lower than those of the control ( $P < 0.05$ ).

Treating effluent with the PFS 83 rate was also effective at reducing the peak concentrations of DRP and TDP, but not to the same extent as with the two higher PFS rates. It resulted in a significant reduction of 90.5% (0.38 mg P/L) and 85.5% (0.71 mg P/L) for the DRP and TDP peak concentrations, respectively. However, these concentrations were significantly higher than the concentrations of the PFS 250, PFS 167, and the control ( $P < 0.05$ ). Furthermore, treating FDE with the PFS 83 rate did not reduce the peak TP concentration in drainage.

The total amount of DRP, TDP, and TP leached from the untreated FDE treatment was 0.80 kg P/ha, 1.13 kg P/ha, and 1.70 kg P/ha, respectively. All three rates of PFS treatment of FDE (PFS 250, PFS 167, and PFS 83) were not significantly different to the control, and resulted in significant reductions in the leaching loss factors from the total amount of DRP leached; 111.13%, 107.77%, and 80.56%, respectively, ( $P < 0.05$ ). Similarly, all three rates of PFS-treated FDE significantly reduced the total amount of TDP leached compared to untreated FDE and were not significantly different to the control. The reductions in the leaching loss factors were of 115.47%, 112.85%, and 80.17%, from the PFS 250, PFS 167, and PFS 83, respectively. The PFS 250 and PFS 167 treatments significantly reduced the leaching loss factors from the total amount of TP in drainage by 85.02% and 90.72%, respectively, and were not significantly different to the control. The total amount of TP in drainage from the PFS 83 showed no significant difference to the untreated FDE or to the control.

In addition, treating FDE with the PFS 250 and PFS 167 treatments reduced the total amount of DRP and TDP in drainage to a lower concentration than the control, showing that these treatments can not only eliminate phosphate leaching from farm dairy effluent application, but also reduce the leaching losses to levels below those of the control (shown by reductions greater than 100%).

These results were attributed to the reactions which occur between the phosphate in effluent and the ferric hydroxides formed in the PFS-treated effluent. These reactions reduce the concentration of DRP in the treated effluent and reduce the mobility of phosphate within the soil matrix when PFS-treated effluent is applied to land.

#### 5.1.2 Effect of different rates of PFS on *E. coli* leaching loss

Results for the *E. coli* concentrations in drainage water in the field trial showed that treating FDE with all three rates of PFS significantly reduced *E. coli* concentrations ( $P < 0.05$ ). The *E. coli* concentrations in the drainage water from the PFS 250, PFS 167, and PFS 83 treatments represented a 99.9%, 99.9%, and 57.9% reduction after the first application and a 99.9%, 99.9%, and 99.4% reduction after the second application, respectively, compared with those from the untreated FDE treatment.

The decrease in *E. coli* concentrations was linked to the interactive effects by the acidic ferric sulphate and the encapsulation of the *E. Coli* within flocculated effluent.

#### 5.1.3 Effect of different rates of PFS on greenhouse gas emissions

The field trial indicated that the cumulative CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> gas emissions from the soil were not significantly different between all three rates of PFS, the control and the FDE. There was an initial increase in N<sub>2</sub>O emissions immediately following the first treatment application under the untreated FDE and PFS-treated effluents, as is expected following the application of cattle excrement to soil.

#### 5.1.4 Effect of different rates of PFS on herbage dry matter yield and N and P uptake

The field trial showed that there were no significant differences in herbage dry matter yield or N and P herbage uptake between treatments. Therefore, pasture production was not affected by the application of PFS-treated effluents at any of the rates tested.

#### 5.1.5 Implications for future farm management

Incorporating and running an EcoPond system on-farm to treat effluent increases management costs. Prior research had demonstrated that poly-ferric sulphate is an effective treatment for the mitigation of phosphate and *E. coli* leaching during the application of effluent to land (Wang et al., 2019; Chisholm et al., 2020; Che et al., 2022) but had not investigated the effects of using lower rates of the treatment. Therefore, the results from the field trial are important because they provide a better understanding of the efficacy of different rates of PFS treatment in mitigating phosphate and *E. coli* leaching losses from the application of effluent to land. The results indicate that lower rates of PFS treatment than previously published could achieve similar results, while not having an effect on pasture yield or greenhouse gas emissions.

The field trial showed that the poly-ferric sulphate rates 250 mg Fe/L and 167 mg Fe/L completely eliminated DRP and TDP leaching, with the concentrations of DRP and TDP in drainage under these treatments being lower than those of the control. These two PFS rates also significantly reduced TP and *E. coli* concentrations in drainage, demonstrating that a lower rate of PFS than 250 mg Fe/L can significantly reduce leaching of *E. coli* and all forms of phosphorus.

The PFS rate 83 mg Fe/L achieved some significant reductions in phosphate leaching and *E. coli*, but it was not as effective as the two higher rates and would therefore be unlikely to be an adequate rate to achieve sufficient reductions in phosphate and *E. coli* leaching losses.

The average dairy herd size in New Zealand is about 440 cows (DairyNZ, 2023). Around 70 L of water is used per cow per day to wash the dairy shed (DairyNZ, 2014). This amounts to 8,316,000 L entering effluent ponds per milking season, for a 270-day milking season. Based on the results of the field trial, a PFS treatment rate closer to 167 mg Fe/L, rather than the current 250 mg Fe/L could be

used by farmers, decreasing the total amount of PFS required by 4,324 L PFS. This would decrease the annual operating expenditure (OPEX) costs of EcoPond technology on-farm.

The loss of contaminants, such as phosphorus and *E. coli* from agricultural land, contributes to the growing pressures on in-stream biological health (Parliamentary Commissioner for the Environment, 2015). With the growing need to produce more food, this pressure is likely to increase, and mitigation activities are required to improve water quality. Awareness of the environmental impacts of nutrient loss from agricultural areas is growing, and with it, legislation concerning the management of farming activities. Recent national policy has set water quality objectives for N, P, and sediment in waterbodies (MfE, 2020c). Regional councils around New Zealand are setting environmental guidelines for the management of DRP in waterways, to reduce the risk of eutrophication and harmful aquatic algal growth. The recent policy frameworks, Te Mana o te Wai, and the National Policy Statement for Freshwater Management (MfE, 2024a) aim to restore and preserve the health of waterways in New Zealand. Under these guidelines, DRP concentrations must be monitored and maintained to their current levels or improved (MfE, 2020a). These policy frameworks are currently under review, but the frameworks which will replace them are likely to support similar objectives for maintaining and improving water quality.

This is especially prominent in areas such as Southland, where rivers and streams have some of the highest levels of sediment, faecal bacteria, nitrogen, and phosphorus in the country (Environment Southland, n.d.). The Proposed Southland Water and Land Plan has been made operative (in part) in 2021 by Environment Southland and outlines guidelines on nutrient losses, including phosphorus, to achieve objectives for macroalgae and phytoplankton reductions (Snelder, 2021; Environment Southland, 2024). Within these guidelines, farmers must ensure farming activities do not increase phosphorus discharge to waterways and avoid, where reasonable, leaching of phosphorus, nitrate, microbial contaminants, and sediment. Freshwater farm plans will need to outline actions undertaken to minimise the risks identified of adverse effects of farming activities such as the leaching of nutrients and contaminants (Kiro, 2023; Environment Southland, 2024). Other areas in New Zealand have also begun introducing freshwater farm plans, namely, parts of Waikato, Otago, the West Coast, and Manawatu-Wanganui (MfE, 2024b) and this will soon progress to every region of New Zealand.

Additionally, public perceptions of what defines 'good' water quality have evolved in recent years, with growing emphasis on food production systems that do not compromise essential resources such as water quality (Stokes et al., 2021). There is a growing incentive for farmers to improve their environmental practices to gain a competitive edge in the food export market. As consumers' awareness about sustainability grows, so does their willingness to pay a premium for products that align with environmentally friendly and sustainable practices. For dairy products, the price premium is of 25% when the product can be labelled as 'Environmentally friendly' (Our Land and Water, 2021). This market price premium could offset the costs of mitigation solutions on-farm, such as the EcoPond technology.

Hence, the EcoPond technology is an effective mitigation tool for treating farm dairy effluent to reduce phosphate and *E. coli* leaching, while not impacting greenhouse gas emissions or pasture production. This contributes to actionable steps farmers can include in their freshwater farm plans to support water quality and health.

## 5.2 Future research

In view of the results obtained from the field trial, it is hypothesised that the 'optimal' PFS rate is around 167mg Fe/L for the conditions under which the trial was performed. The optimal rate of PFS

is likely to be dependent on several parameters including effluent composition, weather, and climate. It is recognised that this study used lysimeters that only represented artificially drained Templeton silt loam soil and it is likely that soil type is also a key parameter.

It is therefore recommended that additional research be conducted to identify the key effluent and environmental parameters which influence the optimum PFS rate and the relative phosphate leaching loss reduction. These parameters may vary based on the farm management system, location of the farm, and the soil characteristic. Consequently, further research is recommended to understand how these factors influence the required rate of PFS to effectively reduce phosphate leaching losses. While it is expected that this rate may not vary significantly between farm locations, this hypothesis should be tested.

Furthermore, three rates of PFS were used in the field trial. It is recommended that further field research is conducted using a greater range of PFS treatment rates to improve the understanding around the effect of PFS rate on phosphate leaching.

Lastly, it is hypothesised that the reduction in phosphate leaching when FDE is treated with PFS could allow farmers to apply more effluent to land at a time, such as to match plant N requirements. Without the PFS treatment of FDE, applying effluent to land in relation to the N requirements of plants results in an application rate of P greater than the plant requirements, and an increased P leaching potential (Sharpley et al., 2000). When FDE is treated with PFS, it could be applied to land at higher rates compared to untreated FDE, with a reduced risk of phosphate leaching. This is only a hypothesis and requires field research to ensure phosphate leaching would be minimised at a higher application rate.

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