# The influence of anaerobic conditions and redox on phosphorus loss from waterlogged soils

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A thesis
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Genevieve J Smith

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# The influence of redox and waterlogging on phosphorus loss risk from poorly drained agricultural soils

by

**Genevieve J Smith**

Diffuse phosphorus (P) loss from agricultural land contributes to surface water quality degradation. To mitigate losses and protect waterways it is important to describe all the ways that P can be mobilised and transported from land. The main aim of this thesis was to investigate P loss associated with the reductive dissolution of iron (Fe) and manganese (Mn) oxides in the soil, due to waterlogging and reducing conditions. The overall hypothesis was that anaerobic and reducing conditions in soils contribute significantly to potential annual P losses. A combination of laboratory analysis and field work was conducted in New Zealand and Ireland.

The first objective was to quantify the potentially reducible phosphorus (P) component in the lab for a range of stored soil samples, and the distribution of reducible P pools relative to known soil maps. In New Zealand, eight stored soils were tested in the laboratory (Andisol, Cambisol, Vitric andisol, Ferrasol, Luvisol, Gleysol, Arenosol/Fluvisol, and Acrisol), and five stored soils were tested in the laboratory from Ireland (Cambisol, Gleysol, Luvisol, Phaeozem, and Podzol). Current models use oxic soil tests, which may not represent anaerobic conditions. Anoxic water extractable P (anoxic WEP) and sodium-bicarbonate-dithionite extractable P (dithionite-P) tests were developed to predict soil P vulnerable to reductive dissolution and potential loss under anaerobic conditions. In New Zealand and Ireland, anoxic WEP and dithionite-P varied by soil order and land use, and anoxic WEP was greater than oxic WEP, which showed the short-term impact of soil anoxia on P release. Models predicting anoxic WEP and dithionite-P at the 1:50,000 scale in New Zealand found relatively small proportions

of agricultural land were enriched in dithionite-P (31% >85 mg kg$^{-1}$) or anoxic WEP (3% >0-0.291 mg L$^{-1}$).

The second objective was to determine if redox reflects changes in P and redox-sensitive components, with attention to the length of time that the soil is saturated, P fertiliser treatment, and temperature. The second laboratory experiment was an incubation comparing the rate and extent of P release across contrasting soil textures (clay loam, silt loam, sandy loam), three long-term P fertiliser levels, at two temperatures (3$^{o}$C v.s. 18$^{o}$C), and two oxygen levels (oxygen < 0.5 mg L$^{-1}$ v.s. > 7 mg L$^{-1}$). The mean dissolved reactive P (DRP) concentration and its rate of release increased with fertiliser application, temperature, and in two soils, anoxic conditions - commensurate with the depletion of nitrate ($NO_3^-$) and the reductive dissolution of Fe and Mn. The release of P was complete within 24 hours, which showed that the reaction, and potential for enhanced P loss, could occur within a day of saturation.

The third objective was to observe trends in the release of P and other redox-sensitive species into soil solution under saturated conditions, during the drainage season. A field experiment monitored a New Zealand soil profile with 16 unsaturated zone samplers installed down to 20 and 80 cm below ground level, from May to September of 2017 and 2019. They were installed to observe P and Fe release as the profile wets up or dries out. Events that saturated soil caused reducing conditions that released up to 77% and 96% greater P and Fe, respectively, than average over the rest of the sample period. Artificial saturation experiments in the laboratory and in the field used the same soil as the field experiment and showed that soils treated with $NO_3^-$ released up to 86% less DRP and 98% less Fe than the soil that received no N. This showed that the reduction reaction was buffered by the presence of $NO_3^-$.

The fourth objective was to determine the role of redox processes in the release of P and other redox species within and across drainage and runoff events. Flow-weighted artificial drainage and runoff samples were collected from four hydrologically-isolated plots on the same slope in Ireland in 2009, 2018 and 2019. They were analysed for P and redox sensitive components and assessed throughout seasons and storm events. At the site used, dissolution of P and Fe dissolution had a stronger relationship in reducing conditions. Additionally, the reaction was not season specific. The main drivers of Fe and P release were the extent of waterlogging in the soil, and levels of $NO_3^-$.

In conclusion, an area that is prone to saturation excess could have increased P loss due to reductive dissolution. The research presents two updated soil test methods and predictive equations that could be used to improve estimations of P loss from poorly drained areas and specific soil types. Laboratory data gives evidence that soil texture, P fertility levels, temperature and oxygen conditions affect the amount and rate of WEP released within 24 hours of waterlogging. Field data shows that the relationship between P and Fe can be seen in soil solution as well as at the drainage output. The present work also shows that waterlogging and $NO_3^-$ levels are key drivers in the occurrence of P and Fe dissolution from soil. Therefore, the research highlights periods where warm temperatures and high moisture conditions coincide as high risk. Having a high P/low $NO_3^-$ system, particularly in sites that are prone to saturation events may exacerbate P release into waterways in the future. The influence of waterlogging and anaerobic conditions on Fe and P should be integrated into current critical source area models and used to inform potential mitigation strategies.

**Keywords:** Anaerobic, saturation, drainage, iron-oxide, phosphorus, WEP, sodium-bicarbonate-ditionite.

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1. AgResearch, Invermay, New Zealand: Project proposal and initial experiments (March-September, 2017)
2. Teagasc, Johnstown Castle, Wexford, Ireland: Experimental phase (September 2017-February 2019)
3. Lincoln University, Canterbury, New Zealand: Experimental phase and thesis write-up (April 2019-November 2020)

Some of the results of this project have been presented in the following conferences:

- G. J. Smith, R. W. McDowell, L. Condron, O. Fenton, P.-E. Mellander, K. Daly, D. Ó hUallacháin (2018) Redox-sensitive phosphorus remobilisation in grassland soils: In progress. Environ2018 Conference, 26-28 March, Cork, Ireland
- G. J. Smith, R. W. McDowell, L. Condron, O. Fenton, P.-E. Mellander, K. Daly, D. Ó hUallacháin (2018) Redox-sensitive phosphorus remobilisation in grassland soils. HighRes2018 Conference, 12-13 June, Clonakilty, Ireland
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Chapters 2 to 5 have been submitted to journals, and the following articles have been published or will be published presently:

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# Abbreviations

| *Abbreviation* | *Definition* |
|---|---|
| BGL | Below ground level |
| $CaCl_2$-P | Phosphorus released in calcium chloride solution, representative of subsurface P release |
| CBD-Fe | Citrate-bicarbonate-dithionite extractable iron |
| CSA | Critical source area |
| DOC | Dissolved organic carbon |
| DRP | Dissolved reactive phosphorus |
| Fe | Iron |
| HSA | Hydrologically sensitive area |
| LiDAR DEM | Light Detection and Ranging Digital Elevation Models |
| $LSD_{05}$ | Least significant difference ($P < 0.05$) |
| Mn | Manganese |
| N | Nitrogen |
| Dithionite-P | Bicarbonate-dithionite extractable phosphorus |
| ORP | Oxidative-reductive potential |
| P | Phosphorus |
| PP | Particulate phosphorus |
| SOM | Soil organic matter |
| STI | Soil topographic index |
| TP | Total phosphorus |
| Anoxic WEP | Water-extractable P in anaerobic conditions |
| Oxic WEP | Water-extractable P in aerobic conditions, representative of surface P release |

# Chapter 1

# Introduction

## 1.1 Background

Projected estimates set the world population at 9.1 billion by 2050, with half of that population being urban (FAO, 2009). There has been a shift in focus to ensuring that the primary sector can provide for this expected demand. Despite cropland and pasture occupying already around 40% of global land area, many countries are reaching (or have reached) their limit of land use, and with an anticipated growing urban population, it is expected that food production would have to increase by 70% between 2005 and 2050 to support the new population estimate (FAO, 2009; The World Bank, 2007). Therefore, there is pressure on farming groups around the world to meet new milestones between now and 2050 (FAO, 2009; MPI, 2020). Alongside this is the growing social pressure to minimise the impact of farming on environmental health. While a variety of activities and urban practices add to water quality degradation, farming has been identified as a main diffuse source of nutrient enrichment (FAO, 2009; Foley et al., 2005; The World Bank, 2007). Current N and P pollution levels may already exceed world sustainability limits (Boretti and Rosa, 2019), and it is expected that, by 2050, nitrogen (N) and phosphorus (P) effluents will increase by 180% and 150%, respectively.

The two goals of increased production and environmental health are driving the move to smarter farming using technology and science to inform sustainable production. Ideally, this would mean the rate of agricultural growth can increase to meet population pressure, without compromising environmental health (FAO, 2009; Foley et al., 2005; Schneider et al., 2011; The World Bank, 2007). In order to achieve this, the behaviour and losses of phosphorus (P) must be fully understood, so that consideration of P can be effectively incorporated into our approach to farming, and its losses mitigated. The main objectives of this review were to identify gaps in current literature about redoximorphic chemistry relating to phosphorus (P) in soil, subsurface losses of mobilised phosphorus, and methods to reduce losses.

The specific goals of this review were to:

- Summarise the key issues associated with environmental P loss from agricultural practices;
- Understand the different pools of P and their mobilisation risk in different soils;
- Identify what soil chemistry is involved in mobilising P to then be lost, and the specific chemistry involved in releasing P associated with iron (Fe) and manganese (Mn) oxides; and,
- Establish the transport pathways and speciation for P, and connectivity to surface water.

Once information was collected and gaps were identified, objectives and the main hypothesis were developed.

### 1.1.1 Case Studies: New Zealand and Ireland

Ireland and New Zealand both have milestones established for increased primary outputs by 2020 and 2025 respectively. The Irish Food Harvest 2020 and Food Wise 2025 schemes set the target of a 33% increase in primary output value compared to the 2007-2009 average, which involves a 50% increase in milk production (DAFM, 2010). Similarly, New Zealand has goals set to double primary exports by 2025 (MPI, 2015; MPI, 2017; OECD, 2017). New Zealand and Ireland have similar populations, climates and export rates. They are also both striving to find a balance between production and the environment, where the primary sector must produce more for growing populations but cannot degrade resources and compromise future national health and production.

Agricultural grassland covers approximately half of both Ireland and New Zealand (Bord Bia, 2020; European Commission, 2019; StatsNZ, 2018). Therefore, research into the behaviour of phosphorus is necessary in order to offset potential impacts of agricultural intensification presently and in the future. Additionally, approximately 14.5% of managed Irish grassland utilises poorly drained soils, and approximately 27.7% of productive land in New Zealand is on very poorly to imperfectly drained soils (Landcare Research, 2017; Newsome et al., 2008; O'Sullivan et al., 2017). The behaviour of phosphorus in saturated and anaerobic conditions is therefore particularly important to both countries.

### Ireland

In 2017, cattle and calves made up 29% of gross output from Ireland, while milk made up 32% (Table 1.1). Dairy products were exported to almost 140 countries that same year (Department of Agriculture, 2018). Irish ground and surface waters are considered 'among the best' compared to other countries in Europe, and there have been promising downward trends in P loss to surface and groundwater (Department of Agriculture, 2018; EPA, 2012; Trodd and O'Boyle, 2018). However, there is the potential for significant unbalancing and degradation if technological and management advancements do not develop alongside primary output targets, particularly if the country is to meet their Food Harvest 2020 targets (ACP, 2012). The country works under the ecologically focused Water Framework Directive (WFD) used by the European Union (EU) and the Nitrates Directive to protect surface water, groundwater and transitional areas (ACP, 2012; EPA, 2006; EPA, 2014).

The WFD also sets objectives for Member States, to prevent further water quality degradation and work to improve areas with poor water status. If Ireland breaches WFD targets as the result of agricultural intensification, it could lose its derogation status to stock livestock above the threshold of 170 kg/ha N which would make achieving policy aims in the future much more difficult (DAFM, 2020). The Agricultural Catchments Programme (ACP) was established to monitor and research different aspects of water quality and farming in 6 catchments, highlighting the importance of catchment-specific nutrient management methods (ACP, 2012).

Table 1.1 Republic of Ireland agricultural land use statistics in 2016 (CSO Ireland, 2018)

| Description | ' 000 Hectares | % Change 2015-2016 |
|---|---|---|
| Cereals | 281.1 | -3.9 |
| Crops, fruit & horticulture | 351.7 | -2.2 |
| Crops & pasture | 3,914.8 | -0.3 |
| Dairy cows | 1,397.9 | 7.9 |
| Other cattle | 1,103.7 | 2.6 |
| Sheep | 5,179.2 | 0.8 |

### New Zealand

Currently, New Zealand stands as the twelfth largest agricultural exporter by value and is the number one dairy product exporter worldwide (MPI, 2020; OECD, 2017). Historically, low intensity sheep and beef farming was a staple of New Zealand farming but, in light of 'economic signals' over the last couple of decades, there has been a significant shift towards higher intensity land uses, particularly in the South Island (Table 1.2) (Environment Southland, 2014; MfE, 2011; Stats NZ, 2015a; Stats NZ, 2015b; StatsNZ, 2018). The decade between 2002 and 2012, there was a 10.8% (1,306,774 ha) decrease in land area dedicated to sheep and beef, and a 28.2% (877,124 ha) increase in the land area used for dairy farming (Stats NZ, 2015b). Accompanying this, the stocking rate has increased, with a 29.8% increase in dairy cattle numbers in New Zealand, representing around 1.5 million cows (Stats NZ, 2015b).

Compared to world standards, New Zealand water bodies are generally of good quality. However, there have been growing issues with water quality over the last fifty years due to increasing pressures from different land uses (MfE, 2017). This is coupled with the increasing pressure from the public to address the impacts on environmental health (OECD, 2017).

New Zealand has the National Policy Statement for freshwater management (NPS-FWM) that sets guidelines and trigger values for each regional council to implement how they see fit (MfE, 2014). Environmental thresholds for nutrients in waterways have been set by the Australian and New Zealand Environment and Conservation Council (ANZECC) to guide water quality regulations and management (e.g. Table 1.3). As a point of comparison, New Zealand's lowland river dissolved reactive phosphorus (DRP) target (0.011 mg DRP $L^{-1}$) is much lower than the EU target of 0.035 mg DRP $L^{-1}$established by the WFD (ACP, 2012; McDowell et al., 2018). It has become a matter of finding ways to 'farm within the limit', and many research institutes are involved in establishing the effects of different practices on nutrient loss and developing possible changes in management. For instance, to offset the influence of dairy intensification on local waterbodies in the Southland region, housing cows and duration-controlled grazing has been deemed a viable method to increase production but meet nutrient output requirements, whereas largescale housing in the past was unheard of (MacDonald et al., 2014).

As well as affecting local organisms and general waterway health, excess nutrient input and waterway pollution affects New Zealand's image. Although this is not as readily quantifiable as the other factors discussed, visually declining water quality can influence local recreation and tourism, affecting community satisfaction and potential revenue from water-based activities and attractions (OECD, 2017). Therefore, there has been significant research into understanding and mitigating P inputs into waterways from agricultural land.

Table 1.2 New Zealand agricultural land use statistics in 2015-16 (Journeaux et al., 2017)

| Description | ' 000 Hectares | % Change 1990-2015 |
|---|---|---|
| Sheep & Beef | 8,035 | -34 |
| Dairy | 2,258 | 67 |
| Deer | 344 | 24 |
| Other | 9 | - |
| Horticulture | 126 | 43.8 |
| Forestry | 1,681 | 28.9 |

Table 1.3 New Zealand default guideline values (DGVs) for phosphorus (McDowell et al., 2018).

| Ecosystem type | TP mg $L^{-1}$ | DRP mg $L^{-1}$ |
|---|---|---|
| Cool wet hill | 0.016 | 0.008 |
| Cool wet low-elevation | 0.018 | 0.011 |
| Cool extremely wet low-elevation | 0.009 | 0.013 |
| Warm wet hill | 0.017 | 0.008 |
| Warm wet low-elevation | 0.024 | 0.014 |
| Warm extremely wet low-elevation | 0.017 | 0.006 |

DRP = dissolved reactive phosphate; TP = total phosphorus

### 1.1.2 Phosphorus in the Environment

Phosphorus is an integral nutrient in animal, microbial and plant processes. In the context of agriculture, it has become an important part of maintaining plant health, quality and yield, and pushing the limits of production to meet new demands (Haygarth et al., 1998; Leinweber et al., 2018). Agricultural systems remove P from the plant-soil continuum when crop and animal products are taken away. Agricultural practices rely on the P supply in the soil being replenished and maintained, so there is a dependence on anthropogenically-sourced P fertilisers (Table 1.4) or manures (Bomans et al., 2005). A key practice in agricultural production is applying nutrients like N and P to crops via fertilisers and manures, particularly under intensified regimes (Leinweber et al., 2018; Leinweber et al., 2002).

Table 1.4 International phosphorus fertiliser demand from 2017 to 2020 (FAO, 2017).

| Region | Demand (thousand tonnes P fertiliser) | | | |
|---|---|---|---|---|
| | 2017 | 2018 | 2019 | 2020 |
| Asia | 24056 | 24544 | 25005 | 25432 |
| Americas | 12060 | 12380 | 12700 | 13009 |
| Europe | 4217 | 4269 | 4319 | 4368 |
| Oceania | 1332 | 1356 | 1376 | 1390 |
| Africa | 1529 | 1571 | 1614 | 1659 |

Total-P (TP) encompasses all forms of aqueous P, and the main forms within this are dissolved reactive P (DRP), dissolved unreactive P (DUP), total dissolved P (TDP), and particulate-P (PP). These terms define the physical chemical characteristics of the P present. Dissolved P persists in solution after being filtered at 0.45µm. The terms also define the reactivity of the forms. DRP will react with reagents used in the Murphy & Riley measurement process, while DUP will not until digested into a reactive form (Watanabe and Olsen, 1965). The sum of the two makes TDP. PP is the organic and inorganic forms of P that would be filtered out of solution at 0.45µm. PP and TDP make up the TP in solution (Leinweber et al., 2002; Selig et al., 2002; Simmonds, 2016).

Approximately three quarters of undesirable periphyton growth in freshwater systems globally is driven by P (King et al., 2015; McDowell et al., 2020). The dissolved (or filterable) forms are associated with increased periphyton and phytoplankton growth particularly in streams and rivers, as they are immediately accessible in solution. Studies suggest that algal growth requires TP concentrations greater than 0.02 mg TP $L^{-1}$, and DRP concentrations beyond 0.01 mg $L^{-1}$, provided other requirements are met (Owens and Shipitalo, 2006). Along with – and due to – the excessive algal and macrophyte growth associated with increased reactive P levels, aquatic ecosystems also develop increased turbidity; poor oxygenation; and biodiversity shifts (Hansen et al., 2002; Heathwaite and Dils, 2000; Leinweber et al., 2018; Leinweber et al., 2002). Dissolved oxygen (DO) in water is affected by aquatic plant photosynthesis, respiration, and death. Plant respiration and microbial decomposition consumes oxygen. Then, depending on how sensitive fish and micro-organisms are to habitat changes, the fluctuations in oxygen levels between oxic, hypoxic and anoxic conditions can cause biodiversity shifts or death (Wright, 2012).

The time of year at which these forms of P are lost and discharged to streams and rivers is important. During winter months when flow rates are fast in rivers and streams and temperatures are low, there is less opportunity for P to make an impact in waterways as it is quickly diluted and flushed from the system. In summer months when streamflow is lower and more sluggish, coupled with greater temperatures and light, P discharged from land will have a greater retention time and the conditions will encourage algal growths. There is also less chance for streams and rivers to be inundated and flushed to clear them of sediment and growths, so nutrients and plants accumulate. Lake systems are more sensitive to nutrient changes and can accumulate PP in lake sediments. Particulate P in sediments will support rooted plant growth and can also be released to replenish available P in the upper layers of a lake system for algal blooms in summer months (Wright, 2012).

Previous studies have shown a clear connection between agriculture and P movement to surface water bodies, via natural rainfall-runoff processes and via the artificial drainage that farms rely on to utilise poorly-drained land in wet periods (Heathwaite and Dils, 2000; Owens and Shipitalo, 2006). In recent years, there has been a focus on mitigating nutrient contributions from different sources. The issue is that losses from agricultural land are largely from diffuse or non-point source (NPS) pollution. This means that, rather than being from one localised site (a point source), P moves from a variety of small sources in the landscape and the amount lost can vary depending on the frequency or intensity of rainfall events. This makes targeted and effective mitigation significantly more difficult (Heathwaite and Dils, 2000; Leinweber et al., 2018; Leinweber et al., 2002).

On agricultural land, P losses can originate from incidental or residual transfers. The former involves recently applied nutrients being moved from source to sink before it can be properly incorporated into the soil, so is an immediate risk. The latter is a more long-term risk, as it involves the transfer of soil nutrient stores that are not being drawn from by crops. Therefore, if the supply in the soil continually outweighs the requirements of crops, the residual source represents a risk until that excess supply can be depleted. The fertiliser history and legacy soil P of a site can contribute significantly to P loss in the long term (Cassidy et al., 2016; Shore et al., 2016). Due to the variability of P bioavailability in soil and the assumption that P remains stable in the subsurface, there has been a tendency for farm managers to overcompensate when making P fertiliser decisions, particularly as the economic benefits of applying extra P outweigh the economic impact of P loss from land (Bomans et al., 2005).

However, there are risks associated with P fertiliser inputs being greater than plant requirements or the ‘agronomic optimum’. If this occurs, the plant response and economic output do not reflect the input. Beyond being wasteful financially, this practice also increases the potential for unutilised available P in soil to move away from the target area and be transported to a waterbody (McDowell and Condron, 2004; Taylor et al., 2016). Even in a well-managed system, the critical concentration of available P required in soil for good crop growth is an order of magnitude greater than the concentrations that will cause issues in waterways (Heathwaite and Dils, 2000; Owens and Shipitalo, 2006). Therefore, agricultural practices that apply in excess and increase the chances of soil P loss and transport will put water bodies at risk.

The amount of P that is transported to waterways, and the forms it is transported as, are highly variable depending on the biogeochemical processes that occur in soil and hillslope hydrology (Heathwaite and Dils, 2000). To improve P loss management, there needs to be an in-depth knowledge of the different flow pathways of P; the opportunities for attenuation in each relevant pathway; and what affects the kinetics of P transfer in soils. This review will explore source, release and transport factors that dictate how much P is lost to the environment and via what pathway.

### 1.1.3 Phosphorus in Soil

Soils are the source of P for plant uptake and for transfer to watercourses. The potentially mobile P fraction and the relevant processes that can influence it need to be defined first before moving on to the hydrological, soil and land use effects (Taylor et al., 2016). When considering the risk of P loss to water, there first needs to be a mobile or potentially mobile soil P fraction that could pose a risk.

There are several forms of phosphorus in soil that can be divided into categories, namely: reactive and unreactive or soluble and insoluble. The categories dictate how available the P is to plant uptake or loss: reactive P is the most readily available, and the unreactive portions represent the soil solid phase (Hansen et al., 2002). The amount of P vulnerable to loss depends on the concentration of P in soil solution (primarily in the form of orthophosphate anions) and the fixation and solubilisation processes that occur in a soil that can remove or release P to the readily-available pool (Figure 1.1). There are three relevant processes that lead to fixation: sorption, precipitation, and immobilisation. With each of these, the reverse processes that can return P to soil solution: desorption, dissolution, and mineralisation, respectively (Lindsay, 1979; Shaheen and Rinklebe, 2015).

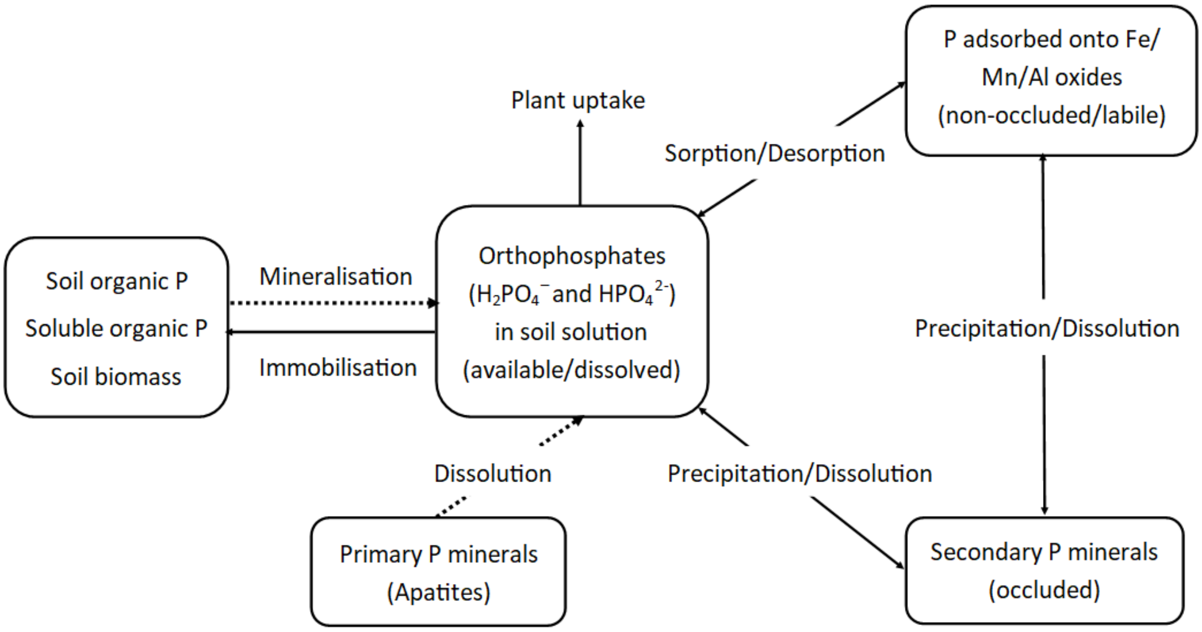

Figure 1.1 Relevant transformations that affect dissolved phosphorus concentrations, adapted from Dodd (2013).

Sorption can happen at variable rates, and involves either adsorption onto solid surfaces or absorption into oxides and minerals to form precipitates (Shaheen and Rinklebe, 2015). In adsorption, orthophosphates bind to the surface of minerals via ligand exchange reactions (*viz.* chelation) (McLaren and Cameron, 1996). Relevant soil cations that P anions can bind to are Fe, aluminium (Al), calcium (Ca), magnesium (Mg), and Mn, but amorphous hydrous oxides of Fe and Al (Fe/Al oxides) and short-range aluminosilicates are the primary contributors to sorption (McLaren and Cameron, 1996). The relative abundance of these materials can dictate the anion sorption capacity (ASC, or P retention) of a soil, and can be an indicator of P loss risk (Hansen et al., 2002; King et al., 2015; Leinweber et al., 2002; Lindsay, 1979; Mackey and Paytan, 2009; McLaren and Cameron, 1996). In the short term, P adsorbed to the surface of oxides and amorphous material is in equilibrium with solution P and, depending on the local conditions, can desorb and re-enter soil solution to replenish soluble P if plant uptake or environmental losses occur. This can occur within seconds to minutes. Therefore, of the sorbed P fraction, this pool presents the greatest potential for becoming readily available and being lost (Haygarth et al., 1998; Haygarth and Jarvis, 1999). The binding efficiency to these materials can be affected by a variety of conditions in the soil, such as pH and the presence of competitive anions. Conditions and factors that influence ASC could therefore affect how much P is left vulnerable to loss via surface and subsurface flow.

Chemical processes can lead to P becoming strongly sorbed or occluded and therefore unreactive, as it is in a more stable form. Occlusion is the term for when phosphate ions either diffuse into soil minerals or if phosphate ions adsorb onto the surface of soil minerals and are then trapped under coatings or concretions of Al- or Fe-oxides (Haygarth et al., 1998; Haygarth and Jarvis, 1999; McLaren and Cameron, 1996). As shown in Figure 1.1, adsorbed P or soil solution P can be precipitated into secondary P minerals by reacting with soluble minerals. These minerals render P insoluble, and potential solubility will vary with pH. Biologically, P can be rendered unreactive via immobilisation (Lindsay, 1979; Mackey and Paytan, 2009). Transitory immobilisation occurs when microbes absorb inorganic P into their cellular biomass to aid tissue synthesis (Mackey and Paytan, 2009). In the process, P is converted to organic forms and can be incorporated into organic matter. This type of immobilisation is restricted to the lifetime of the microbe, so can re-enter the reactive P pool after cell death. The rate of immobilisation and mineralisation is affected by temperature, moisture, organic matter content, and aeration (McLaren and Cameron, 1996).

Unreactive or insoluble forms are technically in equilibrium with reactive forms and can be released and move back into solution via desorption, dissolution, or mineralisation. These are the reverse processes of sorption, precipitation, and immobilisation, respectively. The reactions to remobilise strongly occluded or immobilised P are considered too slow to be significant in farming practices (Hansen et al., 2002; McLaren and Cameron, 1996). However, as stated, organic P immobilisation can vary.

## 1.2 Factors affecting phosphorus availability to transport

### 1.2.1 Phosphorus fertility and saturation

P loss occurs to some extent from most soils. However, when P inputs accumulate on P binding sites, the soil profile can eventually become saturated and lead to increased DRP losses (Bomans et al., 2005; Ekholm et al., 2005; Heckrath et al., 1995a; Sharpley, 1995). In agriculture, fertility is anthropogenically maintained using manures or fertilisers, which increases the fraction of readily available P in the topsoil. In response, fixation reactions will occur that remove P from solution. However, there is a limit to this (Haygarth and Jarvis, 1999).

As discussed, different soil orders in the New Zealand soil classification (IUSS Working Group WRB, 2015) will have varying levels of mineral surfaces or active sites for P anions to react with. Therefore, depending on the quantity of these active sites, different soil orders will have different ASCs, and will reach anion saturation thresholds at different rates (Table 1.5). A profile is never truly saturated, but high saturation levels mean a decreased fixation efficiency. For instance, P saturation may occur relatively quickly in a fragic pallic soil that has an ASC of 20% due to a low quantity of Fe/Al oxides, but there is a high P input (Ekholm et al., 2005). Dissolved P losses are exacerbated in soils with lower ASC (McDowell et al., 2015). Meanwhile, allophanic soils like those in the Waikato region in New Zealand have large amounts of a short-range order aluminosilicate called allophane, which provides a high ASC. Soils with high ASCs can sorb greater quantities of applied P before the profile is considered saturated (Ekholm et al., 2005). The degree of P saturation in different soils is defined by the Equation 1 (Sharpley, 1995):

$$Degree\ P\ Sorption\ saturation\ (\%) = \frac{Olsen\ P}{ASC} * 100 \qquad \text{Eq. 1.1}$$

When there is a high degree of P sorption saturation, the soil’s ability to retain added P in a form that will not easily be carried in runoff or drainage decreases, so the soil has a greater potential to enrich runoff with DRP (Sharpley, 1995). ASCs in specific soil types have been catalogued (Table 1.5). However, this only applies for oxic conditions. Tests conducted in aerobic, controlled conditions may not reflect the variable and dynamic conditions in the field where periods of anoxia often occur (Zhang et al., 2010). Therefore, while we rely on these values to inform fertility management decisions, it is potentially an oversight to not also have a database of capacities when soils are anaerobic.

Table 1.5 Topsoil anion storage capacity categories of soil orders in New Zealand, adapted from McLaren and Cameron (1996) and Saunders (1965)

| P retention/ASC category | Soil order |
|---|---|
| Very low to low (0-30%) | Organic soils |
| Low (0-30%) | Pallic soils<br>Ultic soils<br>Podzols<br>Recent soils<br>Raw soils |
| Medium to high (31-85%) | Brown soils<br>Pumice soils |
| High to very high (86-100 %) | Granular soils<br>Allophanic soils |

Soil tests are used to establish the fraction of P ('soil test P' or STP) in soil that can easily move into soil solution (*viz.* Labile). There are several tests such as Mehlich 3-P or Morgan's P, but New Zealand predominantly uses the Olsen P test. Results from these tests are used to guide fertility management but are also used as a proxy measurement of P loss potential to water (Heckrath et al., 1995a; King et al., 2015; McDowell, 2015; McDowell and Condron, 2004; Taylor et al., 2016). There are several studies that show how Olsen P and ASC influence P loss. The general trend is that increasing Olsen P will increase P loss risk, particularly when coupled with a lower ASC. The risk of P loss in soil typically follows a similar upward curve as Olsen P increases, but at different rates for each soil type.

Specifically concentrating on the study by Simmonds (2016), there is an increase in P loss concentrations with each Olsen P increment from natural Olsen P levels to 80 mg $L^{-1}$ (Figure 1.2, bottom). The increase is particularly notable in the organic soil, which has a significantly lower ASC (5% ASC). The brown soil appeared to exhibit more gradual changes than the Organic soil and required a greater input of P to elicit the same response. It should be noted that the data for the Organic and Brown soil were collected are under lab conditions.

### 1.2.2 Soil pH

Soil pH influences the amount and availability of anions and cations in soil solution. In the context of P, the ratio of $H_2PO_4^-$ : $HPO_4^{2-}$ anions increase in more acidic conditions (pH<7), and vice versa. The soil pH can also influence which metal oxides (Al, Fe, Mn, Mg and Ca) will contribute more significantly to sorption and precipitation, sorption strength, and the solubility of phosphate minerals. Acidic conditions will favour adsorption to colloidal Fe/Al minerals, or precipitation to form Fe/Al phosphate minerals. Meanwhile P in alkaline conditions of around pH 8 will swiftly react with dominant cations $Ca^{2+}$ and $Mg^{2+}$ (Figure 1.2). Dissolution of Ca phosphates will occur in sufficiently acidic soils, while Fe/Al phosphate dissolution will occur in alkaline soils (Simmonds, 2016). Therefore, chemical processes that alter pH can affect a soil's sorption ability, as some soils will have a greater proportion of certain metal oxides than others.

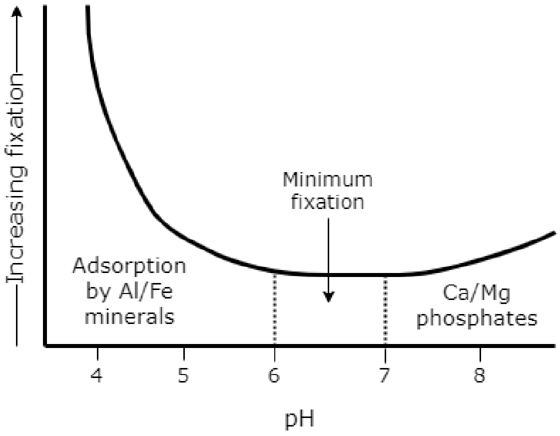

Figure 1.2 Oxide sorption and availability of P from pH 4-8 (McLaren and Cameron, 1996)

Minimum P sorption occurs between pH 6-7, so P availability is at a maximum in this range (Leinweber et al., 2018; Leinweber et al., 2002; Lindsay, 1979; Sato and Comerford, 2005). Studies attribute decreased P sorption as soils' pH increase to two reasons. The first is that the increased pH corresponds with an increase in hydroxyl ($OH^-$) concentrations, which increases the competition for mineral adsorption sites between $OH^-$ and $PO_4^-$ ions. The other is that increasing pH reduces the number of sorption sites available for P, either via the neutralisation and precipitation of cations, or through an increase in negativity on mineral surfaces that would repel phosphate anions (Sato and Comerford, 2005).

### 1.2.3 Redoximorphic reactions

Fe/Al oxides contribute significantly to P retention in acid soils. Therefore, any conditions that compromise the minerals' ability to retain P will influence the readily-available pool (Prem et al., 2014). When soils are anaerobic, natural microbial respiration can lead to the reductive dissolution of Fe (and Mn) compounds, converting them and associated P to soluble forms.

Abiotic or chemical Fe reduction can also occur but is not coupled with reduction of oxygen and $NO_3^-$ like the biotic reaction (Ionescu et al., 2015; Melton et al., 2014). Microbial respiration involves a reaction where an electron donor (e.g. carbon) gives an electron ($e^-$) to a redox-sensitive terminal acceptor. By gaining an electron, the acceptor is converted to a reduced species, and the microbial mediator gains energy from the reaction. Typically, microbial respiration favours oxygen as an electron acceptor as the reaction is energetically more favourable than with other potential acceptors. The hierarchy of preferred electron acceptors is demonstrated in Figure 1.3. In anaerobic conditions, after oxygen is depleted by respiration processes, the next most favourable available acceptor will be used. This continues down the electron acceptor hierarchy (McMahon and Chapelle, 2008).

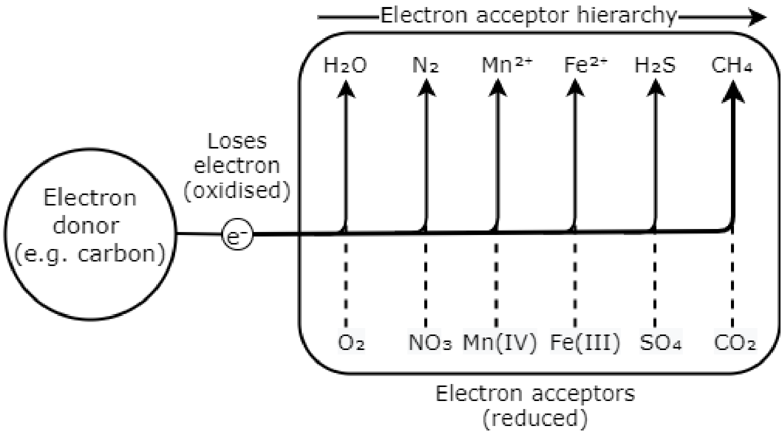

Figure 1.3 The electron acceptor hierarchy in bacterial respiration and redox transformations (McMahon and Chapelle, 2008).

The active form ferric oxyhydroxide (Fe[III]) is redox-sensitive, and can be reduced to its $Fe^{2+}$ species in soil (Lindsay, 1979). P that was coprecipitated in ferric oxyhydroxide (Fe(III) phosphates) will no longer be sorbed and can exchange with soil solution (Holford and Patrick, 1978; Patrick and Khalid, 1974). This fraction of P will be referred to as ‘reducible-P’. Soils can become anaerobic when they are inundated or flooded long enough for oxygen to be depleted, so soils with poor hydraulic conductivity or perched water tables can produce the correct conditions. This poses the question of whether Fe reduction in soil will have an influence on P release and loss, which is a gap in the literature. From this, there are areas that could be investigated to fill the gap. Does this process have enough of an effect to switch a site from a sink for P to a source? Are there spatial and temporal influences that will increase the likelihood, rate, and extent of release? An example of spatial influences could be that soils with a high concentration of Fe oxides would have more potential for P release than a soil with more Al. A temporal influence could be how long the soil remains saturated and anaerobic for P mobilisation to be significant. The effects of reduction on the state of P can be remedied by reoxidation, which occurs when aerobic conditions are re-established (Holford and Patrick, 1978; Patrick and Khalid, 1974). However, would this attenuating feature be relevant if P is moving before aerobic conditions are re-established? It may be possible that areas vulnerable to redox reactions can briefly become sources of P during periods of inundation and remove solubilised P before natural attenuation at the source can occur. This is an area that could be explored further.

## 1.3 Soil inundation and flooding

A soil profile that is prone to regular or prolonged inundation with water is at risk of becoming a source of mobilised P (McDowell and Sharpley, 2002). When soil profiles become saturated, normally air-filled pores are filled with water and the profile cannot be infiltrated further until drainage or evapotranspiration occurs (Houlbrooke and Monaghan, 2009). Profiles that are shallow, are slow-draining, or have high or perched water tables are particularly vulnerable to saturation (Dahlke et al., 2012). In waterlogged soils, microbial activity can quickly induce anaerobic conditions, with timeframes varying from hours to days (Leinweber et al., 2002; McLaren and Cameron, 1996; Zhang et al., 2010). As stated, these conditions can quickly cause the reductive dissolution of Fe(III) and the release of associated P in acid soils. The difference in soluble P levels in oxic versus anoxic soils has been shown to be as much as 10-fold (Holford and Patrick, 1978; Patrick and Khalid, 1974; Scalenghe et al., 2002; Scalenghe et al., 2012). This raises the question of whether, in a scenario where an aerobic soil with good drainage and an anaerobic soil are compared, there would be a significant contrast between P losses at identical Olsen P levels, or whether the poor drainage of the latter soil would mean less of the mobilised P is free to be transported.

One study measured the effects of flooding on Fe at a site in autumn and winter months, when anaerobic conditions were likely to occur. The area was inundated during this period, and the ratio of Fe(III) to Fe(II) measured. The results indicated that the soil was significantly reducing and affected the phase of P (Heiberg et al., 2010). This shows how waterlogging and subsequent reduction can lead to a site switching from being a sink of available P to a source of vulnerable P, especially as this site was adjacent to a river (Prem et al., 2014). Where controlled drainage or sub-irrigation management systems are introduced, there can be regular shifts between reduction and oxidation in the soil profile (Tan and Zhang, 2011). Tan and Zhang (2011) observed a 30% increase in filterable P concentrations in water samples from controlled systems compared to free-draining systems, and attributed this to reduction processes induced by the wetter conditions from retaining the water in the profile rather than having it immediately discharge.

Reduction reactions can lead to an acidic soil's pH increasing to near-neutral (Grybos et al., 2009; Sallade and Sims, 1997a; Scalenghe et al., 2002). As discussed, this pH is when phosphate is at its most available and phosphate minerals' solubility increases (Lindsay, 1979; Sato and Comerford, 2005; Scalenghe et al., 2002). Sallade and Sims (1997a) conducted a study observing changes in soluble Fe and pH in wetted sediments. The general trend of the study was that the redox potential (Eh) of flooded sediments gradually decreased (became more reducing) to a point where Fe compounds could be reduced, which increased pH to near-neutral; increased the soluble Fe component; and paralleled an increase in soluble P. The relationship between an increase in soluble Fe and pH was shown to be positively correlated.

When considering the effects of temperature, there were similar trends of pH increase and Fe solubility at 7°c (simulating winter and spring conditions) and 35°c, though "changes were more rapid and more pronounced" under the latter treatment. In warmer temperatures, Eh decreased within a week. Soluble P and Fe concentration changes were observed in this window, then only slightly changed over the rest of the 42-day period. Meanwhile incubation at 7°c produced more gradual changes over the first 3 weeks, then a sharp increase in soluble Fe and pH during the rest of the period (Sallade and Sims, 1997a). This study represents an extreme temperature that would be unlikely below the soil surface. However, seasonal fluctuations in soil temperature can still be observed in soils up to 10m below ground level, and show a sinusoidal pattern in depths to two metres (Figure 1.4) (Hanova and Dowlatabadi, 2007). Soils with impermeable layers or shallow depths to groundwater at 2m or less could both be prone to having a saturated portion of the soil profile affected by seasonal temperature fluctuations. There is the question of whether it is important to consider the effect of temperature on the rapidity of redox reactions, and whether the effects are significant enough to be considered when planning irrigation on easily-saturated soils in the warmer season.

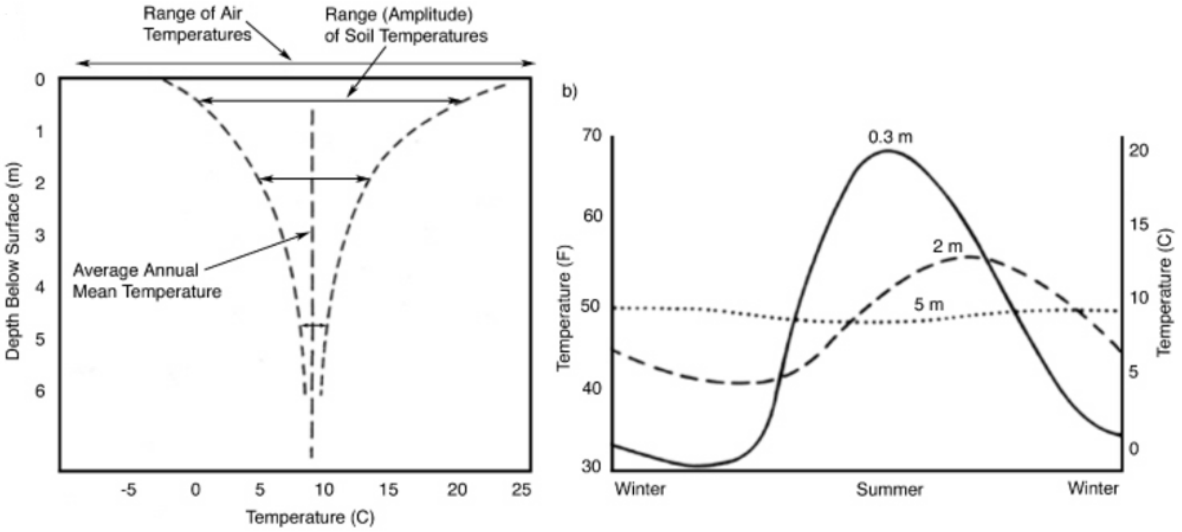

Figure 1.4 Averaged annual data for changes in soil temperature at different depths in Ottawa, Canada (Hanova and Dowlatabadi, 2007).

The impact of redox on P desorption is difficult to generalise, as it can be very spatially and temporally complex on account of variation in the extent of Fe(III) reduction, soil flooding, and timing, particularly due to seasonal and topographic differences (Zhang et al., 2010). Also, as Al is not redox-sensitive, the ratio of Fe oxides ($Fe_{ox}$) to Al oxides ($Al_{ox}$) in soil can define the impact of changes in redox potential on P retention. At similar STP values, DRP release to runoff has been shown to be greater in soils with a larger $Fe_{ox}$:$Al_{ox}$ than soils with a greater proportion of $Al_{ox}$ (Dodd et al., 2014b; McDowell et al., 2020). It could be said that Al is more important for P sorption than Fe if a soil is redox-sensitive. Additionally, knowing the ratio of the two is essential when mapping out soil vulnerability to reductive dissolution and P remobilisation. Natural remediation or attenuation of remobilised P can occur when the soil re-oxidises as the water table lowers and soils dry (Holford and Patrick, 1978; Patrick and Khalid, 1974). However, not all inundation occurs in a controlled system like the study conducted by Tan and Zhang (2011), where the discharge is minimised and remobilised P is somewhat contained until reoxidation occurs. If inundation on a slope combined with preferential flow increases the rate of flux, it is possible that reoxidation during drying would not play a part in attenuating the recently desorbed P (Heiberg et al., 2012; Prem et al., 2014). Overall, this raises the question of whether these types of soils, that are also vulnerable to anaerobic conditions and reduction are potentially significant sources of P loss.

Available organic matter in soil plays a part in driving reductive dissolution. As indicated in Figure 1.3, C is the electron donor and energy source for the microbial respiration reaction (Khan et al., 2019; McMahon and Chapelle, 2008). The effects of C content are dependent on soil type, environmental conditions and the likelihood of flooding at each site. However, a range of studies have investigated the significant positive relationship between C availability and the rate of reactions. For instance. Esberg et al. (2010) and Schmidt et al. (1997) noted a strong positive correlation between C content and increased microbial activity. A study by Chacon et al. (2006) showed that C availability could limit Fe(III) reduction rates. Additionally, they established that natural stocks of labile C in a humic tropical forest would be ample to consistently accelerate the reduction of Fe(III). In subtropical rice paddies, the release of labile C in anoxic conditions is exploited to release Fe and its sorbed P via reductive dissolution for plant growth (Khan et al., 2019). Therefore, there is a known relationship between labile P, redox and the rate or amount of P released.

## 1.4 Transport pathways and speciation

As well as needing an available source, P loss requires a transport pathway (or hydrological pathway) to carry it to the receiving waterbody. P is lost either in dissolved forms (DRP & DUP) or while sorbed to soil material (PP), and can move via different broad pathways: overland flow; shallow subsurface flow or interflow; and deep subsurface flow or groundwater flow (Figure 1.5) (Haygarth and Sharpley, 2000; McDowell and Condron, 2004). Different pathways in a catchment can be affected by a series of variables, such as topography and climate. Depending on landscape features, each possible pathway or mechanism of loss will vary in significance in different catchments, and have different characteristics, transport factors and opportunities for attenuation, which influence the forms and concentrations of P loss to receiving waters (Bomans et al., 2005; Taylor et al., 2016). Table 1.6 indicates how relevant different transport pathways are to different soil P fractions. Interflow represents horizontal flow in surface soil (often included in overland flow measurements) and subsurface flow in drainage representing the faction that is intercepted by subsurface drainage.

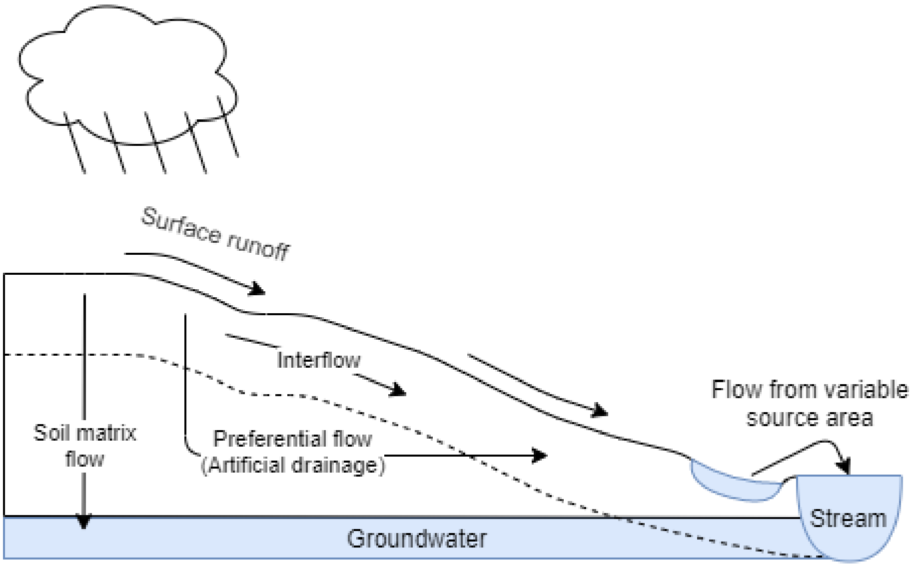

Figure 1.5 Potential flow pathways of P from source to receiving water body in an agricultural catchment, adapted from Houlbrooke, Laurenson, & Carrick, 2011.

Table 1.6 Applicable transport pathways of P fractions* indicated by tick marks, adapted from Simmonds (2016)

| Fractions | Pathways | | | |
|---|---|---|---|---|
| | Leaching | Subsurface flow in drainage | Soil through flow | Overland flow |
| $PP_i$ | ✓ | ✓ | ✓ | ✓ |
| $PP_o$ | - | - | - | ✓ |
| DRP | ✓ | ✓ | ✓ | ✓ |
| DUP | - | ✓ | - | - |

*$PP_i$ = Particulate inorganic phosphorus; $PP_o$ = Particulate organic phosphorus; DRP = Dissolved reactive phosphorus; DUP = Dissolved unreactive phosphorus

### 1.4.1 Surface transport

Surface runoff (*viz.* overland flow) is a broad term given to lateral transport of water and collected solutes over the soil surface (Haygarth and Sharpley, 2000). This pathway is associated with elevated P losses due to the accumulation of nutrients in the topsoil (1-5 cm depth) from agricultural practices and topsoil erodibility (Buda et al., 2009a; Buda et al., 2009b; King et al., 2015). The potential concentration in runoff is greater as STP increases, due to the increased degree of P saturation in the topsoil (Hansen et al., 2002). Runoff typically contributes a significant proportion of P as PP on soil particles from erosion, and the proportion of DRP and DUP is dependent on the amount and reactivity of topsoil P (Hansen et al., 2002; Leinweber et al., 2002; Taylor et al., 2016).

There are two key runoff-generating processes; infiltration-excess overland flow and saturation-excess overland flow. The relative importance and contribution of each process is dependent on spatial and temporal variables like topography, soils and climate (Agnew et al., 2006; Dahlke et al., 2012). Infiltration-excess or Hortonian flow occurs when rainfall intensity exceeds the soil's infiltration capacity, either because the rainfall intensity is high or the soil's infiltration capacity is very low (Agnew et al., 2006; McDowell, 2015). Saturation-excess overland flow occurs only when the soil becomes saturated. As this process of runoff-generation is dependent on landscape wetness and profile inundation, saturation-excess is dependent on landscape features that would encourage convergence and inundation, and seasonal fluctuations or random rainfall events. It is more likely to occur in winter and spring; in easily-saturatable or slowly-permeable soils; areas with high water tables; or near stream channels (Agnew et al., 2006; Dahlke et al., 2012; McDowell, 2015).

There is conflicting evidence for whether saturation-excess or infiltration-excess mechanisms induce greater P concentrations in runoff. Findings by Buda et al. (2009a) suggested that, while saturation-excess processes produced greater runoff volumes, the relative P concentration was less than infiltration-excess processes. Meanwhile, Zheng et al. (2004) and Sanchez and Boll (2005) show that the contact time between saturation-excess runoff and an inundated and P-saturated soil profile will give greater P concentrations than infiltration-excess processes.

The issue with investigating transport pathways is that the pathways are dynamic, and the importance of each pathway is highly spatially and temporally variable. A small rainfall event or short, heavy rainstorm could only result in subsurface flow, while a much heavier or longer rainstorm could either result in infiltration-excess or saturation-excess overland flow depending on factors like antecedent moisture content, topography and slope, soil type and infiltration capacities (Bomans et al., 2005; Samper et al., 2015). Buda et al. (2009a) found that, on specific hillslope sites, at least 80% of the runoff events were generated as infiltration-excess runoff, with small runoff volumes but high P concentrations. However, on a specific north slope, saturation-excess runoff volumes were 19 times greater than infiltration excess runoff volumes. This means P loads from saturation-excess was greater than from infiltration-excess. Differences were attributed to the influence of upslope soil profiles that contained a fragipan (i.e. an impermeable layer). Therefore, generalisations about hillslope hydrology such as assuming that water flow is uniformly in one direction over a wide landscape, or that one runoff-generating mechanism explains transport in a catchment can be very inaccurate. Factors that will influence the threshold of activation of each pathway are important to acknowledge when attempting to establish their relative importance to P transport (Heathwaite and Dils, 2000).

### 1.4.2 Subsurface transport

Traditionally, contributions from subsurface flow were considered unimportant due to P adsorption in soil and P losses were not agronomically-significant (King et al., 2015; Taylor et al., 2016). However, as the focus of nutrient management has moved more towards environmental considerations, the amounts lost from subsurface pathways that would previously have been considered negligible would now be considered a threat to receiving waters (Haygarth et al., 1998). Efforts have been made to identify and model runoff pathways and potential means of P transport from source to sink (Thomas et al., 2016), to better inform mitigation strategies. However, modelling requires “realistic representation of hydrological transport” (Thomas et al., 2016). Assuming isotropic conditions (uniform flow in one direction) when making hydrologic models can be detrimental. Therefore, evaluating and applying the effects of subsurface conditions is very important.

Subsurface pathways can be significant contributors to contamination in situations with high STP levels, poor ASC, reducing conditions, and preferential flow, but also offer opportunities for resorption into the soil matrix if the P moves into a P-deficient subsoil (King et al., 2015; Sims et al., 1998). Characteristics in soil horizons can alter subsurface hydrology and affect where and how P moves from source to sink. Preferential flow occurs due to the presence of macropores or cracks, artificial drainage, or low permeability layers in soil profiles (King et al., 2015; Kramers et al., 2009; McDowell and Sharpley, 2004; Stamm et al., 1998; Svanbäck et al., 2014). The subsurface pathways to consider are: lateral flow (interflow); vertical drainage; or preferential flow via macropores, cracks and artificial drainage (Dahlke et al., 2012; Du et al., 2016; Enright and Madramootoo, 2004; Klaiber, 2016; Tan and Zhang, 2011; Ward and Robinson, 2000).

### Preferential flow

This term describes the movement of solutes and water through a more favourable pathway such as macropores, cracks, along low permeability layers, and via artificial drainage. It presents issues for nutrient management as preferential flow does not provide the same opportunities for sorption like in matrix flow where solutes are exposed to more of the soil matrix (Houlbrooke and Monaghan, 2009). Heathwaite and Dils (2000) conducted a study in the Pistern Hill catchment (Leicestershire, UK) and observed that TP losses in preferential flow were more than twice the losses in matrix flow. Preferential flow can cause water to move through only a small portion of the soil profile, reducing contact time and residence time (Taylor et al., 2016). There may be a point in a rainstorm event where vertical drainage flow shifts more towards macropore rather than matrix flow, which will influence the terminal P load (Heathwaite and Dils, 2000).

Also, rapid flow through larger pores and cracks can give rise to erosion within the soil profile. This can contribute significant amounts of fine, colloidal particles carrying PP (Leinweber et al., 2002). If there is an artificial drainage system in place, these particles can then be carried out of the profile and directly to a receiving environment. In profiles with preferential flow and artificial drainage, it is common to have greater quantities of PP in drainage than in a profile with matrix flow (King et al., 2015).

### Low permeability layers and lateral flow

Impermeable subsurface soil layers – like a fragipan – can define how sensitive a catchment area is to perching, saturation, subsurface lateral flow and runoff generation during rainfall (Thomas et al., 2017). Low permeability layers or restricting layers are dense horizons in the soil profile with high bulk density and low saturated hydraulic conductivity ($K_S$) compared to adjacent horizons. They can take various forms and are given different names like duripans, plough pans and fragipans depending on how they are formed (Bockheim and Hartemink, 2013). A specific example of a low permeability layer in soils is the fragic pallic soils that are present in 12% of New Zealand, and have a compact pan in the subsurface (Landcare Research, 2016). They can reduce the vertical conductivity down the profile, resulting in either the profile above the layer developing a perched water table and becoming saturated, or can increase the flow of water via the path of least resistance - generally laterally, parallel to the impeding horizon (King et al., 2015; McDaniel et al., 2008; Zhang et al., 2010). This preferred flow pathway is typically termed interflow, throughflow or subsurface stormflow (Du et al., 2016; Ward and Robinson, 2000). Interflow requires:

- Steep slopes that increase movement in the lateral direction rather than via profile vertical flow; and,
- Thin soil layers overlying low-permeability layers, shallow sub-horizontal rock fractures, or bedrocks (Samper et al., 2015).

The presence of an impermeable layer plays a significant part in shaping hydrological pathways. As well as inducing lateral flow in the subsurface, interflow is an important precursor to surface flow generation. Dahlke et al. (2012) demonstrated how catchments with fragipans will generate twice the amount of runoff than soils without fragipans. This is supported by observations in other studies that lateral flow over a fragipan can account for more than 80% of the runoff on a site (Buda et al., 2009a; McDaniel et al., 2008). Gburek et al. (2006) ascertained that areas in a Pennsylvanian catchment that had fragipans exhibited saturation-excess overland flow, while other areas in the same catchment without a fragipan generated “little or no runoff”.

Overall, impermeable layers create the conditions that would be conducive to the mobilisation of reducible P: an area vulnerable to saturation and a tendency to generate lateral flow via interflow and runoff. Therefore, these areas are of potential interest to study, to find their influence on P loss via redox.

***Artificial drainage***

Poor natural drainage and high water tables reduce land use productivity, and increase the potential for P loss via surface flow (Bomans et al., 2005). There are ways to mitigate the effects of poor drainage, including breaking up poorly permeable layers via ripping and flipping, or installing artificial subsurface drainage. Ripping and flipping involves deep cultivation that break up the problem impermeable layer, to encourage percolation to depth. These mitigation strategies can be costly, but will improve land capabilities (Government of Western Australia, 2017). Artificial drainage involves altering the landscape by installing tile or pipe drainage for water to flow into, so that it can increase the storage capacity in the spaces above the tiles and in the pipes, and direct the excess water to a receiving environment (increase saturated hydraulic conductivity ($K_s$)) rather than leaving it to perch above the layer

(Figure 1.5) (Christianson and Harmel, 2015). This practice is relatively widespread. Around 43 million ha and 16 million ha has or needs artificial drainage in the USA and Canada respectively (Enright and Madramootoo, 2004). Some Irish and New Zealand soils are also commonly artificially drained to improve water flow, such as the surface water gleys and gleyic luvisols of Ireland, and the pallic soils found predominantly along the eastern side of New Zealand (Kramers et al., 2009; Landcare Research, 2016).

Introducing artificial drainage has been shown to increase crop yields by 5-25% annually, increase the number of days field activities can occur, improve infiltration, and decrease surface runoff volume, soil compaction and erosion (Bomans et al., 2005; Christianson and Harmel, 2015; King et al., 2015). While P loss via surface runoff and erosion can decrease after installation, tile drainage can increase the amount of discharge that is contributed to a stream via subsurface flow in comparison to surface flow (King et al., 2015). Soluble P loads and concentrations in drainage water are greater in tile-drained soils than in natural soils, as the artificial system decreases the potential retention and contact time of water and solutes in a profile, and there is less opportunity for natural P-attenuating processes to occur. One study showed that, on an undrained plot, there were twice the annual average losses via surface runoff than on a drained plot (0.86 and 0.44 kg P/ha respectively). While losses still occurred via the installed drainage, these were significantly lower (Sharpley and Syers, 1979). In saying this, the losses are still significant environmentally, and the amount of P that arrives at the drain from the profile does depend on factors like depth to the tiles (where shallower tiles can produce greater P losses) and the soil texture (where clay soils with cracking and significant bypass flow to drains will have greater contributions than soils with better matrix flow) (Bomans et al., 2005; King et al., 2015). Artificial drainage systems can also be installed that restricts drainage to periods when excess water would be damaging to plant growth or inhibit farm practices. Below this level, water is retained in the profile to minimise nutrient loss. There have been previous studies undertaken by Tan and Zhang (2011) that have shown how altering the landscape and hydrology in this manner lends itself to creating redoximorphic conditions in the subsurface. In these studies, controlled drainage increased the filterable-P component when compared to a typical free-draining system (King et al., 2015).

Artificial drainage offers the opportunity to compare a soil that is drained and undrained to observe and measure the influences on aerobic and anaerobic conditions in the landscape. Through this, there is the potential to see whether more P is lost from a reduced soil compared to aerobic soils of same Olsen P concentrations, or whether the limited discharge of saturated soils mean they lose less P than free-draining soils.

### 1.4.3 Connectivity

In a certain amount of land that drains to a receiving waterbody, it is possible that maybe 10% of it can contribute 80% of the P lost to waterways (Dahlke et al., 2012). That 10% is termed the critical source areas (CSAs) (McDowell and Sharpley, 2004). To be a risk, CSAs need to have a large pollutant source, a high mobility risk, and hydrologically sensitive areas (HSAs). In turn, to be hydrologically sensitive, there needs to be a high transport risk and connectivity to receiving surface waters (Thomas et al., 2016). Any of the reactions described in section 1.3 can occur to render P potentially mobile but, without a means to move to a receiving waterbody, the site where these reactions occur do not represent a mobility risk and are not a critical source area (CSA). Therefore, a key component of P transport is the connectivity of CSAs to a sink, and how immediate this connection is. An important question is to ask how strong the connection is between sources and a sink. In an instance with artificial drainage, there is a conduit for water flow, and a strong connectivity between source and sink would be expected. In a perfect world, different variables and influences like depth to pans and subsurface topography would be catalogued and applied to each hillslope to establish the level of hydrological connectivity. Then, the actual risk of P loss from different areas can be quantified and targeted accordingly based on that level or risk.

Transport pathways are not isolated, so although water and associated solutes may be carried by a pathway, it does not mean that this one pathway will carry those solutes the entire distance from source to sink. In general, the areas that would generate lateral flow would be spatially and temporally complex, so the relative importance of these areas and this pathway may vary, particularly between seasons (Haygarth and Sharpley, 2000). For instance, although there is evidence of very rapid solute transport over a fragipan in soil (McDaniel et al., 2008), if the lateral hydraulic conductivity above the fragipan is poor, this may not be the case (Dahlke et al., 2012). Some interflow does not directly discharge to stream channels but can return to the surface as overland flow and continue via this pathway, particularly in very shallow soil profiles (Ward and Robinson, 2000). As the water flow moves to the surface, the influences of subsurface biochemical processes may not play as large a part in exacerbating P loss or attenuating nutrients (Vero et al., 2017). Studies such as those by Thomas et al. (2017)

used modelling to develop HSA maps that incorporate depth to bedrock or a restrictive layer in their equations. However, an identified drawback in this study was that the presence of and the depth to potential fragipans at their sites were not accounted for due to time constraints. For the time being, it was assumed that they were not present. Part of the model equation involves defining the mean soil saturated hydraulic conductivity ($K_s$) above a local soil depth to the restrictive layer (D). Therefore, for improved accuracy, developing a way to identify fragipans, assess their contribution to P loss, and incorporate them into the runoff modelling is a step forward.

Another possibility is that solutes could simply be transported in the subsurface to another part of the soil profile and not move to a waterbody, due to a disconnection between upper and lower landscape positions, as was demonstrated in the study by Buda et al. (2009a); Buda et al. (2009b). In these situations, a segmented conveyance process could come into play, where subsurface P transfers take more than one event to be transferred to a waterway. In the instances where lateral flow is transferring upslope P to a downslope position, there is the question of whether there is an accumulation of P in the downslope positions that can be remobilised when saturated and pose a risk again, particularly as convergence of water flow in lower slope positions is likely to lead to saturation (Buda et al., 2009a; Dahlke et al., 2012; Ward and Robinson, 2000).

## 1.5 Summary

The literature highlights several potential information gaps regarding the influence of anaerobic conditions on P mobility and the potential for this newly mobilised P to be transported to waterways. There are variable results regarding the influence of redox on reducible-P co-precipitated with soil Fe, therefore it would be useful to carry out an investigation on a larger database of soils to clarify this. It would also be useful for identifying whether having a database of ASC values in anaerobic conditions would be beneficial to fertility management decisions. In-field factors should also be explored, such as whether the period of inundation and reduction significantly influences the quantity of remobilised P, the importance of the $Fe_{ox}$:$Al_{ox}$ ratio to release, and whether seasonal changes in natural soil temperatures play a part in accelerating reduction processes.

Impermeable layers and perched water tables represent a likely environment for inundation and redoximorphic processes, as well as a tendency to generate lateral flow via interflow and runoff. Therefore, their influence and importance to these processes should be assessed and compared to a drained site to inform model development in the future. Finally, due to the incredible variability of transport between source and sink in a landscape, the influence of dissolution from these sites to a receiving water body should be investigated to assess whether remobilised reducible-P can be identified in output.

Taking these gaps into consideration, this research aims to clarify the role of anaerobic conditions (and therefore redox) on P release and load in a catchment by exploring spatial influences like soil Fe concentrations, impeding layers, artificial drainage, and vulnerability to saturation; temporal changes like length of inundation and regularity of rainfall events within and between seasons; and the connectivity between these sites and receiving water bodies. The underlying rationale behind this is that, although technology could be developed to accurately describe subsurface fragipan topography and therefore surface load, the actual chemical reactions in the fragipanic soil need to be assessed to understand P mobilisation and load.

## 1.6 Research Aim and Objectives

Based on the literature, the overall hypothesis was established:

*Anaerobic conditions in soils will contribute significantly to potential annual P losses.*

The following four specific objectives were carried out to assess this hypothesis:

I. Quantify the potentially reducible phosphorus (P) component in the lab for a range of stored soil samples, and the distribution of reducible P pools relative to known soil maps,
II. Determine if redox reflects changes in P (and other redox-sensitive components such as Fe and Mn) with attention to the length of time that the soil is saturated, P fertiliser treatment, and temperature,
III. Observe trends of the release of P and other redox-sensitive species into soil solution under saturated conditions, during the drainage season,
IV. Determine the role of redox processes in the release of P and other redox species within and across drainage and runoff events.

The objectives, once completed, were intended to be integrated into current critical source area models and used to develop potential mitigation strategies. Field and laboratory experiments were employed to explore the relationship between periodic and/or seasonal saturation and the release of Fe and associated P into soil water and surface water. Soil extractions and incubations were conducted in the laboratory in controlled conditions, and monitoring sites were established to identify anticipated trends as the *in situ* soil profiles were wetted up and dried out over seasons and storm events.

## 1.7 Layout of the Thesis

The thesis contains nine chapters. Following this introduction, **Chapters 2 to 5** are a collection of experiments presented as papers: **Chapter 2** explores the redox-sensitive phosphorus in dried archived soils, as a laboratory technique to measure the potential P release in easily saturated land; **Chapter 3** assesses the potential for reduction releasing P and Fe from soil in ideal reducing conditions, achieved under laboratory incubation conditions; **Chapter 4** explores the *in situ* influence of redox potential on soil Fe-phosphorus loss in a soil profile; and, **Chapter 5** assesses the reduction and P release into surface and subsurface drainage losses in the Southeast of Ireland. Finally, **Chapter 6** is an overall discussion of the results and implications for land management and farming going forward, and possible areas of future work.

The contribution of each objective to publications are outlined in Figure 1.6. The experiments outlined in Chapters 4 to 7 were carried out in both New Zealand and the Republic of Ireland. In New Zealand, laboratory and field work was carried out in Agresearch Invermay and Mossburn Southland, respectively, as well as in Lincoln University, Lincoln. In the Republic of Ireland, laboratory and field work was carried out in Teagasc Johnstown Castle.

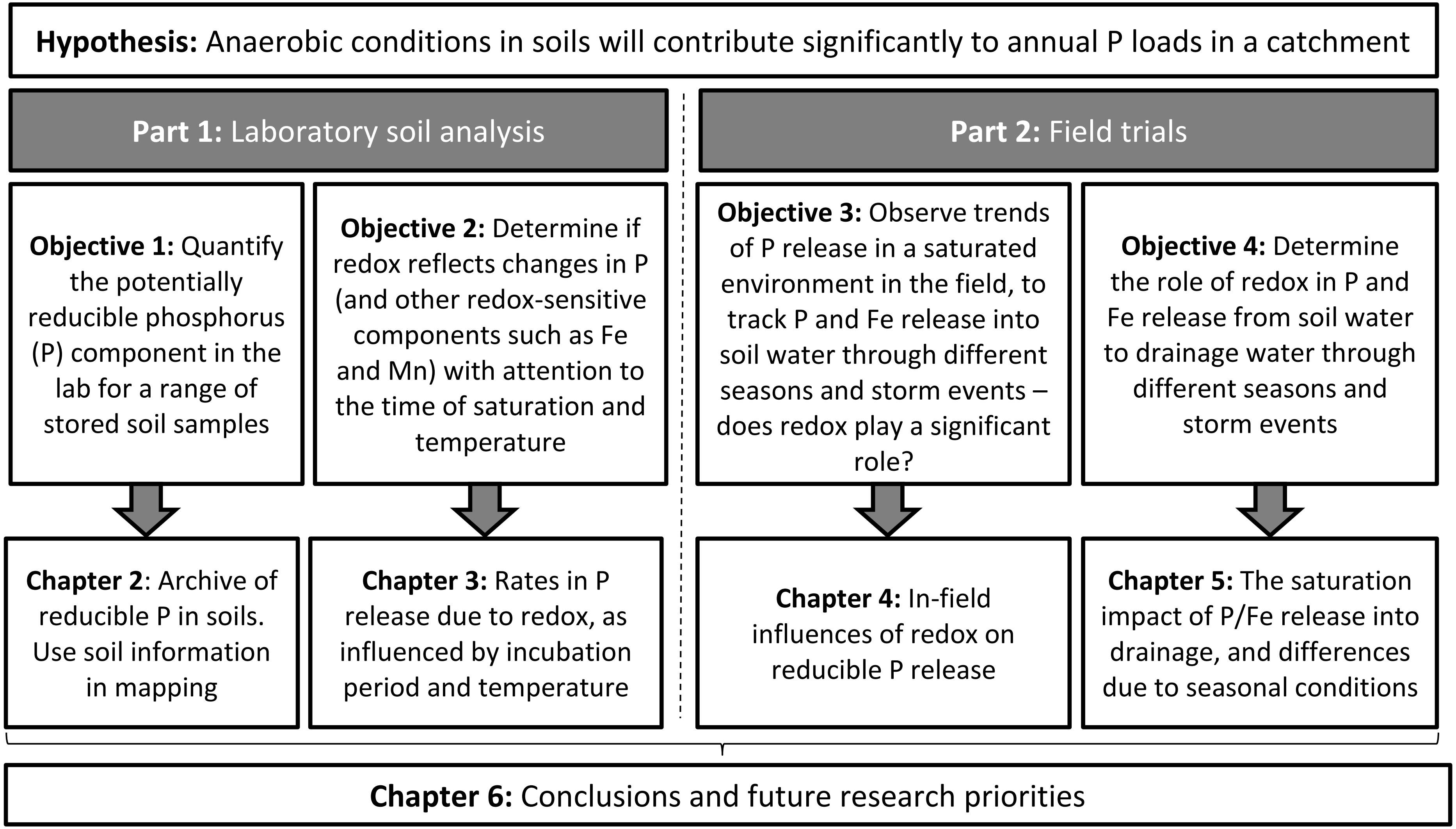

Figure 1.6 Objectives and their relationship to chapters and thesis structure

# Chapter 2

# Estimating and modelling the risk of redox-sensitive phosphorus loss from saturated soils using common soil tests

## 2.1 Introduction

Phosphorus (P) loss from agricultural soils can negatively affect water quality through eutrophication and excessive aquatic plant growth (Hansen et al., 2002; Heathwaite and Dils, 2000; Leinweber et al., 2018; Leinweber et al., 2002; Owens and Shipitalo, 2006). To decrease losses, a greater understanding of the mechanisms of P loss and flow pathways from different soils to waterways is required (Gillingham and Thorrold, 2000; Hansen et al., 2002; Leinweber et al., 2018; Owens and Shipitalo, 2006). One way to understand flow pathway behaviour and P contributions is critical source area (CSA) modelling. In CSAs, sources of mobile P coincide with hydrologically sensitive areas (HSAs) in a landscape. They account for the majority of P loss from a farm or catchment but come from a minority of the farm or catchment's area (Dahlke et al., 2012; McDowell et al., 2016).

The CSA models rely on estimates of soil P tests such as water extractable P (WEP), Olsen P or Mehlich-P (McDowell and Condron, 2004). Thomas et al. (2016) created models using WEP and Morgan's P to estimate potential P losses due to saturation-excess overland flow. Using WEP may be problematic, as the amount of P released under oxic conditions may not represent P release from saturated soils that could become anoxic. Some studies (Gu et al., 2019; Prem et al., 2014) suggest that saturated, anoxic conditions can release greater dissolved reactive P (DRP) than oxic conditions (Gu et al., 2019; Heiberg et al., 2012; Heiberg et al., 2010). Saturated soils can become anoxic from microbial respiration (Zhang et al., 2010). During respiration, microbial communities mediate oxidative-reductive (redox) reactions to make energy. They preferentially use oxygen as an electron acceptor – as it is the most energetically favourable in a system – followed by nitrate ($NO_3^-$), manganese ($Mn^{3+}$), and then iron ($Fe^{3+}$) ($O_2$ > $NO_3^-$ > $Mn^{3+}$ > $Fe^{3+}$ > $SO_4^{2-}$). When $Fe^{3+}$ and $Mn^{3+}$ are used as electron acceptors, they become reduced, and are dissolved into solution (*viz.* reductive dissolution) (Hansen et al., 2002; Martynova, 2010). Fe and Mn hydroxides and oxyhydroxides (*viz.* Fe- or Mn-oxides) can significantly contribute to P retention in non-calcareous soils, so their reduction could enhance P loss risk (Baken et al., 2015; Brand-Klibanksi et al., 2007; Heiberg et al., 2012; Zhang et al., 2010).

To successfully predict P losses in periodically saturated soils, a soil test should simulate the maximum potential reductive dissolution of Fe, Mn and associated P across a variety of soil types. This paper developed a modified WEP test conducted in anoxic conditions (anoxic WEP) to represent immediate loss risk in saturated soils and compared this to oxic WEP. Additionally, sodium-bicarbonate-dithionite ($Na_2S_2O_4$) – a strong reducing agent – was proposed to estimate the maximum potential reducible P pools (*viz.* Dithionite-P) (Jensen and Thamdrup, 1993; Psenner and Pusckso, 1988). Soils from New Zealand and Ireland were taken as case studies, two temperate countries where approximately 27.7% and 14.5% of productive land, respectively, utilises imperfectly to poorly-drained soil (European Commission, 2019; StatsNZ, 2018); (Landcare Research, 2017; Newsome et al., 2008; O'Sullivan et al., 2017). In the present study, the overall objective was to predict the pools of reducible P (Dithionite-P and anoxic WEP) across New Zealand and Ireland, in an effort to provide a means to improve the estimation of P losses over current tests. Selected soils were used from national soil archives to: 1) determine Dithionite-P pools across New Zealand and Ireland as a measure of maximum potentially reducible metal oxide-bound P; 2) show the potential immediate P loss risk in saturated conditions via WEP tests in anoxic conditions, and compare results to normal oxic WEP; 3) create prediction equations for Dithionite-P and anoxic P using proxy soil tests from the New Zealand and Irish soil archive databases; and 4) create a map for the distribution of Dithionite-P and anoxic WEP pools across New Zealand. No map was produced for Ireland owing to a lack of spatial data. The present study posits that predictive equations and maps of Dithionite-P and anoxic WEP can be used to show if significant pools of reducible P intersect with CSAs. Therefore, they would aid in improving land management decisions to decrease P loss (Leinweber et al., 2018; Thomas et al., 2016).

## 2.2 Materials and methods

### 2.2.1 Soil archives

Over three hundred soil samples from across New Zealand and Ireland were used for the purposes of this study, covering a variety of soil types and land uses (Tables 2.1 and 2.2). The limitation of the datasets used is that it is topsoil data. Therefore, it may not be fully representative of the subsoil environment and the behaviour of WEP in this scenario. However, a compromise was made in order to have more ancillary data to create models with. The following is a summary of the dataset:

1. *500 Soils project archive:* 500 soil samples were taken during a nation-wide survey by Landcare Research from 1998-2002, to explore all soil types and land uses as evenly as possible (Hill et al., 2003; Sparling and Schipper, 2002). The samples represented the top 10 cm of soil from each site, and the co-ordinates from each sample site were recorded. The dataset covers the following soil orders, with NZ soil classification (Hewitt, 2010) and associated World Reference Base (WRB) classification (IUSS Working Group WRB, 2015) in parentheses: Allophanic soils (Andisols); Brown soils (Cambisols); Gley soils (Gleysols); Granular soils (Ferrasols); Pallic soils (Luvisols); Podzols (Podzols); Pumice soils (Vitric andisols); Recent soils (Arenosols & Fluvisols); & Ultic soils (Acrisols). The database also included ancillary data on each soil sample, the averages of which are included in Table 2.1. A subset including 134 of these soils were chosen to represent a range of soil orders and land use and where enough sample remained.

2. *Irish Soil Information System (Irish SIS) archive:* This archive was a collection of composite samples taken from the first horizon (between 0-15 or 40 cm below ground level) of grassland soils around Ireland. 106 samples were used. These soils were classified in this report according to their FAO classification: Cambisols, Gleysols, Luvisols, Phaeozems, and Podzols. Ancillary data was available for each sample, the averages of which are listed in Table 2.2.

Table 2.1 Mean topsoil (0-10cm) chemical parameters[1] for eight Food and Agriculture Organization (FAO) soil groups, corresponding New Zealand soil orders[2] and land uses in the New Zealand archive (n = 134). The significance of soil group, land use, and the interaction of soil group and land use is given by *P* values[3] (n = number of samples). A t-test compared the total dataset (n = 526) and this subset, to find if the subset was representative of the archive.

| FAO Group | NZ Soil Order | Land use | n | Dithionite-P mg kg$^{-1}$ | WEP mg L$^{-1}$ | Olsen P mg kg$^{-1}$ | CBD-Fe mg kg$^{-1}$ | TC Mg ha$^{-1}$ | TN Mg ha$^{-1}$ | pH | CEC cmol kg$^{-1}$ | ASC % | Ca cmol kg$^{-1}$ | Mg cmol kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Andisol | Allophanic | Crop | 7 | 53 | 0.07 | 53 | 1001 | 32 | 2.8 | 6.4 | 24 | 55 | 14 | 1.5 |
|  |  | Pasture | 18 | 59 | 0.10 | 38 | 637 | 50 | 4.8 | 5.9 | 28 | 47 | 10 | 1.3 |
| Cambisol | Brown | Pasture | 15 | 91 | 0.10 | 22 | 852 | 35 | 2.8 | 5.7 | 28 | 24 | 1 | 1.4 |
| Vitric Andisol | Pumice | Pasture | 10 | 29 | 0.26 | 40 | 318 | 49 | 3.6 | 5.8 | 14 | 27 | 7 | 0.7 |
| Ferrasol | Granular | Crop | 4 | 63 | 0.11 | 100 | 1678 | 8 | 0.7 | 6.4 | 22 | 19 | 14 | 1.1 |
|  |  | Pasture | 9 | 124 | 0.10 | 46 | 1567 | 50 | 4.3 | 6.1 | 26 | 34 | 13 | 1.8 |
| Luvisol | Pallic | Crop | 7 | 253 | 0.15 | 21 | 582 | 34 | 2.8 | 6.0 | 20 | 11 | 13 | 1.5 |
|  |  | Pasture | 9 | 273 | 0.17 | 26 | 573 | 41 | 3.5 | 5.8 | 23 | 17 | 15 | 3.3 |
| Gleysol | Gley | Crop | 12 | 362 | 0.18 | 56 | 673 | 23 | 2.0 | 6.1 | 21 | 16 | 14 | 3.0 |
|  |  | Pasture | 15 | 313 | 0.14 | 45 | 526 | 46 | 4.1 | 5.7 | 24 | 28 | 12 | 2.1 |
| Arenosol / Fluvisol | Recent | Crop | 7 | 257 | 0.26 | 72 | 510 | 44 | 3.4 | 6.6 | 19 | 10 | 16 | 1.7 |
|  |  | Pasture | 14 | 183 | 0.20 | 40 | 717 | 42 | 3.6 | 6.0 | 21 | 13 | 12 | 2.3 |
| Acrisol | Ultic | Pasture | 7 | 211 | 0.13 | 28 | 652 | 62 | 5.0 | 5.8 | 22 | 15 | 14 | 1.9 |
| $P_{\textit{soil order}}$ |  |  |  | <0.001 | <0.05 | <0.001 | <0.001 | ns[4] | ns | <0.05 | <0.001 | <0.001 | <0.05 | <0.001 |
| $P_{\textit{land use}}$ |  |  |  | ns | ns | <0.001 | ns | <0.001 | <0.001 | <0.001 | ns | ns | <0.05 | ns |
| $P_{\textit{soil order x land use}}$ |  |  |  | <0.001 | ns | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.01 | ns | <0.05 |
| *t-test* $_{\textit{subset x full archive}}$ |  |  |  | ns | ns | ns | -[5] | ns | <0.01 | ns | ns | - | ns | ns |

[1] Abbreviations for chemical parameters are: WEP = Water extractable phosphorus; CBD-Fe = Citrate-bicarbonate-dithionite Iron; TC = Total carbon; TN = Total nitrogen; CEC = Cation exchange capacity; ASC = Anion storage capacity; Ca = Exchangeable calcium; Mg = Exchangeable magnesium

[2] Hewitt, 2010

[3] *P* values for parametric data = two-way ANOVA

[4] ns = not significant.

[5] Not included in original dataset

Table 2.2 Mean first horizon chemical parameters[1] for different Food and Agriculture Organization (FAO) soil groups[2] by land use in the Irish Soil Information System project archive (n = 106). The significance of soil group, land use, and the interaction of soil group and land use is given by *P* values[3] (n = number of samples)

| FAO soil group[2] | Land use | n | Dithionite-P mg kg$^{-1}$ | WEP mg L$^{-1}$ | Morgan's P mg kg$^{-1}$ | Mehlich-P mg kg$^{-1}$ | Mehlich-Fe mg kg$^{-1}$ | Mehlich-Al mg kg$^{-1}$ | TC Mg/ha | TN Mg/ha | pH | CEC cmol kg$^{-1}$ | PSI mg kg$^{-1}$ | Bulk density g/cm$^3$ | Ca cmol kg$^{-1}$ | Mg cmol kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cambisol | Arable | 6 | 61 | 0.04 | 4.3 | 44 | 309 | 957 | 43 | 4.2 | 5.9 | 15 | 15 | 1.04 | 11 | 1.9 |
| | Pasture | 27 | 92 | 0.05 | 6.2 | 55 | 345 | 1079 | 47 | 4.0 | 6.1 | 14 | 21 | 1.00 | 11 | 1.4 |
| Gleysol | Arable | 1 | 84 | 0.07 | 9.0 | 41 | 337 | 705 | 45 | 4.6 | 6.6 | 19 | 9 | 1.04 | 16 | 4.0 |
| | Pasture | 39 | 107 | 0.06 | 7.4 | 58 | 395 | 979 | 61 | 4.7 | 5.8 | 16 | 21 | 0.94 | 13 | 1.3 |
| Luvisol | Arable | 1 | 193 | 0.06 | 8.9 | 57 | 584 | 785 | 43 | 4.5 | 5.3 | 13 | 27 | 1.04 | 8 | 2.0 |
| | Pasture | 8 | 88 | 0.06 | 4.7 | 44 | 366 | 922 | 43 | 4.0 | 6.0 | 13 | 21 | 1.00 | 10 | 1.1 |
| Phaeozem | Pasture | 17 | 100 | 0.05 | 5.3 | 58 | 399 | 1098 | 45 | 3.9 | 6.0 | 13 | 28 | 1.01 | 11 | 1.1 |
| Podzol | Pasture | 7 | 24 | 0.04 | 6.3 | 33 | 335 | 1384 | 120 | 6.8 | 4.9 | 13 | 29 | 1.00 | 5 | 1.5 |
| $P_{\text{soil order}}$ | | | ns[4] | ns | ns | ns | ns | <0.01 | <0.001 | <0.05 | <0.001 | ns | <0.05 | ns | <0.05 | ns |
| $P_{\text{land use}}$ | | | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| $P_{\text{soil order x land use}}$ | | | ns | ns | ns | ns | <0.05 | <0.01 | <0.01 | ns | <0.001 | ns | <0.05 | ns | ns | ns |

[1] Abbreviations for chemical parameters are: WEP = water extractable P; TC = Total carbon; TN = Total nitrogen; CEC = cation exchange capacity; PSI = P sorption index; Ca = Exchangeable calcium; Mg = Exchangeable magnesium

[2] from Creamer et al. (2007).

[3] *P* values for parametric data = two-way ANOVA; nonparametric data = Kruskal-Wallis Chi-sq

[4] ns = not significant

### 2.2.2 Laboratory analysis

**A method to quantify maximum potentially reducible P**

A method was refined from other works (Jensen and Thamdrup, 1993; Lukkari et al., 2007b; Psenner and Pusckso, 1988) to determine the pool of P that could be released under anaerobic conditions, using a sodium dithionite-bicarbonate buffered solution. An alternative test for amorphous Fe oxides is extracting with hydroxylamine-HCl. The P extracted using dithionite is bound to amorphous and slightly crystalline Fe- and Mn-oxides in soil (Dithionite-P). The dithionite-bicarbonate test is widely used in P fractionation methods and lake sediment studies, but not typically in a solitary soil profile test. Some limitations of the test are:

a. Dithionite-bicarbonate solution can extract slightly crystalline Fe oxides, which may result in over-estimating the readily-reducible Fe fraction;
b. The extractant may produce variable results or may have impaired efficiency depending on different soil types and pH levels (Rennert, 2019).

In the present study, a buffered solution of 0.11 M sodium dithionite ($Na_2S_2O_4$)/0.11 M sodium bicarbonate ($NaHCO_3$) (*viz. Na-Dithionite)* was added to soil (air-dried, <2 mm) at a soil to solution ratio of 1:100, shaken end-over-end for 1 hour, centrifuged and the supernatant removed for analysis.

Initial method development involved testing different procedures on a subset of seven soils – representing seven soil groups – from the New Zealand archive (Table 2.3). The aim was to find the most reproducible and effective method of detecting orthophosphate via colorimetry. Colorimetry was used as a cheaper and faster method of detecting orthophosphate P in solution than other methods such as ion chromatography.

The addition of molybdate-based acid colorimetry reagents to Na-dithionite extracts cause elemental sulphur (S) to precipitate which impair the detection of P via colorimetry (Loeppert and Inskeep, 1996). Hence, Na-dithionite needed to be oxidised by aeration to minimise the formation of S precipitate. A trial was run with triplicate samples of seven air-dried soils, aerating the extract post-shaking for four different periods (0 minutes, and 1, 2 and 4 hours, Fig. 2.1). Regardless of aeration period, a precipitate formed. To resolve this problem Jensen and Thamdrup (1993) left the precipitate to settle over days, while Lukkari et al. (2007b) bubbled the supernatant with compressed air to accelerate dithionite oxidation. They noted that, when oxidation was not complete, precipitation of S occurred. Others have used trisodium citrate or ethylenediaminetetraacetic acid (EDTA) to inhibit S precipitation (Alexander and Robertson, 1972; Kowalenko and Babuin, 2007). However, these compounds require long colour development times that could enhance the acid-mediated oxidation of organic P thus overestimating the fraction under consideration. Therefore, potassium persulfate ($K_2S_2O_8$), an oxidiser, was used to keep S in a soluble $SO_4$ form (Kronholm et al., 2000; Nimesh, 2013). Given that $K_2S_2O_8$ is used to digest solutions at high temperatures for total P analysis (Dayton et al., 2017) it was necessary to investigate if the addition of $K_2S_2O_8$ just prior to detection and at a low temperature would avoid significant oxidation of organic P and detection as orthophosphate. A second trial aerated the Dithionite-P extracts of nine soils from the New Zealand archive, which were selected to cover both a range of soil groups, and contrast of chemical characteristics within a soil group (Fig. 2.2). They were aerated for 2 hours, adding 1ml of $K_2S_2O_8$ dissolved in 0.5 M sulphuric acid ($H_2SO_4$) and added the Mo-reagent followed by pH adjustment with NaOH, to detect orthophosphate immediately (0 min), after 60 min, or after heating the mixture to 120°C for 2 hours as per a full digestion (Dayton et al., 2017).

The maximum amount of orthophosphate detected in the Na-Dithionite extracts occurred after 2 hours of aeration and oxidation, after which concentrations in solution declined (Fig. 2.1). The decline was assumed to be caused by the production of a S precipitate (Jensen and Thamdrup, 1993; Loeppert and Inskeep, 1996; Lukkari et al., 2007a). Acidified-

$K_2S_2O_8$ was tested to see if it would partially digest organic P into solution and over-estimate orthophosphate (Fig. 2.2). Across all soils there was no significant difference in orthophosphate detected between soils that had been extracted in Na-Dithionite for 2 hr and in contact with acidified-$K_2S_2O_8$ for zero or for 60 minutes. However, the digested sample had greater orthophosphate detected than both time treatments. This increase demonstrated that the addition of acidified-$K_2S_2O_8$ without heating did not digest organic P and over-estimate orthophosphate.

Based on these results, the final method involved aerating 20 mL of supernatant in a fume hood for 2 hours, adding 1 mL of $K_2S_2O_8$ dissolved in 0.5 M sulphuric acid ($H_2SO_4$), adjusting pH to > 7 with 4 M NaOH and analysing for orthophosphate using the procedure of Watanabe and Olsen (1965).

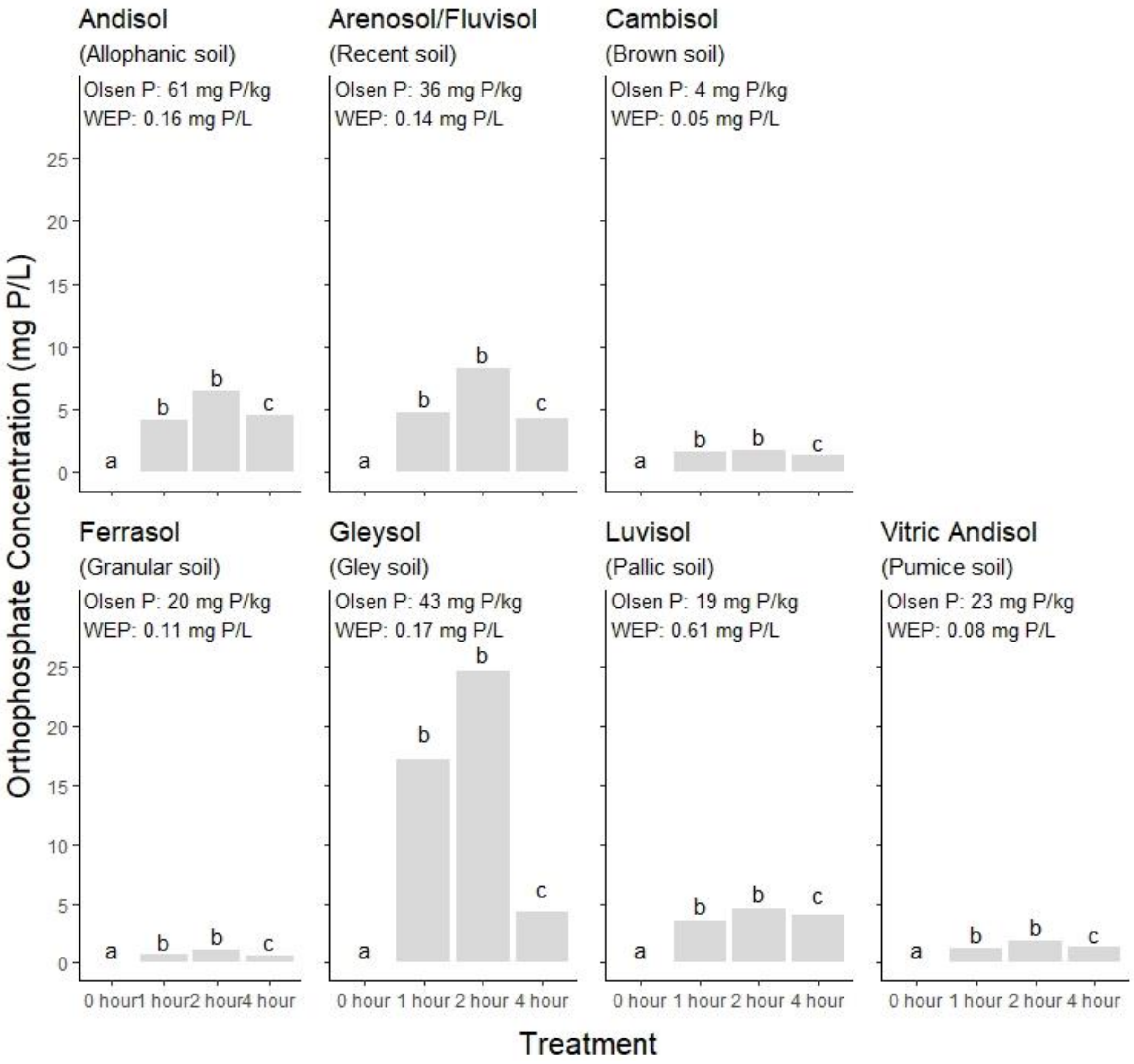

Figure 2.1 Mean orthophosphate concentrations in sodium bicarbonate-dithionite extracts of seven New Zealand soils that have been aerated for 0, 1, 2 and 4 hours prior to analysis. Means with different letters indicate a significant difference between the treatments using Tukey's Honestly Significant Difference test.

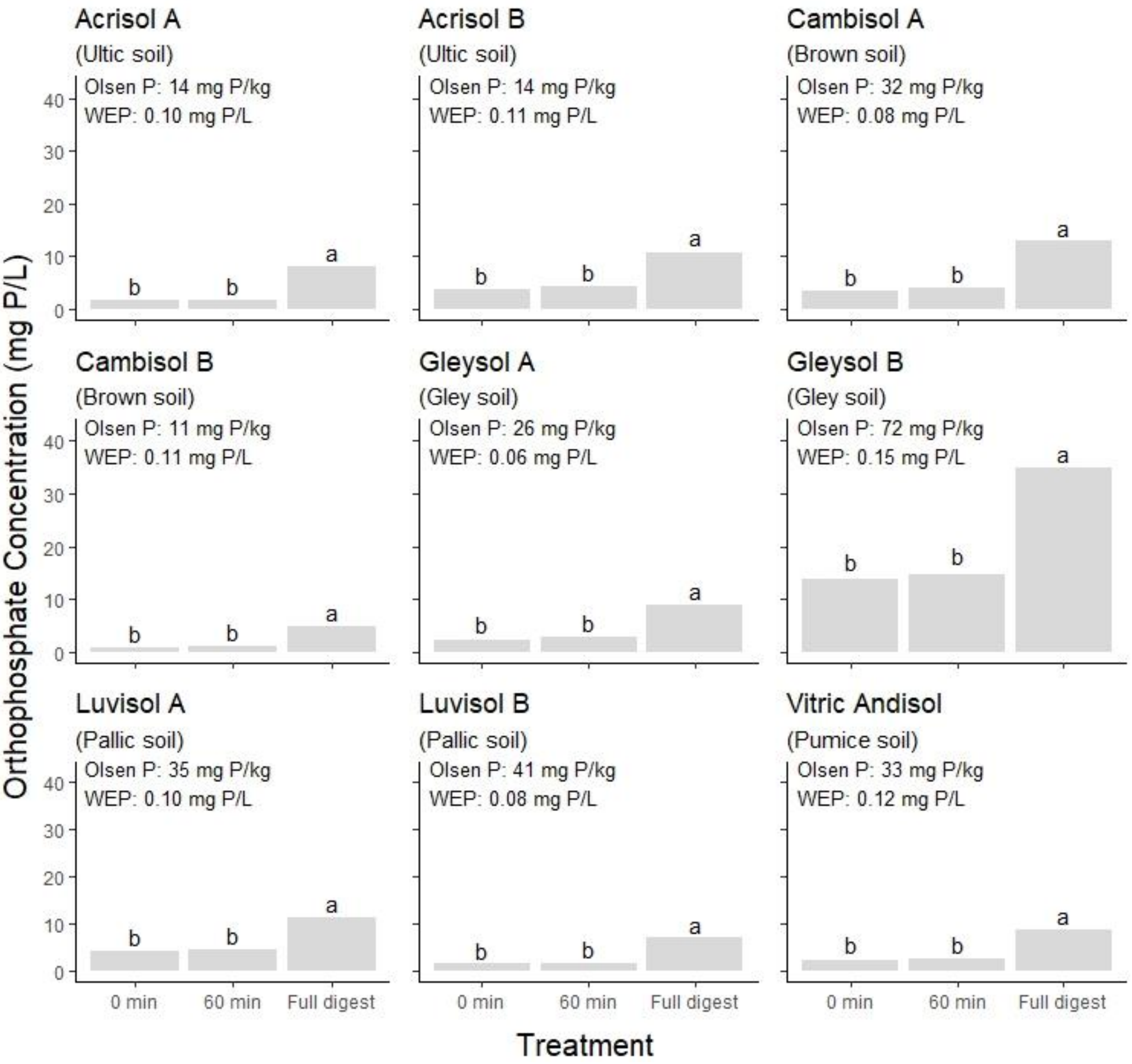

Figure 2.2 Mean orthophosphate concentrations in sodium bicarbonate-dithionite extracts (Dithionite-P) of nine New Zealand soils that have been aerated for 2 hours and left in contact with acidified-potassium persulfate for 0 or 60 minutes or subjected to a complete digestion ('Full digest'). Means with different letters indicate a significant difference between the treatments using Tukey's Honestly Significant Difference test.

### WEP by anaerobic and aerobic incubation in New Zealand soils

To demonstrate the effect of anaerobic conditions on the potential for P loss in runoff, WEP was measured using the method of McDowell and Condron (2004) with oxic and anoxic water. Specifically, soil was extracted using deionised (DI) water for 1 hour at a ratio of 1:300, respectively. Soil samples were selected from the described New Zealand archive. For that purpose, at least eight samples were selected per soil group (supplementary table 1), to identify the behaviour of each group in anaerobic conditions. In the anoxic treatment, all sample handling after weighing occurred in an anoxic glove box that was purged with helium (He). Anoxic water (<0.5 mg dissolved oxygen (DO)/L) was prepared by bubbling helium through the water. After extraction and filtering, the sample was kept anoxic by minimising the headspace in the sample tube until analysis. Oxic water had a DO of >7 mg DO/L, and the samples were prepared and handled as normal in ambient laboratory conditions. The resulting anoxic- and oxic-P concentrations of each soil group were checked for outliers based on Cook's Distance (Cook and Weisberg, 1984), which were removed. The two treatments were then compared to establish whether a difference in the extent of P release existed after 1 hour of extraction, within and between soil groups.

### Additional Analysis

The soils from New Zealand and Ireland were also tested for measures of P sorption capacity using the P sorption index (PSI) (Graetz and Nair, 2009; McDowell and Condron, 2004) and anion storage capacity (ASC) tests (Saunders, 1965). The citrate-bicarbonate-dithionite reducible Fe in the New Zealand soils was also tested (Loeppert and Inskeep, 1996).

Table 2.3 Mean Na-Dithionite-extractable P (dithionite-P), citrate-dithionite-extractable P (CBD-Fe), anion sorption capacity (ASC), total carbon (TC) and pH, for representative New Zealand soil orders (n = 83) extracted by water under anaerobic and aerobic conditions. The *P* value[1] is given to test for differences between soil orders and a t-test to determine if the mean of these soils were different to that in the full archive. Means within a column with the same letter are not significantly different from one another according to post hoc tests[2].

| FAO soil group | NZ soil order | n | Olsen P $\text{mg kg}^{-1}$ | ASC % | pH | TC Mg/ha | Dithionite-P $\text{mg kg}^{-1}$ | CBD-Fe $\text{mg kg}^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Andisol | Allophanic | 9 | $35^{b}$ | $54^{c}$ | 5.8 | $74^{b}$ | $51^{a}$ | $794^{b}$ |
| Cambisol | Brown | 10 | $10^{a}$ | $33^{abc}$ | 5.6 | $42^{a}$ | $53^{a}$ | $553^{b}$ |
| Gleysol | Gley | 10 | $52^{b}$ | $33^{abc}$ | 5.7 | $49^{a}$ | $381^{b}$ | $481^{ab}$ |
| Ferrasol | Granular | 12 | $30^{ab}$ | $40^{bc}$ | 6.0 | $70^{b}$ | $122^{ab}$ | $933^{b}$ |
| Luvisol | Pallic | 9 | $26^{ab}$ | $17^{ab}$ | 5.8 | $41^{a}$ | $277^{ab}$ | $240^{a}$ |
| Vitric andisol | Pumice | 8 | $36^{b}$ | $34^{abc}$ | 5.7 | $59^{ab}$ | $28^{a}$ | $209^{a}$ |
| Arenosol / Fluvisol | Recent | 16 | $39^{b}$ | $18^{a}$ | 6.0 | $45^{a}$ | $218^{ab}$ | $411^{ab}$ |
| Acrisol | Ultic | 9 | 24 | $15^{a}$ | 5.8 | $58^{ab}$ | $225^{ab}$ | $407^{ab}$ |
| ***P*** *soil order*[1] | | | <0.001 | <0.001 | ns | <0.001 | <0.001 | <0.001 |
| ***t-test*** *WEP soils vs archive (n=186)* | | | ns | ns | ns | <0.01 | ns | ns |

[1] *P* value for parametric data = two-way ANOVA; non-parametric data = Kruskall-Wallis Chi-sq.

[2] Post hoc for parametric data = Tukey's Honestly Significant Difference; non-parametric data = Kruskall-Wallis post hoc.

### 2.2.3 Statistical Analysis

Statistical analyses were conducted in three phases. The first phase involved comparing the means for each parameter between soil groups, land use and the interaction of soil group and land use via a two-way analysis of variance (ANOVA). The second phase compared oxic WEP and anoxic WEP concentrations on a subset ($n = 83$) of the New Zealand soils ($n = 134$) and used an analysis of covariance (ANCOVA) to determine if the slope of the linear relationship between a select group of soils extracted for oxic WEP and Dithionite-P was different to that between anoxic WEP and Dithionite-P by soil group. If the slope differs, then the interaction between the two WEP forms and Dithionite-P differ. The third phase determined whether soil data could be combined in a stepwise regression to predict Dithionite-P or anoxic WEP. The performance of the stepwise models ($\alpha = 0.05$) was assessed by choosing the model with the fewest predicting parameters and the smallest Mallows Cp value.

All data were checked for normality using the Shapiro-Wilkes test and log- or square root-transformed if necessary. Analyses were conducted using R Studio, or Minitab where specified (Minitab, 2018; R Development Core Team, 2010). All differences are only discussed if significant at the $P<0.05$ level or greater.

### 2.2.4 Model and mapping anoxic WEP and dithionite-P concentrations

Equations from the stepwise regression were used to create GIS maps of anoxic WEP and Dithionite-P concentrations. Dithionite-P concentrations were categorised by soil order in New Zealand and Ireland using hierarchical cluster analysis. The output was clustered into the best number of groups according to the Elbow method in R studio. This cluster analysis separated the data into three ranges of Dithionite-P pool size.

For New Zealand, spatial data was available to model and map the size of P pools at the national scale. For the New Zealand data, the equation from the stepwise regression model were used to predict pool categories of Dithionite-P at the 1:50,000 scale across productive land (12.1M ha) (Statistics New Zealand, 2014) using ArcGIS software, national chemical data from the New Zealand 500 Soils project, data from fundamental soil layers (Newsome et al., 2008) and the land cover database (Landcare Research, 2017). The same process was carried out for the oxic WEP, anoxic WEP and anoxic WEP – oxic WEP data. The final map indicated the predicted size of anoxic WEP and Dithionite-P pools via colour-coding based on the hierarchical cluster analysis. The predictions of Dithionite-P and anoxic WEP were also intersected by soil drainage class (LRIS, 2010).

As there was no national spatial data available from Ireland at the time of this study to use for prediction and mapping, equations were the final product. These were produced using the data in the Irish-SIS to predict Dithionite-P, and using the parameters specified by Thomas et al. (2016). These equations will potentially benefit other models being developed at the smaller scale (Thomas et al., 2016).

## 2.3 Results

### 2.3.1 Soil characteristics

In New Zealand, mean values of all the chemical parameters except TN and TC were different at the soil order level (Table 2.1). Land uses were different from one another for Olsen P, TC, TN, pH, bulk density, Ca and Mg. The interaction of soil order by land use showed means were different for all parameters but WEP. In Ireland, none of soil P tests exhibited differences between soil orders, land uses, or for the interaction of soil order and land use (Table 2.2). This can be attributed to two facts about the Irish soil archive data. The first was that soil orders and land uses were heavily skewed towards Gleysols and Cambisols, and grassland, respectively. The second was that the Irish soils were sampled from the top horizon (up to 40 cm deep) where P enrichment would be diluted compared to a shallower 10 cm topsoil sample (Sharpley, 2003a).

### 2.3.2 Dithionite-P and WEP

In New Zealand, mean Dithionite-P concentrations by WRB soil group ranged from 29-362 mg P/kg, with Vitric andisols under pasture having lowest mean concentration and cropped Gleysols having the greatest (Table 2.1). Significant differences occurred in mean Dithionite-P between soil groups and for the interaction of soil group by land use, but not for different land uses. Olsen P and ASC both have significantly different mean concentrations at the soil group and soil group by land use level, but Olsen P is the only one significant at the land use level (Table 2.1). Mean WEP concentrations ranged from 0.07 to 0.26 mg P/L, with the lowest mean concentration from the Andisol under cropping, and the greatest WEP means in Vitric andisols and Arenosol/Fluvisols under cropping. Mean WEP concentrations in New Zealand were different between soil groups but not for land uses nor for the interaction of soil group by land use.

In Ireland, at horizon level, the lowest mean concentration of Dithionite-P was from Podzols under pasture (24 mg P/kg) and the highest mean concentrations were from Luvisols under arable production (193 mg P/kg) (Table 2.2). The WEP ranged from 0.04-0.07 mg P/L across the first horizons. No significant differences were noted for Dithionite-P or WEP between soil groups, land uses or for their interaction. However, this does not preclude additional relationships to be explored via regression analysis.

### 2.3.3 Oxic and anoxic WEP in New Zealand soils

Mean anoxic WEP was significantly greater than mean oxic WEP for the Andisols, Cambisols, Luvisols, Acrisols, Ferrasols and Gleysols tested (Table 2.4, Fig. 2.4). However, this increase relative to oxic WEP was only paralleled by an increase in Dithionite-P for Cambisols, Gleysols and Luvisols, as the slopes of anoxic WEP versus Dithionite-P were significant ($P < 0.05$) only for these three soils (Table 2.4, Fig. 2.3 & Fig. 2.5). To get a better picture of the magnitude of P that could be quickly released under reducing conditions to sub-surface flow or surface runoff, anoxic WEP was calculated relative to the total reducible P pool - Dithionite-P. The mean anoxic WEP proportions ranged from 12% (Acrisol) to 159% (Andisol). The unusual behaviour of WEP versus Dithionite-P in the Andisol samples may be due to allophane occluding P. Allophane would not behave like metal oxides in reducing conditions. However, more in-depth research is required to understand the minute behaviours of each soil and their constituents in reducing conditions. The mean proportions of the Andisols and Vitric andisols were significantly different ($P < 0.001$) from the mean proportions from Gleysols, Luvisols, Arenosols and Acrisols.

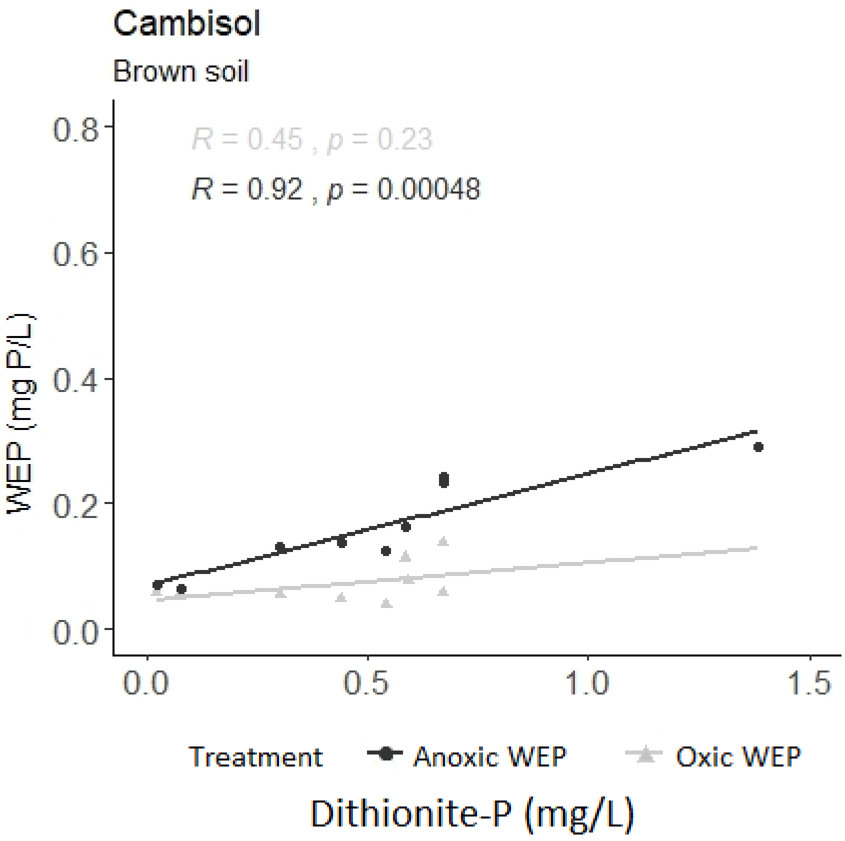

Figure 2.3 Relationship between water extractable P (WEP) extracted under anaerobic (oxygen < 0.05 mg $L^{-1}$) and aerobic (oxygen >0.05 mg $L^{-1}$) conditions, and Na-dithionite-extractable P (dithionite-P) concentrations for Cambisols (Brown soils) from the New Zealand archive. R and *P* values indicate the strength and significance of the relationship, respectively.

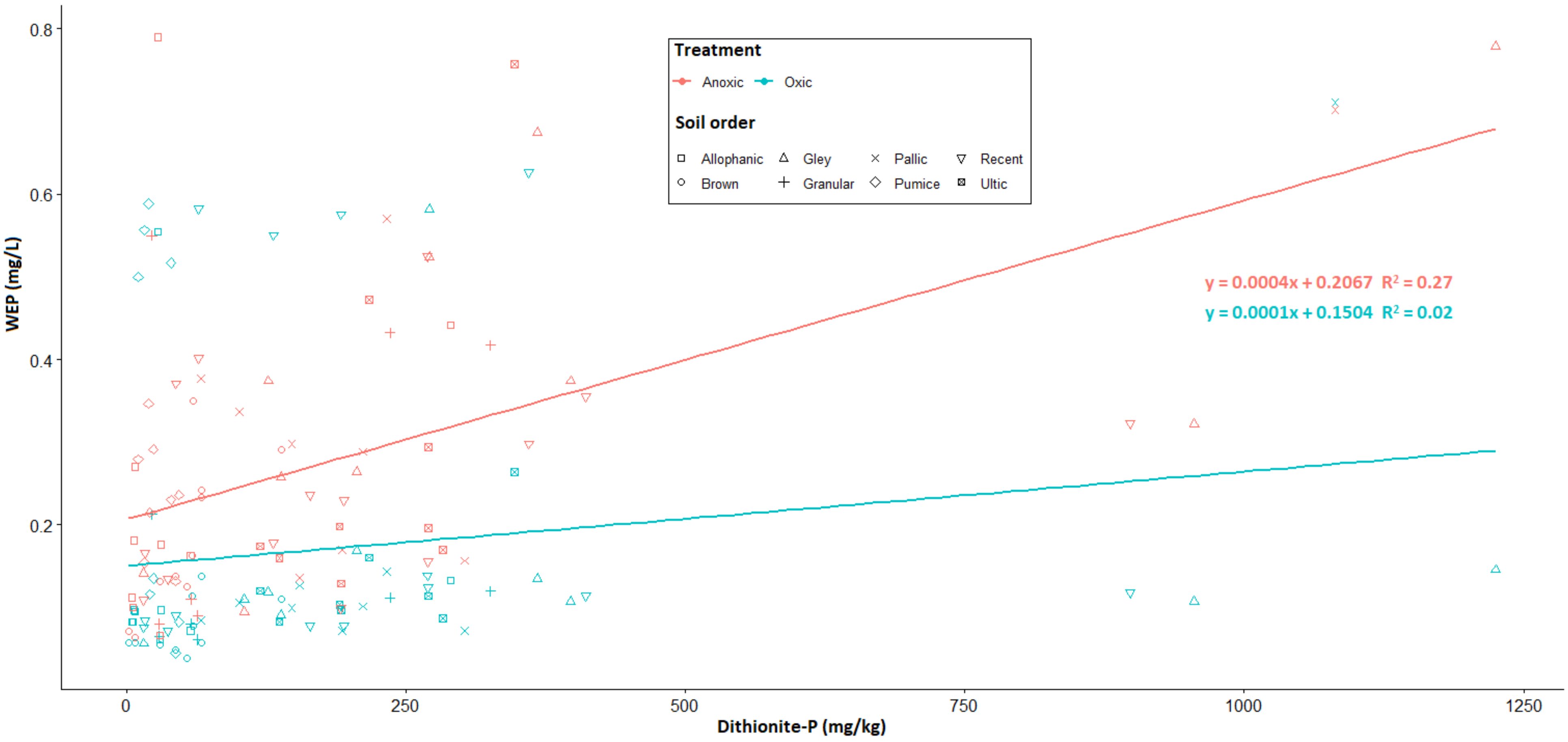

Figure 2.4 Relationship between water extractable P (WEP) extracted under anaerobic (oxygen < 0.05 mg/L) and aerobic (oxygen >0.05 mg/L) conditions, and Na-Dithionite extractable P (Dithionite-P) concentrations of New Zealand soils

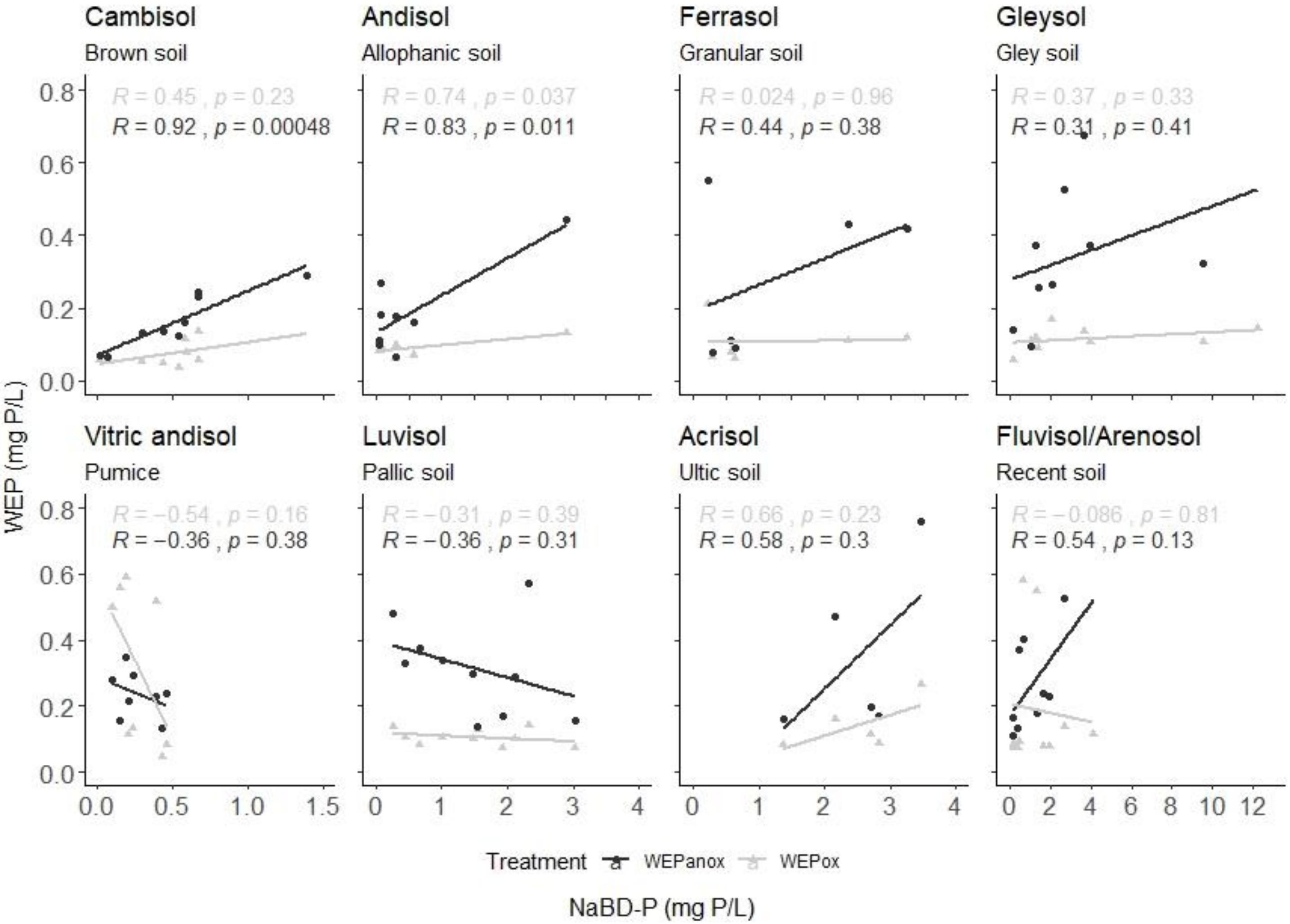

Figure 2.5 Relationship between water extractable P (WEP) extracted under anaerobic (WEP$_{anox}$, oxygen < 0.05 mg/L) and aerobic (WEP$_{ox}$, oxygen >0.05 mg/L) conditions, and Na-Dithionite extractable P (NaBD-P) concentrations for different soil orders in the New Zealand archive. Note scales are of different size.

Table 2.4 Mean water-extractable P (WEP) of New Zealand soils from each soil group extracted under aerobic WEP (>0.5 mg dissolved oxygen (DO)/L) or anoxic WEP (<0.5 mg DO/L) conditions, the output of an analysis of covariance yielding the slope of a regression against Na-dithionite-extractable P, and the proportion of anoxic WEP relative to the total Dithionite-P pool. Lettering[1] indicates significant difference between groups via Tukey's Honestly Significant Difference.

| FAO soil group | NZ soil order | n | WEP (mg/L) | | Slope | $R^2$ | % Anoxic WEP as Dithionite -P |
|---|---|---|---|---|---|---|---|
| Andisol | Allophanic | 9 | Oxic | 0.14*[2] | 0.0000 | 0.74 | $159^{a}$ [1] |
| | | | Anoxic | 0.26 | 0.0008 | 0.83 | |
| Cambisol | Brown | 10 | Oxic | 0.08* | 0.0005*[3] | 0.45 | $66^{ab}$ |
| | | | Anoxic | 0.18 | 0.0019 | 0.92 | |
| Gleysol | Gley | 10 | Oxic | 0.16** | -0.0000* | 0.37 | $22^{bc}$ |
| | | | Anoxic | 0.38 | 0.0004 | 0.31 | |
| Ferrasol | Granular | 12 | Oxic | 0.10** | 0.0000 | 0.02 | $56^{abc}$ |
| | | | Anoxic | 0.25 | 0.0007 | 0.44 | |
| Luvisol | Pallic | 9 | Oxic | 0.17* | 0.0004* | -0.31 | $20^{bc}$ |
| | | | Anoxic | 0.34 | 0.0006 | -0.32 | |
| Vitric andisol | Pumice | 8 | Oxic | 0.32 | -0.0095 | -0.54 | $113^{a}$ |
| | | | Anoxic | 0.24 | -0.0019 | -0.36 | |
| Arenosol / Fluvisol | Recent | 16 | Oxic | 0.25 | -0.0001 | -0.09 | $32^{bc}$ |
| | | | Anoxic | 0.25 | 0.0002 | 0.54 | |
| Acrisol | Ultic | 9 | Oxic | 0.13* | 0.0004 | 0.66 | $12^{c}$ |
| | | | Anoxic | 0.28 | 0.0018 | 0.58 | |

[2] Tests for the significant differences in means between oxic WEP and anoxic WEP within a soil order as *** = *P*<0.001, ** = *P*<0.01, * = *P*<0.05

[3] Significant difference (*P*<0.05) between slopes of oxic WEP and anoxic WEP

### 2.3.4 Estimating anoxic WEP and dithionite-P

Equations were generated from stepwise regression using a range of parameters (e.g. ASC, Olsen P, pH, soil group, land use) to find the best predictors for anoxic WEP and Dithionite-P. Predictors for the normal WEP test under oxic conditions were also established using stepwise regression analysis. These equations were used to map the likely concentrations of different P pools across New Zealand. Assumptions were that the prediction errors are independent, follow a normal distribution, and have homoscedasticity. Outliers were tested for (via Cooke's Distance) and removed. The models are limited by the sample size for each soil group and the soil groups available from the two countries and is therefore not exhaustive.

Stepwise regression analysis (Table 2.5) showed that normal oxic WEP was best, but weakly, predicted by ASC and Olsen P ($R^2$ 37%, Mallow's Cp: 6.9, $\alpha < 0.05$; Eq 2.1). Anoxic WEP was also best predicted by Olsen P and ASC ($R^2$ 53%, Mallow's Cp: 0.6, Eq. 2.2). Categorical predictors (i.e. land use or soil group) were not significant in any case.

$$\frac{1}{\sqrt{\text{Oxic WEP}}} = (0.1171\sqrt{\text{ASC}}) - (1.253 \text{ Log Olsen P}) + 4.156 \qquad \text{Eq. 2.1}$$

$$\sqrt{\text{Anoxic WEP}} = (0.4404 \text{ Log Olsen P}) - (0.0371\sqrt{\text{ASC}}) - 1.057 \qquad \text{Eq. 2.2}$$

Stepwise regression analysis of Dithionite-P identified Olsen P, ASC, pH, land use as two categories (arable and pasture), and soil group in the New Zealand model as key predictors (Eq. 2.3), with the smallest Mallow's CP value and the best R-squared prediction percentage of 44% ($R^2$ 54%, Mallow's Cp: 12, Table 2.6).

$$\text{Log Dithionite P} = -0.928 + (0.397\ \text{Log Olsen P}) - (0.00626\ \text{ASC}) + 0.3196\ \text{pH} + 0.0\ \text{Andisol} + 0.369\ \text{Cambisol} + 0.658\ \text{Gleysol} + 0.150\ \text{Ferrasol} + 0.797\ \text{Luvisol} - 0.160\ \text{Vitric Andisol} + 0.386\ \text{Recent} + 0.729\ \text{Acrisol} + 0.0\ \text{Arable} + 0.1932\ \text{Pasture}$$

Eq. 2.3

For the Irish soils, no groupings were made by land use or the soil by land use interaction, reducing the model to soil group and terms for Morgan's P and Mehlich-Al (Table 2.6; Eq. 2.4). The larger coefficient for the Morgan's test implies that it exerts greater control of Na-Dithionite than other variables. The homogeneity of land use in Ireland likely caused the lack of significance of land use in the constructed model. This model explained 52% of the variation in Dithionite-P concentration and had a Mallow's CP of 7. The soils were also grouped into 3 clusters by Dithionite-P concentrations and gave ranges of: 0-108 mg kg$^{-1}$; 108.1-324 mg kg$^{-1}$; and <324 mg Dithionite-P kg$^{-1}$.

$$\text{Log (Dithionite P)} = 0.79\ \text{Log (Morgan's P)} - 0.0005\ \text{Mehlich Al} - 0.13\ \text{Gleysol} + 0.17\ \text{Luvisol} + 0.14\ \text{Phaeozem} - 0.15\ \text{Podzol} - 0.25$$

Eq. 2.4

If the prediction parameters were selected to match those identified by Thomas et al. (2016), namely WEP and Morgan's P and included soil group, they explained 50% of the variation in the model and had a Mallow's CP of 7 (Eq. 2.5, Table 2.7).

$$\text{Log(Dithionite P)} = 0.52\ \text{Log (Morgan's P)} + 0.21\ \text{Log (WEP)} - 0.12\ \text{Gleysol} + 0.16\ \text{Luvisol} + 0.07\ \text{Phaeozem} - 0.38\ \text{Podzol} + 0.12$$

Eq. 2.5

Table 2.5 Stepwise effect on the coefficient of determination and the degree of fit (via Mallows' Cp) of different parameters for the prediction of oxically-extracted water-extractable phosphorus (oxic WEP), anoxically-extracted water-extractable phosphorus (anoxic WEP) in New Zealand soil samples (n=81).

| Country / parameter | -----Step 1----- | -----Step 2----- |
|---|---|---|
| *Oxic WEP* | | |
| Constant | 4.88 | 4.16 |
| Olsen P | -1.34$^{***1}$ | -1.25$^{***}$ |
| ASC | | 0.112* |
| R-sq | 31% | 37% |
| Mallows' Cp | 11.85 | 6.91 |
| *Anoxic WEP* | | |
| Constant | -1.289 | -1.067 |
| Olsen P | 0.47$^{***}$ | 0.44$^{***}$ |
| ASC | | -0.0371$^{**}$ |
| R-sq | 46% | 53% |
| Mallow's CP | 9.02 | 0.60 |

[1] P values indicating significance of 0.001, 0.01 and 0.05 are shown with ***, **, and *, respectively

Table 2.6 Forward stepwise effect on the coefficient of determination and the degree of fit (via Mallows' Cp) of different parameters for New Zealand (anion sorption capacity (ASC), Olsen P, pH, soil order, and land use, n = 134) and Ireland (Morgan's P, Mehlich Al, and soil order, n=106) on predicting sodium bicarbonate-dithionite extractable P (Dithionite-P).

| Country / parameter | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 |
|---|---|---|---|---|---|
| *New Zealand* | | | | | |
| Constant | 2.25 | 1.89 | -0.02 | -0.40 | -0.93 |
| ASC | -0.01*** | -0.01*** | -0.01*** | -0.01** | -0.01** |
| Soil group | | 0.54*** | 0.65*** | 0.76*** | 0.80*** |
| pH | | | 0.31*** | 0.27*** | 0.32*** |
| Olsen P | | | | 0.35** | 0.40*** |
| Land use | | | | | 0.19* |
| R-sq % | 25% | 42% | 49% | 52% | 54% |
| R-Sq Pred[2] | 23% | 34% | 40% | 43% | 44% |
| M Cp[3] | 66 | 36 | 21 | 14 | 12 |
| *Ireland* | | | | | |
| Constant | -0.80 | -0.25 | -0.25 | | |
| Morgan's P | 0.82$^{***}$ | 0.75$^{***}$ | 0.79$^{***}$ | | |
| Mehlich-Al | | -0.0005$^{***}$ | -0.0005$^{**}$ | | |
| Soil group | | | 0.17$^{*}$ | | |
| R-sq % | 40% | 47% | 52% | | |
| M Cp | 23 | 10 | 7 | | |

[1] *P* values indicating significance of 0.001, 0.01 and 0.05 are shown with ***, **, and *, respectively

[2] R-Sq Pred = determines how well the model predicts a removed observation

[3] M Cp = Mallow's Cp

Table 2.7 Forward stepwise effect on the coefficient of determination and the degree of fit (via Mallows' Cp) of parameters used by Thomas et al. (2016), using the Irish Soil Information System data (n = 106).

| Parameter | -----Step 1----- | -----Step 2----- | ------Step 3----- |
|---|---|---|---|
| Constant | -0.78 | 0.19 | 0.12 |
| Log Morgan's P | 0.82$^{***}$ | 0.46$^{**}$ | 0.52$^{***}$ |
| Log WEP 1:300 | | 0.55$^{**}$ | 0.49$^{**}$ |
| Soil group | | | -0.38$^{*}$ |
| R-sq % | 40% | 44% | 50% |
| Mallows' Cp | 18 | 11 | 7 |

$^{1}$*P* values indicating significance of 0.001, 0.01 and 0.05 are shown with ***, **, and *, respectively.

### 2.3.5 Spatial coverage of dithionite-P and anoxic WEP

Based on the stepwise regression analysis, using equations 2.2 and 2.3, anoxic WEP and Dithionite-P were mapped for productive land of New Zealand (Fig. 2.6) using input data from the New Zealand 500 Soils project and the FSL soil drainage layer (LRIS, 2010). Hierarchical cluster analysis (via the Elbow method) accounting for soil order grouped the Dithionite-P pools in New Zealand in soil into three clusters: 0-170 mg kg$^{-1}$; 171-600 mg kg$^{-1}$; and >600 mg kg$^{-1}$. For anoxic WEP, the clusters were identified as: 0-0.291 mg P/L; 0.291-0.570 mg P/L; and >0.570 mg P/L. However, all the predicted anoxic WEP values were predicted to be less than 0.57 mg P/L. In the original dataset, 5 of the 83 samples tested were greater than 0.57 mg P/L. Therefore, this may indicate a weakness in the model to predict more extreme concentrations. Each cluster was rescaled into two (Table 2.8) to allow for more detailed mapping, due to the large ranges the clusters encompassed and the lack of definition in the resulting map (Fig. 2.6). For instance, when dividing by only the three Dithionite-P pool clusters at a 1:50,000 scale in New Zealand, 85% of the productive land fell within the first Dithionite-P cluster. Therefore, while working at the 1:50,000 scale, more detail was required to give any definition while mapping.

Table 2.8 The percentage within a drainage class in New Zealand that occurs within the assigned ranges of sodium-bicarbonate-dithionite extractable P (Dithionite-P) pool size and anoxic WEP pool size, from overlaying the created Dithionite-P and anoxic WEP maps with a New Zealand drainage class map (Landcare Research, 2018).

| | Very poor | Poor | Imperfect | Moderately well | Well | Total land area per P range (ha) |
|---|---|---|---|---|---|---|
| *Dithionite-P range (mg P/kg)* | ---------- % Dithionite-P fraction within drainage class ---------- | | | | | |
| 0 – 85 | 2.3 | 3.3 | 9.9 | 23.5 | 61.1 | 7,795,343 |
| 86 – 170 | 1.0 | 20.9 | 38.2 | 15.8 | 24.1 | 1,752,184 |
| 171 – 390 | 1.2 | 19.1 | 29.3 | 30.1 | 20.3 | 1,627,048 |
| 391 – 600 | 0 | 14.0 | 48.8 | 5.8 | 31.4 | 100,682 |
| 601 – 900 | 0 | 12.3 | 0 | 87.7 | 0 | 7,074 |
| 901 + | 0 | 0 | 0 | 100 | 0 | 6,344 |
| *Anoxic WEP range (mg P/L)* | ---------- % Anoxic WEP fraction within drainage class ---------- | | | | | |
| 0.000 – 0.145 | <0.1 | <0.1 | 1.7 | 30.8 | 59.5 | 278,195 |
| 0.146 – 0.291 | <0.1 | 8.2 | 17.7 | 23.5 | 49.5 | 10,634,054 |
| 0.292 – 0.430 | <0.1 | 20.0 | 21.1 | 9.1 | 31.5 | 376,246 |
| 0.431 – 0.570 | 0 | 13.8 | 20.5 | 26.9 | 38.9 | 179 |
| *Total area in NZ per drainage class (ha)* | 214,256 | 945,904 | 1,969,757 | 2,614,880 | 5,543,877 | |

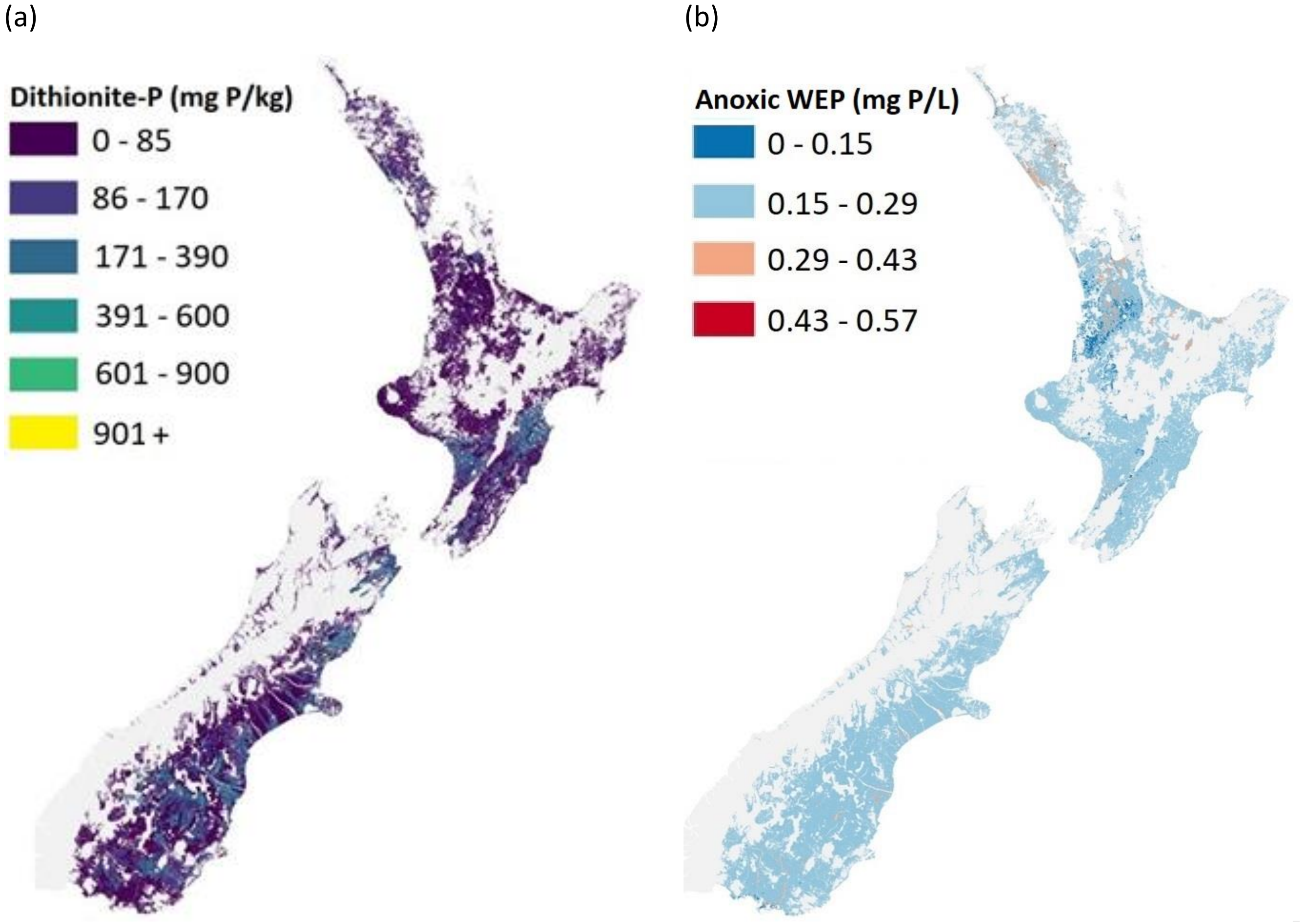

Figure 2.6 New Zealand productive land maps of (a) sodium-bicarbonate-dithionite extractable phosphorus (Dithionite-P), and (b) Water Extractable Phosphorus (anoxic WEP) pool sizes, using equations 2.2 and 2.3.

After intersecting the six Na-Dithionite concentration ranges with the five New Zealand soil drainage classes from very poor to well drained (LRIS, 2010), there was an even spread of low (0-85 and 85-170 mg kg$^{-1}$) Dithionite-P across all drainage classes but the spread became narrower and more likely to be within poorer drainage classes as concentrations increased (Table 2.8). A similar spread was noted for anoxic WEP. All the anoxic WEP values were predicted to be less than 0.57 mg P/L. In the original dataset, 5 of the 83 samples tested were greater than 0.57 mg P/L.

For clarity; the results produced in Figure 2.6 are not a risk map. The map indicates pool sizes and the amount of redox-sensitive P in the soil at a site. However, many of areas (e.g. in Central Otago, Canterbury) have typically high soil moisture deficits (due to lower rainfall). Therefore, this may be why there is also higher WEP – as it has not been flushed out by regular rainfall – and/or soil types (e.g. alluvial gravels) that are not conducive to maintaining soil saturation to enhance WEP. A potential improvement would be to include number of saturation days or climatic data.

## 2.4

### 2.4.1 Relative size importance of dithionite-P

Na-Dithionite targets P that is attached to total free iron oxides in soils and is intended to artificially mimic reduction that occurs naturally (Jensen and Thamdrup, 1993; Lehtoranta et al., 2015; Loeppert and Inskeep, 1996). It can reduce and release 100% of exchangeable iron and amorphous iron oxides (ferrihydrite), and between 50 and 100% of crystalline iron oxides (goethite and hematite) (Colombo et al., 2014; Fan et al., 2016; Scalenghe et al., 2012; Van Bodegom et al., 2003). Therefore, any P associated with these forms of Fe would be released into solution. This test significantly differs from the others in its effect on Fe, as crystalline Fe minerals generally have very low solubility in soils. So a soil with a greater abundance of amorphous Fe (e.g. a Gleysol) would be more prone to reductive dissolution during initial reactions after saturation (Colombo et al., 2014; Lindsay, 1979).

Some studies have used dithionite-extractable P to draw connections between hypoxia and P release from tidal flats, assessing P attached to soil iron oxides and, in the relationship between iron oxides and P sorption. Concentrations vary widely depending on the source and soil group. In the tidal flat areas of Japan, the amount of dithionite-extractable P ranged between 120-200 mg P/kg (Tanaka et al., 2007). Extractions conducted in the United States of America on Acrisol, and Podzoluvisols yielded 308 and 18 mg P/kg, respectively (Hass et al., 2011; IUSS Working Group WRB, 2015). In a study conducted in Pakistan and Germany, a Phaeozem, Cambisol and two Luvisols extracted 18, 61 and 181 and 46 mg P/kg, respectively (Memon, 2008). Although each study used slightly different extraction times and extractants, the magnitude of P extracted is in line with that measured here.

### 2.4.2 Relative size importance of oxic and anoxic WEP

Oxic WEP tests are an environmental indicator of the soluble P that is likely to be desorbed from soil into surface runoff during a rainfall event (Self-Davis et al., 2009). Anoxic WEP is intended to mimic saturated and reducing conditions in the field. Gotoh and Patrick (1974) showed that water-soluble Fe extraction under a negative redox potential (i.e. reduced conditions) and pH<7 significantly increased extractable Fe compared to a positive redox potential of the same pH (e.g., 1493 mg/L Fe at -250 mV vs. < 1 mg/L Fe at +300 mV). As there is a strong relationship between P and active Fe (Jiang et al., 2015), conditions that influence Fe dissolution will also influence P release.

The experiment showed that anoxic WEP concentrations were greater than oxic WEP, supporting the premise that saturated and anoxic conditions would lead to more P dissolving into solution. Experiments such as those by Lai and Lam (2008) and Li et al. (2013) also show anoxic conditions and subsequent decreasing redox potentials induces WEP release. In an experiment on US sediments, Rahutomo et al. (2019) showed a significant increase in WEP in anaerobic conditions compared to aerobic conditions. Additionally, Maftoun et al. (2003) and Ekpete (1976) tested a variety of soil P tests in oxidised and reduced conditions. They both demonstrated that, while Olsen P could predict plant growth parameters in either redox state, other soil tests showed poorer correlation under reducing conditions. These studies suggest that not accounting for reducing conditions can lead to inaccuracies in plant growth modelling. The present study asserts that a similar inaccuracy is likely in catchment maps and models in areas known to exhibit saturation conditions but predict P losses via oxic WEP (Thomas et al., 2016).

While there was a difference in mean oxic WEP and anoxic WEP for most soil groups, no difference was noted in Arenosols and Vitric andisols (Table 2.4). These are coarse-textured soils unlikely to have a much reducible-Fe due to their youth and minimal development (Craft, 2016; Hewitt, 2010). Also, these soils have the highest overall WEP concentrations, on average (0.26 mg P/L). This suggests that the WEP is extracting P that is likely to be loosely held and not as susceptible to reducing conditions.

### 2.4.3 Predicting dithionite-P and anoxic WEP

In the New Zealand soils, the two soil tests important in predicting oxic WEP and anoxic WEP were Olsen P and ASC. Olsen P is usually interpreted as the plant-available inorganic P fraction but has also been correlated to P loss in runoff (Heckrath et al., 1995b). Soil ASC is a measure of the aluminium (Al) and Fe oxide concentration, as measured by the soil's ability to sorb and retain added phosphorus (Saunders, 1965). As ASC increases, P sorption increases and P desorption decreases. If two soils were to have the same Olsen P, the soil with the lower ASC would release more P into solution, which is supported by the equations in the present study. Previous work has shown Olsen P and ASC can predict WEP under oxic conditions (Simmonds et al., 2013). The equation of McDowell and Condron (2004), oxic WEP = 0.03(Olsen P/ASC) +

0.03 is different to that in this study (Eq. 2.2) for oxic WEP, and substantially different to that in Eq. 2.3 for anoxic WEP. This questions the validity of models that use the equation of McDowell and Condron (2004) to predict farm P losses to water under saturated conditions (Gray et al., 2016a). Two limitations of the model presented here are: using an archive of topsoil samples (as discussed); and not including site specific hydro-climatic data in the model's construction.

Variables important in determining Dithionite-P were Olsen P, pH, ASC and land use and soil order. Olsen P has previously been shown to be correlated with Dithionite-P, presumably as a result of extracting similar, but perhaps not the same, Fe-P compounds (Olsen et al., 1954; Wuenscher et al., 2015). Soil pH affects whether P is sorbed to Al, Fe or Ca (Lindsay, 1979). According to the equation for Dithionite-P (Eq. 2.3), Dithionite-P increased with pH. The positive relationship can be explained by the fact that P solubility increases as soils approach pH 6-6.5 and that all soils were pH <6.5 (Table 2.1). Finally, Eq. 2.2 and 2.3 indicated that a greater ASC will result in a smaller Dithionite-P. However, the coefficient was small indicating that the role of ASC in determining Dithionite-P was weak.

Soil group was also important in determining Dithionite-P. This concurs with other studies where P desorption was linked to soil type (Daly et al., 2001). Those New Zealand soils that have the greatest Dithionite-P were Luvisols, Gleysols, Acrisols and Fluvisols (Table 2.1). All these orders have undergone some form of periodic saturation and/or fluvial processing. Saturation converts Fe to amorphous forms (e.g. ferrihydrite) that are more sensitive changes in redox conditions (Colombo et al., 2014; Lindsay, 1979). This cycling is likely to solubilise and precipitate Fe and associated P into Na-Dithionite-extractable P forms. In contrast, the lowest Dithionite-P concentrations were exhibited in soil groups primarily of volcanic origin – the Andisols, Ferrasols and Vitric andisols. Weathered New Zealand volcanic soils contain aluminosilicate clay minerals such as allophane, which are highly P-sorptive due to the presence of Al not Na-Dithionite-extractable Fe (Molloy, 1998).

Land use may reflect the large soil management differences in pH and Olsen P. In a study by McDowell et al. (2020), soil P accumulation was connected to the soil order and the farm type. Dividing the land uses into pasture versus crop, the means of Olsen P, ASC and pH were significantly different (Table 2.1). Particularly in the volcanic soils, the cropped soils had a greater mean Olsen P and lower pH within a soil order compared to the same soil under pasture. It would be beneficial to integrate hydro-climatic parameters into future work. Including them would strengthen WEP predictions at the catchment scale, as conditions such as rainfall or soil moisture may affect the accuracy of predictions.

Only Dithionite-P was predicted in the Irish soils. The inclusion of Ireland provides an interesting contrast between two countries. In New Zealand, there are contrasting soil types (e.g. andisols versus gleysols) and land uses (e.g. arable land versus drystock land). Meanwhile in Ireland, the land uses are heavily skewed towards grassland, and the soil characteristics are more homogenous. Therefore, this demonstrates that reducible Fe and P will have a variable level of importance in different countries. In Ireland, the important variables were Morgan's P and Mehlich-3 extractable Al. Morgan's P test is used to predict plant growth potential and therefore can be expected to extract a similar P fraction as Olsen P. This concurs with other research where Morgan's P was identified as a good indicator of P loss from soil to water (Daly and Casey, 2005). Mehlich-3 extractable Al was an unexpected predictor, as Al is not expected to be affected by redox, but rather subsequent changes in other parameters such as pH (Husson, 2013). However, the equation coefficient is small, and its inclusion in the model may reflect its importance in contributing to a soil's ASC (Daly et al., 2015).

### 2.4.4 Utility of dithionite-P and anoxic WEP estimates

The models can be used to create a GIS layer that can inform future modelling and decision support tools (DST) designed to aid management at a catchment scale. However, unless robust data are available, caution should be employed when using the predictions at a farm scale. For instance, many national soil surveys will have spatial data at a resolution > 1:50,000 (Landcare Research, 2014). Furthermore, saturated areas expand and contract dependent upon soil moisture conditions and the amount and intensity of rainfall (Doody et al., 2006; Gburek et al., 2002; Thompson et al., 2012). This scale and the variable nature of saturated areas may not relate to management decisions on farm. Therefore, local knowledge of where and when saturated areas exist on farm should be the first step in refining the need and placement of management decisions to prevent P loss under saturated conditions. The risk of P loss and need for remedial action could then be further refined with Dithionite-P and anoxic WEP tests.

Excluding spatial scale, caution should also be employed when using these equations to predict anoxic WEP. These equations contain error and therefore should be calibrated against a subset of samples representative of soil types and land uses in the region. However, if management requires detailed knowledge of saturated areas it may be worth the additional time and resources to measure anoxic WEP than predict it. Such a situation may arise if, for example, decisions need to be made regarding the renovation of artificial drainage networks in catchments with P-sensitive receiving waters.

Several practices are available to decrease P losses from saturated grassland soils. These range from lowering soil Olsen P concentrations buy reducing P fertiliser inputs (Morton et al., 2003), to restricting or avoiding their use either for the application of farm dairy effluent or grazing – especially in winter (McDowell et al., 2005; Monaghan et al., 2010). Deceases in P losses range from 5 to 40% but may also result in losses occurring in other parts of the farm if not designed well. For instance, restricting the grazing of winter forage crops by cattle to 3-4 hrs requires stock to be in another part of the farm where dung can be captured and not lost to water (McDowell, 2006). Greater decreases occur where the risk of saturation and runoff is considered. For instance, in a catchment trial in Otago, New Zealand, a critical source area for P loss was identified as the saturated near stream area which lost most P in winter and spring. McDowell et al. (2014) modelled this area, and enriched Olsen P concentrations decreased by half through inversion tillage. Through a lower need for P fertiliser, soil Olsen P and replanting the area in a low-P tolerant ryegrass, milk production was improved while dissolved reactive P concentration decreased by 38% (McDowell et al., 2014).

As noted above, successfully managing P losses from CSAs, requires knowledge of where and how often saturation zones occur and the size of the pool of P available for loss (Doody et al., 2010). Hydrologic models exist at the farm scale (Thomas et al., 2016; Thompson et al., 2012). Data on soil P fertility have been used as a proxy to estimate the availability of P to loss, but with variable results (Page et al., 2005). It is proposed that a better estimate of risk may incorporate P availability via anoxic WEP in the short-term and Dithionite-P in the long-term, although additional work is required to confirm this.

Accuracy of the anoxic WEP and Dithionite-P tests may vary depending on factors such as geographic location, soil type, the depth at which soil samples are taken. The models created here used soil samples collected from the first horizon. However, it may be more beneficial to investigate the relationship to depth where saturation could occur more regularly. We also assumed that the form and behaviour of P and Fe in soil samples were not affected by being sieved and stored before analysis. If a soil was originally anaerobic and dried in the presence of oxygen, soil P and Fe availability may change. Additional work is required to determine if these factors impair the utility of the tests. Another factor to consider is that this work has been presented at the 1:50,000 scale and it is unknown if the processes are at play at larger scales over a farm or sub-catchment. Bol et al. (2018) noted that modelling relies on assumptions such as a constant availability of P to loss, and that not accounting for variation can lead to ambiguities in identifying P sources. Therefore, to be useful in informing models and management of P losses, further work is required relating these lab tests to field data.

## 2.5 Conclusions

This study showed that exposing soil to an anoxic environment increases WEP, in comparison to normal, oxic WEP tests. Therefore, there is a need to include the influence of anoxic conditions on P release in periodically saturated farmland. It is recommended to determine anoxic P directly or conduct a calibration step to make a more accurate model for the specific soils or site in question. However, the present study shows that concentrations could be predicted with moderate confidence ($R^2$ 53%) with an array of readily available soil tests (Olsen P, ASC, and pH). Similar predictions were possible for Dithionite-P.

Readily available soil test data was used to demonstrate the risk of short- and long-term P loss from soils that are periodically saturated. These data could be used as an indication of where additional, finer scale anoxic WEP and Dithionite-P tests, should be collected. These fine scale data will help improve the isolation of CSAs of P loss due to saturated conditions and the targeting of strategies to mitigate loss.  Further study should look to include this method into current or developing models predicting P release at the paddock to small catchment scale and compare predictive data with field data, thus establishing its validity and usefulness in a practical setting.

# Chapter 3

# Shallow subsurface phosphorus losses in grassland soils as influenced by oxygen, temperature, superphosphate and soil texture

## 3.1 Introduction

Globally, phosphorus (P) is essential for productive agriculture, and regular fertiliser P inputs into agricultural soils are necessary to maintain that productivity (Bomans et al., 2005; Haygarth et al., 1998; Leinweber et al., 2002). However, P from agricultural soils can be lost to local surface water bodies via subsurface and surface pathways, leading to water quality issues such as eutrophication and excessive aquatic plant growth (Hansen et al., 2002; Heathwaite and Dils, 2000; Leinweber et al., 2002; Owens and Shipitalo, 2006). Many studies have concentrated on characterising losses of phosphorus (P) in particulate and dissolved forms via surface or subsurface pathways (Dupas et al., 2017; Fenton et al., 2017; McDowell et al., 2015; Monaghan et al., 2016; Thomas et al., 2017; Thomas et al., 2016). The storage of DRP and kinetics of release in near-surface, saturated lateral pathways have not received much attention. Such pathways are highly relevant to P losses in grassland soils that are poorly drained, shallow, have a perched water table, or where there is a large seasonal difference in water table levels and where sites are predisposed to saturation-excess runoff (Thomas et al., 2017).

Saturation excess conditions could cause changes in P loss kinetics along lateral and vertical pathways via a process called reductive dissolution (Gu et al., 2019; Warrinnier et al., 2020). When a soil becomes saturated, respiring microbial communities will quickly deplete oxygen ($O_2$) and $NO_3^-$ sources for energy by reducing them to solubilised forms via redox reactions. When these are depleted, the soil profile becomes anoxic and microbes rely on reducing P-sorptive Mn- and Fe-oxides to create energy (McMahon and Chapelle, 2008). Any P sorbed to Mn- and Fe-oxides are dissolved with the Fe and Mn. However, current tests, such as water extraction, predict the potential for P loss to runoff in oxic conditions (McDowell and Condron, 2004), and therefore may underestimate P loss under saturated conditions. More recent tests have tried to overcome this by quantifying P that is released from reduced Fe and Mn over the long-term, referred to as “reducible-P” (or R-P) (Smith et al., 2021).

In laboratory incubations, microbial activity can quickly (within hours) induce anoxic conditions (Holford and Patrick, 1978; Leinweber et al., 2002; Patrick and Khalid, 1974; Zhang et al., 2010). For instance, Gu et al. (2019) incubated riparian wetland soils and sediments in a soil to solution ratio of 1:20 at room temperature and found DRP release plateaued after 24 hours. However, Heiberg et al. (2012) incubated peat and sand under cereal crop rotation and found that, reduction of Fe(III) began immediately after incubation, and DRP release under anoxic conditions levelled off after 45 days at room temperature (23$^{o}$C). Clearly, more information is required on how fast anoxic conditions will cause P release in soils, especially grassland soils. It is important to know if the period of saturation expected in grassland soils is long enough that DRP release under anoxic conditions is significant.

As redox is typically microbially-mediated, local soil temperature would influence the rate or occurrence of Fe-P dissolution. Sallade and Sims (1997b) demonstrated that there was more rapid and pronounced Fe dissolution at an incubation temperature of 35$^{o}$C compared to 7$^{o}$C. However, the cooler temperature is warmer than that exhibited in many temperate grassland soils during late autumn to early spring. For instance, at this time, most soils under grassland in Ireland and southern New Zealand would have a temperature range of 2-10$^{o}$C, in the top metre of soil (Ceccon et al., 2011; Huang et al., 2014). More importantly, this is also when saturated conditions and P loss are most likely (Srinivasan and McDowell, 2009) leading to the question of whether this cooler temperature significantly reduces the rate of P release under anoxic conditions?

Long term P fertiliser practices may also affect P losses. Previous work has shown a relationship between Olsen P concentrations and surface and subsurface P loss (McDowell and Condron, 2004). However, it is unclear how soils of different Olsen P would release DRP under anoxic conditions.

To address these issues, a soil coring study was conducted in Ireland to establish that (a) there was a redox-sensitive form of P that should be investigated, and (b) that this redox-sensitive form behaves differently than a typical water extractable P (WEP) test. Following the results of this, an incubation study was conducted using field-moist grassland soils from sites in Ireland and New Zealand, in order to further establish differences in P loss due to oxygen conditions. Ireland and New Zealand were selected, as grassland agriculture accounts for nearly half of each country’s land use (European Commission, 2019; StatsNZ, 2018). The objectives of the incubation study were to: (a) determine the concentration and kinetics of P release in water extracts under anoxic and oxic conditions over a 24-hour period – deemed representative of a subsurface flow producing rainfall event; and (b) to establish the importance of temperature and soil P fertility, representative of winter and summer seasons and typical P application rates (0-60 kg P $ha^{-1}$ $yr^{-1}$). These results will give some indication whether anoxically-induced P release would contribute to P loss within the day of saturation and compliment the soil coring study.

## 3.2 Materials and Methods

### 3.2.1 Soil profile vertical distribution study

To give credence to the suggestion that Oxic WEP does not extract redox-sensitive P, the vertical distribution of P via two soil tests were conducted. To determine the availability of P for loss, five soil profile cores were taken every 30 m along a 100 m transect across a hillslope grassland paddock at Johnstown Castle, Wexford (Ireland) with known shallow subsurface pathways (Ibrahim et al., 2013). Cores were taken to 250 cm below ground level, to intercept characterised subsurface transport pathways and capture the distribution of P above and below an installed artificial drainage system at 100 cm and any perched water tables. Each profile core was divided into 0-10, 10-45, 45-70, 70-100, 100-130, 130-150, 150-175, 175-200, 200-215, and 215-250 cm below ground level, air-dried, sieved (<2 mm) and analysed for water extractable P (Oxic WEP) and sodium-bicarbonate-dithionite extractable P (Dithionite-P). The Oxic WEP tests represents the readily available P in soil, while the Dithionite-P test represents the long-term pool of reducible P (Smith et al., 2021).

Additional data were collected to establish the likelihood of saturation occurring at the site. Within 200 cm of each cored point, the soil water table data was collected daily from November 2017 to March 2019 using water level data loggers (TD-Divers, Eijkelkamp Soil & Water, Netherlands) inside of piezometers drilled to 300-400 cm below ground level. Soil profiles were cored adjacent to these piezometers on the slope. Alongside this, soil moisture deficit (SMD) data was used to estimate how often the site would reach saturation excess (Met Éireann, 2020).

A subsample of the core was analysed (air-dried, < 2mm sieved, Table 3.1) for analysis of: water extractable P (WEP) at a 1:300 soil to solution ratio (McDowell and Condron, 2004); Olsen P (Olsen et al., 1954); anion sorption capacity (ASC) – a measure of the soil's P sorption capacity (Saunders, 1965); pH, total nitrogen (TN) and total carbon (TC) by LECO C/N analyser, and; particle size (Gee and Bauder, 1986). The soils were also extracted at a 1:100 soil to solution ratio with sodium-bicarbonate-dithionite.

### 3.2.2 Incubation trial

Following the results of the vertical distribution study, three different grassland sites were sampled over 2018 and 2019 - two in Ireland and one in New Zealand. They will be referred to by their textural class: clay loam; sandy loam; and silt loam. The sites were classified using the New Zealand (Hewitt, 2010) or the Irish soil classification system and the equivalent FAO classification (IUSS Working Group WRB, 2006) in parentheses. The clay loam (from Co. Wexford in Ireland) was a moderately-drained Stagnic Brown Earth (Cambisol) and was the same soil used in the preliminary soil profile study. The sandy loam (from Co. Cork in Ireland) was a well-drained Typical Brown Earth (Cambisol). The silt loam was a well-drained Pallic Firm Brown soil (Cambisol) from Canterbury in New Zealand. Soils were given a textural class according to previous work in the same locations (Ibrahim et al., 2013; Rickard and Moss, 2012).

Initial soil test P values are listed in Table 3.2. The clay loam and sandy loam each have had three P treatments for a decade, receiving annual P applications of 20, 40 or 60 kg P ha$^{-1}$yr$^{-1}$. Each soil site selected had received the same nitrogen treatment (300 kg N ha$^{-1}$). Grass was not grazed but periodically harvested for hay/silage. There were three replicates for each treatment. The silt loam had three treatments receiving annual applications of single superphosphate (SSP) for over 60 years at rates of 10, 20, 30 kg P ha$^{-1}$ yr$^{-1}$. Each SSP treatment had 4 replicate plots and were grazed by separate flocks of sheep at 10, 14 and 18 stock units ha$^{-1}$, respectively (McDowell and Condron, 2012).

Ten fresh, field-moist topsoil cores (0-10 cm) were taken in each plot with a hand auger from random points in each plot and bulked. A subsample of the bulked cores was analysed (air-dried, < 2mm sieved, Table 3.1) for: water extractable P (WEP) at a 1:300 soil to solution ratio (McDowell and Condron, 2004); Olsen P (Olsen et al., 1954); anion sorption capacity (ASC) – a measure of the soil's P sorption capacity (Saunders, 1965); pH, total nitrogen (TN) and total carbon (TC) by LECO C/N analyser, and; particle size (Gee and Bauder, 1986). The soils were also extracted at a 1:100 soil to solution ratio with sodium-bicarbonate-dithionite.

The laboratory treatments used in the incubation were oxygen content (oxic vs. anoxic); temperature (3°C vs. 18°C); and fertiliser rate (20, 40 or 60 kg P $ha^{-1}$ $yr^{-1}$ for the clay loam and sandy loam, and 10, 20 and 30 kg P $ha^{-1}$ $yr^{-1}$ for the silt loam), with four replicates per treatment combination. Each bulked field-moist soil sample was sieved to <4 cm and homogenised. Samples of 2 g were weighed into containers and prepared in either an anoxic glove box purged with nitrogen gas ($N_2$), or in ambient air. In the glove box, deionised (DI) water was bubbled for 20 minutes with $N_2$ until anoxic (<0.5 mg dissolved oxygen $L^{-1}$), added to the soil to reach a ratio of 1:20 dry weight soil to DI water, stirred, and sealed before removal. Samples were placed on orbital shakers (170 rpm) and shaken and incubated in the dark at 18°C or 3°C. The same process was carried out for the oxic treatment, but in ambient air (> 7 mg DO $L^{-1}$) with untreated deionised water. Chloroform was not used to sterilize soils, as it may have affected the ability of the soils to maintain an anoxic environment and have increased P concentrations by lysing microbial cells (Reddy et al., 1998a). The four resulting treatment combinations (oxic 3°C, anoxic 3 °C, oxic 18 °C, and anoxic 18 °C) were sampled sacrificially in triplicate at each time point (0, 60, 240, 480 and 1440 minutes).

Samples were filtered to 0.45 µm, acidified (1 mL 10% HCl) to prevent precipitation of redox sensitive species (Gu et al., 2019) and analysed immediately for DRP using a standard colorimetric procedure (Watanabe and Olsen, 1965). The main constituent in DRP is thought to be orthophosphate, although it is recognised that some organic P species may undergo acid hydrolysis and increase orthophosphate measurements by 10-20% (McDowell and Sharpley, 2001). Redox sensitive cations ($Fe^{2+}$ and $Fe^{3+}$, $Mn^{2+}$) were analysed via inductively coupled plasma optical emission spectrometry (ICP-OES), and anions ($NO_3^-$, $SO_4^{2-}$) using Dionex suppressed ion-exchange chromatography.

The amounts ($q_t$, mg $kg^{-1}$) of DRP desorbed were calculated after fitting an Elovich equation using Curve Expert 14.0. The Elovich equation is widely used in the study of P release from soils and sediments (Sparks, 2003). The Elovich model was selected as it fit the data better ($r^2$ and standard error [SE]) than other commonly used models (pseudo first-order and second-order equations) (Table 3.3). For each treatment, the natural log of time, ln($t$), was plotted against $q_t$, and the following Elovich model applied (Eq. 3.1):

$$q_t = (1/\beta) \ln(\alpha \beta) + (1/\beta) \ln t \qquad \text{Eq. 3.1}$$

The model gives the rate of reaction (mg kg min) via the equation constants, α and β, which represent initial chemisorption rate (mg $g^{-1}$ min), and extent of surface coverage and activation energy of chemisorption (g $mg^{-1}$), respectively (Inyinbor et al., 2016; McCallister, 2015; Ramachandran et al., 2011). The slope from the Elovich equation (1/ β) is equivalent to the desorption rate, and the intercept ('(1/ β)ln(αβ)') is an approximation of the amount of P that is desorbable at time zero (McCallister, 2015). Other studies have quoted decreasing β values and increasing α values as an indication of an increase in reaction rate, but the validity of this is not robust (Chien and Clayton, 1980; Sparks, 2003).

### 3.2.3 Statistical Analysis

Analyses were conducted using R Studio and Minitab or Curve Expert 14.0 where specified (Minitab, 2018; R Development Core Team, 2010). A two-way analysis of variance (ANOVA) was used to compare mean soil P test concentrations, and Tukey's Honestly Significant Difference post hoc test was used to find specific significant differences between chemical parameters in the three soil groups.

Analysis by repeated measures was carried out via a general linear model (GLM) applied to each of the three soils to identify the influence of oxygen, temperature, and fertiliser as factors (and their interactions) on mean DRP, Fe, Mn and $NO_3$ concentrations measured over 24 hrs, and on the P desorption rate (1/β from the Elovich model). A crossed method was selected as all combinations of factors are represented in the experimental design. Interactions between factors in their influence on P, Fe, Mn and $NO_3$ were calculated via a two-way ANOVA.

Table 3.1 Mean soil chemical[1] and physical parameters of the three sites used in the incubation of field-moist soils

| Texture profile[2] | Location | FAO Soil Group[3] | Irish / NZ Soil classification § | Temp | Rainfall | pH | TN | TC | ASC | Particle Size | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | °C | mm yr$^{-1}$ | | g kg$^{-1}$ | g kg$^{-1}$ | % | Sand % | Clay % |
| Clay loam | Co. Wexford, Ireland | Cambisol | Stagnic Brown | 10 | 1060 | 6.0 | 2.2 | 27 | 18 | 50 | 19 |
| Sandy loam | Co. Cork, Ireland | Cambisol | Typical Brown | 10 | 1029 | 6.8 | 3.0 | 42 | 14 | 62 | 15 |
| Silty loam | Canterbury, NZ | Cambisol | Pallic firm brown | 11 | 781 | 5.4 | 3.9 | 43 | 26 | 30 | 25 |

[1] TN – Total Nitrogen, TC – Total Carbon, ASC – Anion sorption capacity,

[2] Sourced from: Teagasc & Cranfield University (2007) and Landcare Research (2020)

[3] (IUSS Working Group WRB, 2015)

Table 3.2 Soil phosphorus tests[1] for each soil and fertiliser treatment (n = 3 per soil x fertiliser treatment). Means (±SE) are contrasted via a two-way analysis of variance. Lettering indicates significant differences in means within a fertiliser treatment, according to Tukey's Honestly Significant Difference (Tukey HSD).

| Soil texture | P Fertiliser treatment | Oxic WEP | Dithionite-P | Olsen P |
|---|---|---|---|---|
| | kg ha$^{-1}$ yr$^{-1}$ | mg L$^{-1}$ | mg kg$^{-1}$ | mg kg$^{-1}$ |
| Clay loam | 20 | 0.07$^{a}$ (0.003) | 50$^{a}$ (0.8) | 31$^{a}$ (0.5) |
| | 40 | 0.07$^{a}$ (0.005) | 66$^{b}$ (1.0) | 33$^{a}$ (1.4) |
| | 60 | 0.16$^{b}$ (0.015) | 68$^{b}$ (0.1) | 47$^{b}$ (0.8) |
| Sandy loam | 20 | 0.10$^{a}$ (0.002) | 70$^{a}$ (0.2) | 52$^{a}$ (0.9) |
| | 40 | 0.16$^{b}$ (0.008) | 73$^{b}$ (1.3) | 58$^{b}$ (0.4) |
| | 60 | 0.15$^{b}$ (0.003) | 88$^{c}$ (0.3) | 70$^{c}$ (1.5) |
| Silt loam | 10 | 0.11$^{a}$ (0.020) | 55$^{a}$ (0.4) | 27$^{a}$ (1.3) |
| | 20 | 0.09$^{a}$ (0.005) | 66$^{b}$ (0.9) | 39$^{b}$ (1.5) |
| | 30 | 0.22$^{b}$ (0.002) | 103$^{c}$ (0.9) | 50$^{c}$ (0.7) |
| ***P*** Soils | | <0.01 | <0.001 | <0.001 |
| ***P*** Fertiliser | | <0.001 | <0.001 | <0.001 |
| ***P*** Soils × fertiliser | | ns | ns | ns |

[1] WEP = Water extractable P; Dithionite-P = Sodium-bicarbonate-dithionite extractable P

Table 3.3 Fit (coefficient of determination and standard error) desorption rate (mg $kg^{-1}$ $min^{-1}$) of first order, second order and Elovich equation to dissolved reactive P measured over time for the site A (clay loam) soil receiving 20 kg $ha^{-1}$ $yr^{-1}$.

| Model | Treatment | b [1] | $R^2$ | SE |
|---|---|---|---|---|
| First order | Anoxic (3°C) | 0.78 | 0.54 | 0.40 |
| | Oxic (3°C) | 0.89 | 0.58 | 0.45 |
| | Anoxic (18°C) | 0.76 | 0.57 | 0.38 |
| | Oxic (18°C) | 0.85 | 0.61 | 0.37 |
| Second order | Anoxic (3°C) | 0.59 | 0.99 | 54.9 |
| | Oxic (3°C) | 0.34 | 0.98 | 41.5 |
| | Anoxic (18°C) | 0.61 | 0.96 | 94.8 |
| | Oxic (18°C) | 0.42 | 0.98 | 46.3 |
| Elovich | Anoxic (3°C) | 0.22 | 0.99 | 0.11 |
| | Oxic (3°C) | 0.38 | 0.99 | 0.23 |
| | Anoxic (18°C) | 0.20 | 0.97 | 0.19 |
| | Oxic (18°C) | 0.30 | 0.98 | 0.20 |

[1] b = $k_1$ for first order, $k_2$ for second order, and $\beta$ for Elovich equations.

## 3.3 Results

### 3.3.1 Soil profile vertical distribution study

The investigation shows that there was a difference in P behavior under normal versus reducing conditions. For WEP, the amount of extracted P was greatest in the topsoil and decreased with depth. In contrast, Dithionite-P decreased with depth to 60 cm then gradually increased to concentrations like those recorded in the topsoil (0-10 cm) and coincident with the location of artificial drainage pipes (100-150 cm) (Figure 3.1). The greatest Dithionite-P value at depth was found in the soil cores taken from the bottom of the slope (i.e. 124 mg P kg$^{-1}$), which was at least twice the amount found in the soil cores from the middle and top of the slope. These data provide context for the potential of short and long-term pools of P to influence P losses. More specifically, they suggest that while drainage may be influenced by P that is susceptible to loss under long-term reducing conditions, surface runoff may be influenced by P that is susceptible to loss in the short-term. The possibility of short-term changes (e.g. over 24-hour periods) is prudent in such systems.

Between November 2017 and March 2019, the average soil water table level was 260 cm below ground level but at some locations in the slope the water table level would periodically come to within to 40 cm of the soil surface (Figure 3.1). At the bottom of the slope, the water table was between 100 and 250 cm below ground level for 27% of the period sampled. More importantly, for surface runoff, mean SMD indicated that topsoil was either at or in excess of field capacity for 60% of the year between 2017-2019, meaning that surface runoff was likely to be as frequent as drainage (Met Éireann, 2020). Therefore, as there was a difference in the vertical distribution of the two P forms and the site is regularly saturated, the study reinforced the necessity to conduct a 24-hour incubation study that clarified the influence of oxygen conditions on P release.

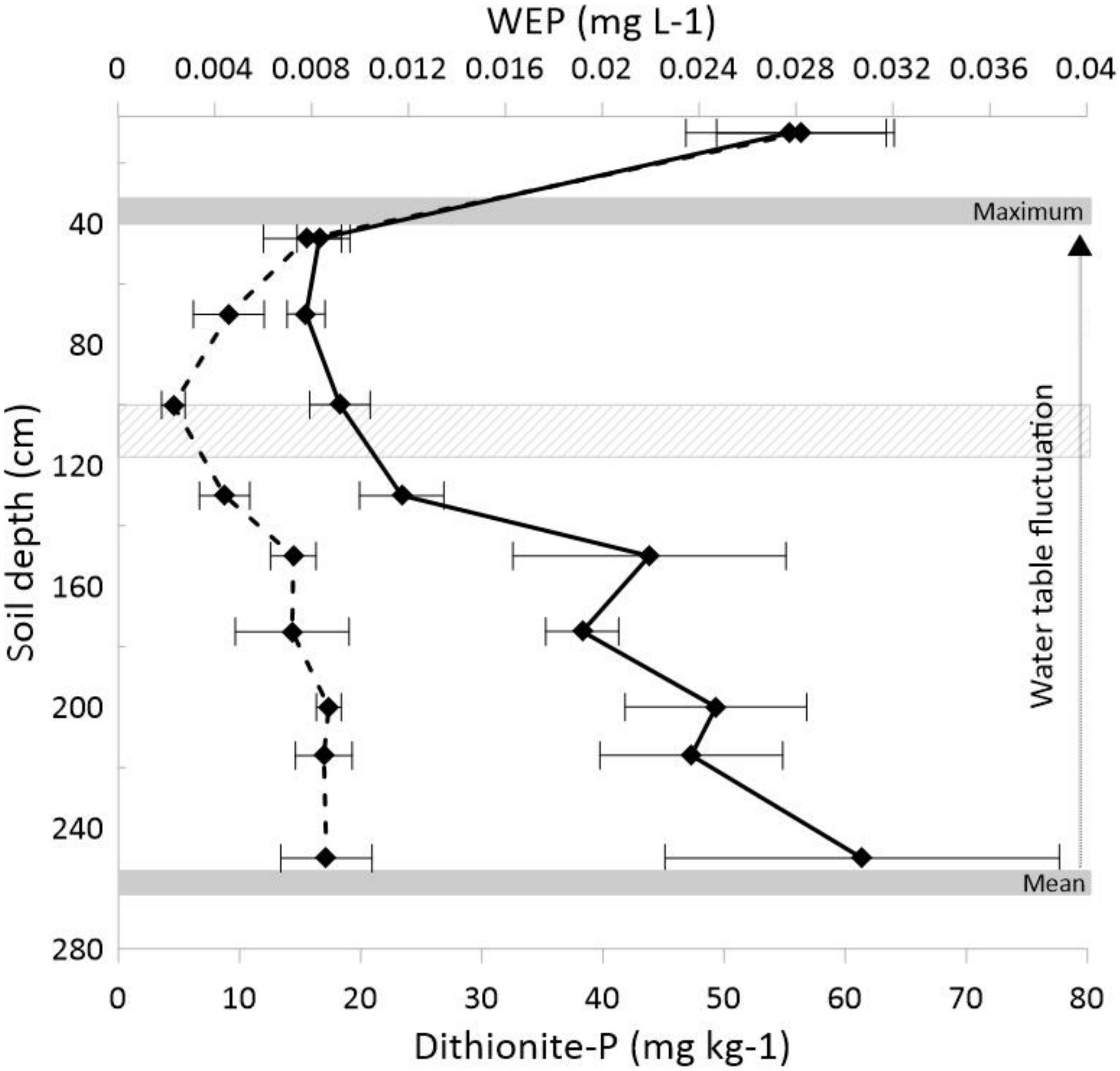

Figure 3.1 Averaged vertical distribution of sodium-bicarbonate-dithionite extractable P (Dithionite-P, solid line) and water extractable P (WEP, dashed line) to 250 cm below ground level. Error bars show the standard error of the mean at each depth. Soil profile samples were taken from the same farm as the soils used in the clay loam incubation. Grey polygons indicate the mean and maximum water table level over the five soil profiles from September 2017 to March 2019. The shaded area at 100 cm below ground level indicates the location of artificial drainage. Note that the x-axis scales are not the same.

### 3.3.2 Incubation soil characteristics

Mean Olsen P concentrations were enriched above those deemed necessary for optimal pasture production (20-40 mg kg$^{-1}$) for drystock and dairy farming, which may explain why WEP concentrations were high (Table 3.2) (Morton and Roberts, 2016; Roberts and Morton, 2009). Concentrations of Dithionite-P in the New Zealand soil (silt loam) were between 55-103 mg kg$^{-1}$. Concentrations of Dithionite-P were below the average of similar soils in national soil surveys from New Zealand (91 mg kg$^{-1}$) and Ireland (92 mg kg$^{-1}$) (Smith et al., 2021).

The proportion of sand across the soils ranged from 30% in the silt loam to 62% in the sandy loam, and clay ranged from 15% to 25% (Table 3.1). Values of pH ranged from 5.4 to 6.8, with the silt loam being the most acidic, but still within the range considered optimal for pasture production (5.5-7.0) (Morton and Roberts, 2016). The total N and C concentrations were lowest in the clay loam at 1.8 and 26 g kg$^{-1}$, respectively. The ASC was low compared to soils used for grazed grassland farming in New Zealand (McDowell and Condron, 2004). Owing to the chemical and physical differences demonstrated between the soils (Tables 3.1 & 3.2), and slightly different fertiliser treatments, analysis was carried out on each soil's data individually.

### 3.3.3 Overall incubation DRP release and kinetics

Table 3.4 shows the mean solution DRP concentration after 1440 minutes (24 hours), with the *P* values of a GLM. DRP concentrations increased with fertiliser inputs in the clay loam, sandy loam and silt loam. The warmer temperature significantly increased DRP concentrations in sandy ($P < 0.001$), silt loams ($P<0.001$) and clay loam ($P<0.001$). There was a significant fertiliser by temperature interaction and fertiliser by temperature by oxygen interaction on DRP in the silt loam. There were no significant interaction impacts for the clay loam or sandy loam.

Examples of DRP release over time are given in Figures 3.2-3.4 for each of the soils at the same fertiliser rate (20 kg ha$^{-1}$). Between 40 and 100% of cumulative DRP desorbed from each treatment occurred within the first 60 minutes of incubation. However, this varied between the soils. For instance, within 60 minutes, the sandy loam released between 80-100% of its cumulative DRP, particularly as the fertiliser treatment increased. Meanwhile about 50% of cumulative DRP was released from the clay loam in the first 60 minutes. Compared to the other two soils, DRP release from the silt loam was more gradual, especially with those treated with 3°C. The patterns of Fe and Mn release were like those for P across all soils (Figures 3.2-3.4).

The Elovich model was applied to all soils and the slope (1/β) used to statistically compare the desorption rate (mg $g^{-1}$ min) of DRP across treatments within soils (Table 3.5). A higher value was indicative of a faster release rate (McCallister, 2015). Desorption rates increased significantly with fertiliser rate and temperature for all soils. There was also a significant increase under anoxia in the clay and sandy loams, but not so for silt loam soils. Interactions were significant between fertiliser, temperature and oxygen (Table 3.5). By averaging all desorption rates of each treatment across all soil textural classes and fertiliser treatments, the mean P desorption rate from lowest to highest was Oxic 3°C < Anoxic 3°C ≤ Oxic 18°C < Anoxic 18°C.

### 3.3.4 Factors controlling DRP release during the incubation

The response of redox sensitive parameters was not as clear as that for DRP (Tables 3.6-3.8). Nitrate was enriched in the clay loam under oxic and cold conditions but depleted at higher temperatures or under anoxic conditions (Table 3.6). The sandy loam maintained between 0.2 and 0.4 mg $L^{-1}$ $NO_3^-$ in solution between 60 minutes and 24 hours (Figure 3.2). The silt loam, with the highest initial $NO_3^-$ concentration, maintained >0.8 mg $L^{-1}$ $NO_3^-$ (Figure 3.4). In contrast, the clay loam nearly exhausted $NO_3$ within the first 60 minutes in the anoxic treatments (Figure 3.3).

The overall concentrations of Fe and Mn, like P, increased with temperature in the sandy and silt loam soils but not in the clay loam (Tables 3.7-3.8; Figures 3.2-3.4). The clay loam exhibited a difference between temperature treatments by the end of the incubation, but not overall. Apart from an enrichment under anoxia in the sandy loam no differences were noted for the other soils or treatments.

Table 3.4 Mean solution DRP concentrations (mg L$^{-1}$, standard errors of the means in parentheses) over 1440 minutes for each soil and fertiliser rate under anoxic or oxic conditions at 3 or 18$^{o}$C. The *P* value of general linear model (GLM) of the averaged solution DRP concentrations within a soil group is given for each treatment and their interaction. Treatments with different letters are significantly different.

| Site | -------- Clay loam -------- | | | -------- Sandy loam -------- | | | -------- Silt loam -------- | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertiliser | 20 | 40 | 60 | 20 | 40 | 60 | 10 | 20 | 30 |
| kg ha$^{-1}$ yr$^{-1}$ | | | | | | | | | |
| Anoxic (3$^{o}$C) | $0.05^{a}$<br>(0.007) | $0.08^{a}$<br>(0.020) | 0.19<br>(0.028) | $0.08^{ab}$<br>(0.014) | $0.11^{a}$<br>(0.009) | 0.11<br>(0.049) | $0.17^{a}$<br>(0.021) | $0.38^{a}$<br>(0.035) | $0.86^{b}$<br>(0.079) |
| Oxic (3$^{o}$C) | $0.05^{a}$<br>(0.007) | $0.06^{a}$<br>(0.006) | 0.17<br>(0.025) | $0.07^{a}$<br>(0.012) | $0.06^{a}$<br>(0.007) | 0.08<br>(0.051) | $0.16^{a}$<br>(0.027) | $0.37^{a}$<br>(0.026) | $0.41^{a}$<br>(0.068) |
| Anoxic (18$^{o}$C) | $0.09^{b}$<br>(0.013) | $0.14^{b}$<br>(0.011) | 0.21<br>(0.027) | $0.14^{b}$<br>(0.021) | $0.16^{b}$<br>(0.017) | 0.18<br>(0.051) | $0.26^{b}$<br>(0.035) | $0.46^{b}$<br>(0.027) | $0.81^{b}$<br>(0.078) |
| Oxic (18$^{o}$C) | $0.07^{ab}$<br>(0.075) | $0.08^{a}$<br>(0.009) | 0.27<br>(0.060) | $0.14^{b}$<br>(0.022) | $0.15^{b}$<br>(0.021) | 0.15<br>(0.048) | $0.24^{b}$<br>(0.026) | $0.41^{ab}$<br>(0.034) | $0.63^{ab}$<br>(0.093) |
| $\boldsymbol{P}_{\text{Fertiliser}}$ | | <0.001 | | | <0.001 | | | <0.001 | |
| $\boldsymbol{P}_{\text{Temperature}}$ | | <0.05 | | | <0.001 | | | <0.001 | |
| $\boldsymbol{P}_{\text{Oxygen}}$ | | ns | | | ns | | | ns | |
| $\boldsymbol{P}_{\text{Fertiliser} \times \text{temperature}}$ | | ns | | | ns | | | <0.05 | |
| $\boldsymbol{P}_{\text{Fertiliser} \times \text{oxygen}}$ | | ns | | | ns | | | ns | |
| $\boldsymbol{P}_{\text{Temperature} \times \text{oxygen}}$ | | ns | | | ns | | | ns | |
| $\boldsymbol{P}_{\text{Fertiliser} \times \text{temperature} \times \textit{oxygen}}$ | | ns | | | ns | | | <0.05 | |

Table 3.5 A comparison of mean DRP desorption rates ($1/\beta$, mg g$^{-1}$ min$^{-1}$) calculated via the Elovich model after 1440 minutes for each soil and fertiliser (Fert) rate under or oxic (Ox) conditions at 3 or 18°C. The *P* value of general linear model (GLM) of the mean DRP desorption rates within a soil group is given for each treatment and their interaction. Treatments with different letters are significantly different via Tukey's Honestly Significant Difference.

| Site | ---- Clay loam ---- | | | ---- Sandy loam ---- | | | ---- Silt loam ---- | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertiliser kg ha$^{-1}$ yr$^{-1}$ | 20 | 40 | 60 | 20 | 40 | 60 | 10 | 20 | 30 |
| Anoxic (3°C) | $0.21^{a}$ | $0.26^{b}$ | $0.77^{ab}$ | $0.45^{b}$ | $0.31^{b}$ | 0.16 | $0.63^{a}$ | $0.71^{ab}$ | 0.46 |
| | (0.008) | (0.009) | (0.095) | (0.007) | (0.005) | (0.002) | (0.054) | (0.055) | (0.458) |
| Oxic (3°C) | $0.20^{a}$ | $0.16^{a}$ | $0.66^{a}$ | $0.32^{a}$ | $0.22^{a}$ | 0.16 | $0.63^{a}$ | $0.59^{a}$ | 0.51 |
| | (0.203) | (0.016) | (0.021) | (0.009) | (0.016) | (0.005) | (0.635) | (0.061) | (0.053) |
| Anoxic (18°C) | $0.37^{b}$ | $0.31^{b}$ | $0.75^{ab}$ | $0.66^{c}$ | $0.51^{c}$ | 0.16 | $1.07^{b}$ | $0.89^{bc}$ | 0.84 |
| | (0.023) | (0.026) | (0.073) | (0.024) | (0.034) | (0.003) | (0.127) | (0.010) | (0.244) |
| Oxic (18°C) | $0.30^{b}$ | $0.23^{ab}$ | $1.04^{b}$ | $0.63^{c}$ | $0.52^{c}$ | 0.17 | $0.97^{ab}$ | $1.09^{c}$ | 0.45 |
| | (0.019) | (0.024) | (0.081) | (0.012) | (0.031) | (0.002) | (0.975) | (0.051) | (0.011) |
| ***P*** Fertiliser | | <0.001 | | | <0.001 | | | <0.001 | |
| ***P*** Temperature | | <0.001 | | | <0.001 | | | <0.001 | |
| ***P*** Oxygen | | <0.01 | | | <0.001 | | | ns | |
| ***P*** Fertiliser × temp | | ns | | | <0.001 | | | ns | |
| ***P*** Fertiliser × oxygen | | <0.01 | | | <0.01 | | | ns | |
| ***P*** Temp × oxygen | | ns | | | <0.001 | | | ns | |
| ***P*** Fertiliser × temp ***×*** *oxygen* | | <0.05 | | | <0.001 | | | <0.01 | |

Table 3.6 Mean solution nitrate ($NO_3^-$) concentrations (mg L$^{-1}$) over 1440 minutes for each soil and fertiliser rate under anoxic or oxic conditions at 3 or 18$^{o}$C. The *P* value of general linear model (GLM) within a soil group is given for each factor, as well as the significance of interactions between factors. No treatments were significantly different via Tukey's Honestly Significant Difference.

| Site | ------ Clay loam ------ | | | ----- Sandy loam ----- | | | -------- Silt loam -------- | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertiliser kg ha$^{-1}$ yr$^{-1}$ | 20 | 40 | 60 | 20 | 40 | 60 | 10 | 20 | 30 |
| Anoxic (3$^{o}$C) | 0.11<br>(0.073) | 0.14<br>(0.085) | 0.12<br>(0.078) | 0.29<br>(0.048) | 0.50<br>(0.044) | 0.40<br>(0.060) | 1.76<br>(0.130) | 1.89<br>(0.179) | 2.29<br>(0.064) |
| Oxic (3$^{o}$C) | 0.76<br>(0.439) | 0.13<br>(0.088) | 0.57<br>(0.514) | 0.31<br>(0.040) | 0.50<br>(0.035) | 0.37<br>(0.050) | 1.83<br>(0.152) | 1.62<br>(0.226) | 2.17<br>(0.063) |
| Anoxic (18$^{o}$C) | 0.11<br>(0.070) | 0.15<br>(0.073) | 0.11<br>(0.073) | 0.33<br>(0.041) | 0.50<br>(0.034) | 0.52<br>(0.072) | 1.65<br>(0.152) | 1.91<br>(0.148) | 1.87<br>(0.037) |
| Oxic (18$^{o}$C) | 0.07<br>(0.071) | 0.20<br>(0.064) | 0.13<br>(0.076) | 0.35<br>(0.051) | 0.50<br>(0.041) | 0.38<br>(0.061) | 1.63<br>(0.144) | 2.23<br>(0.148) | 2.32<br>(0.036) |
| $P_{\text{Fertiliser}}$ | | ns | | | ns | | | <0.001 | |
| $P_{\text{Temperature}}$ | | <0.05 | | | ns | | | ns | |
| $P_{\text{Oxygen}}$ | | <0.05 | | | ns | | | ns | |
| $P_{\text{Fertiliser × temperature}}$ | | ns | | | ns | | | ns | |
| $P_{\text{Fertiliser × oxygen}}$ | | ns | | | ns | | | ns | |
| $P_{\text{Temperature × oxygen}}$ | | ns | | | ns | | | ns | |
| $P_{\text{Fertiliser × temperature × } \textit{oxygen}}$ | | ns | | | ns | | | ns | |

Table 3.7 Mean solution iron (Fe) concentrations (mg L$^{-1}$) over 1440 minutes for each soil and fertiliser rate under anoxic or oxic conditions at 3 or 18$^{o}$C. The *P* value of general linear model (GLM) within a soil group is given for each factor, as well as the significance of interactions between factors. Treatments with different letters are significantly different via Tukey's Honestly Significant Difference.

| Site | ------- Clay loam ------- | | | ------ Sandy loam ------ | | | ------- Silt loam ------- | | |
|---|---|---|---|---|---|---|---|---|---|
| Fertiliser kg ha$^{-1}$ yr$^{-1}$ | 20 | 40 | 60 | 20 | 40 | 60 | 10 | 20 | 30 |
| Anoxic (3$^{o}$C) | 0.82<br>(0.097) | 0.46<br>(0.073) | 0.45<br>(0.082) | 0.52$^{a}$<br>(0.059) | 0.55<br>(0.090) | 0.55$^{bc}$<br>(0.063) | 0.72<br>(0.135) | 0.74$^{ab}$<br>(0.087) | 1.21<br>(0.118) |
| Oxic (3$^{o}$C) | 0.98<br>(0.147) | 0.54<br>(0.132) | 0.40<br>(0.060) | 0.35$^{ab}$<br>(0.062) | 0.38<br>(0.054) | 0.39$^{c}$<br>(0.042) | 0.79<br>(0.197) | 0.72$^{b}$<br>(0.078) | 0.86<br>(0.152) |
| Anoxic (18$^{o}$C) | 1.48<br>(0.280) | 0.57<br>(0.107) | 0.43<br>(0.062) | 0.93$^{ab}$<br>(0.116) | 0.80<br>(0.123) | 1.16$^{a}$<br>(0.134) | 1.34<br>(0.285) | 1.05$^{a}$<br>(0.079) | 0.95<br>(0.131) |
| Oxic (18$^{o}$C) | 1.41<br>(0.224) | 0.44<br>(0.092) | 0.48<br>(0.079) | 0.69$^{b}$<br>(0.110) | 0.62<br>(0.097) | 0.99$^{ab}$<br>(0.114) | 1.16<br>(0.173) | 1.16$^{a}$<br>(0.146) | 1.17<br>(0.142) |
| ***P*** Fertiliser | | <0.001 | | | ns | | | ns | |
| ***P*** Temperature | | ns | | | <0.05 | | | <0.001 | |
| ***P*** Oxygen | | ns | | | <0.05 | | | ns | |
| ***P*** Fertiliser × temperature | | ns | | | <0.01 | | | ns | |
| ***P*** Fertiliser × oxygen | | ns | | | ns | | | ns | |
| ***P*** Temperature × oxygen | | ns | | | ns | | | ns | |
| ***P*** Fertiliser × temperature × *oxygen* | | ns | | | ns | | | ns | |

Table 3.8 Mean solution manganese (Mn) concentrations (mg L$^{-1}$) over 1440 minutes for each soil and fertiliser rate under anoxic or oxic conditions at 3 or 18$^{o}$C. The *P* value of general linear model (GLM) within a soil group is given for each factor, as well as the significance of interactions between factors. Treatments with different letters are significantly different via Tukey's Honestly Significant Difference.

| Site | | ------ Clay loam ------ | | | ----- Sandy loam ----- | | | -------- Silt loam -------- | |
|---|---|---|---|---|---|---|---|---|---|
| Fertiliser kg ha$^{-1}$ yr$^{-1}$ | 20 | 40 | 60 | 20 | 40 | 60 | 10 | 20 | 30 |
| Anoxic (3$^{o}$C) | 0.02<br>(0.002) | 0.04<br>(0.017) | 0.03<br>(0.007) | $0.04^{ab}$<br>(0.005) | $0.03^{ab}$<br>(0.006) | $0.03^{bc}$<br>(0.003) | $0.01^{ab}$<br>(0.002) | 0.01<br>(0.001) | 0.01<br>(0.002) |
| Oxic (3$^{o}$C) | 0.03<br>(0.006) | 0.02<br>(0.002) | 0.02<br>(0.003) | $0.02^{b}$<br>(0.005) | $0.02^{b}$<br>(0.004) | $0.02^{c}$<br>(0.002) | $0.01^{b}$<br>(0.002) | 0.01<br>(0.001) | 0.01<br>(0.001) |
| Anoxic (18$^{o}$C) | 0.06<br>(0.014) | 0.03<br>(0.006) | 0.03<br>(0.005) | $0.07^{a}$<br>(0.010) | $0.06^{a}$<br>(0.008) | $0.07^{a}$<br>(0.010) | $0.02^{a}$<br>(0.004) | 0.01<br>(0.002) | 0.01<br>(0.002) |
| Oxic (18$^{o}$C) | 0.05<br>(0.009) | 0.02<br>(0.003) | 0.08<br>(0.030) | $0.05^{ab}$<br>(0.010) | $0.07^{a}$<br>(0.011) | $0.06^{ab}$<br>(0.007) | $0.02^{a}$<br>(0.002) | 0.01<br>(0.003) | 0.01<br>(0.002) |
| ***P*** Fertiliser | | ns | | | ns | | | <0.01 | |
| ***P*** Temperature | | ns | | | <0.001 | | | <0.001 | |
| ***P*** Oxygen | | ns | | | ns | | | ns | |
| ***P*** Fertiliser × temperature | | ns | | | ns | | | ns | |
| ***P*** Fertiliser × oxygen | | ns | | | ns | | | ns | |
| ***P*** Temperature × oxygen | | ns | | | ns | | | ns | |
| ***P*** Fertiliser × temperature **×** *oxygen* | | ns | | | ns | | | ns | |

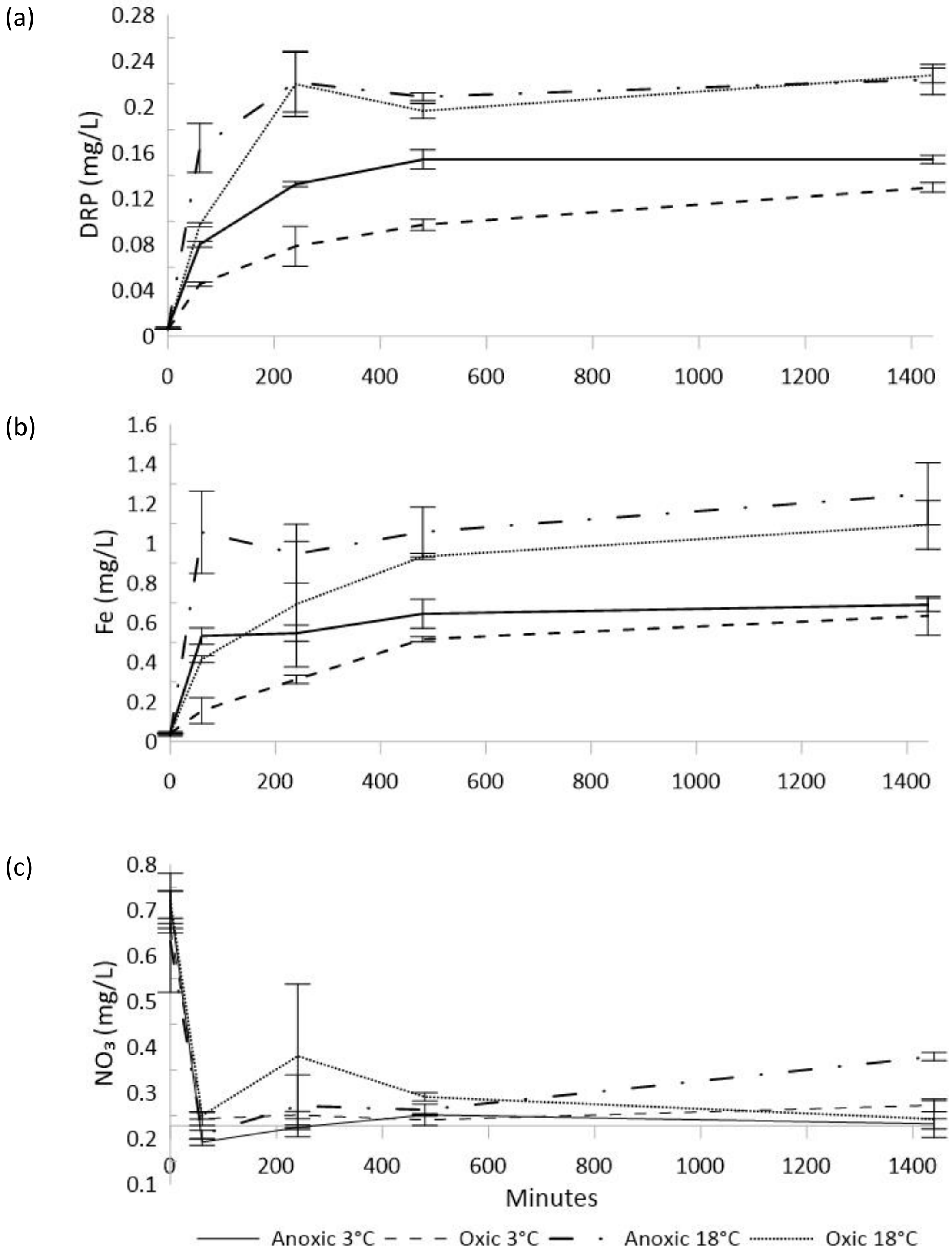

Figure 3.2 Example of (a) dissolved reactive P (DRP), (b) dissolved iron (Fe), and (c) Nitrate-N ($NO_3^-$) concentrations detected over time under the various temperature and oxygen treatments for the sandy loam receiving 20 kg ha$^{-1}$ yr$^{-1}$. Error bars represent the 95% confidence interval.

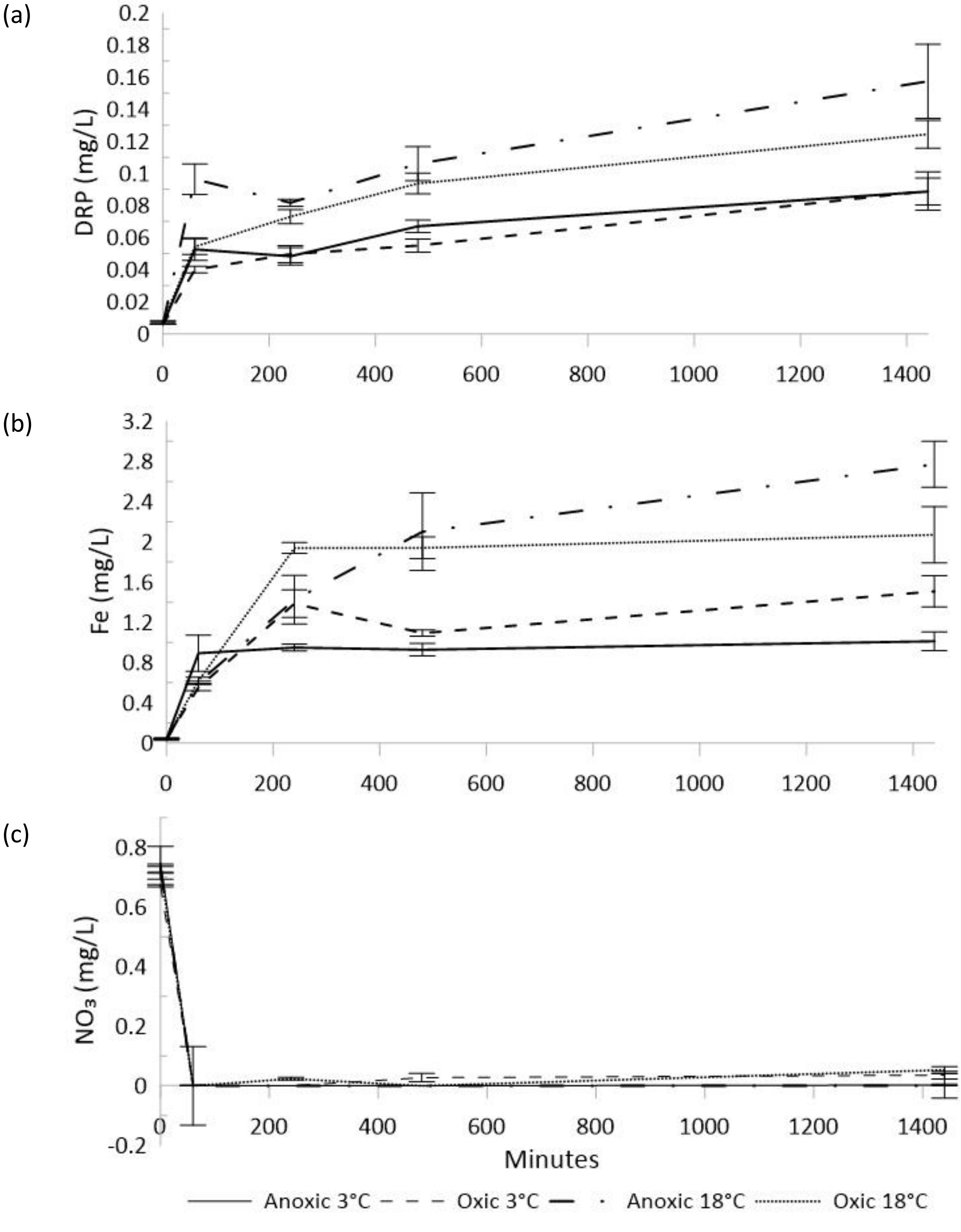

Figure 3.3 Example of the (a) dissolved reactive P (DRP), (b) dissolved iron (Fe), and (c) Nitrate-N ($NO_3^-$) concentrations detected over time under the various temperature and oxygen treatments for the clay loam receiving 20 kg ha$^{-1}$ yr$^{-1}$. Error bars represent the 95% confidence interval.

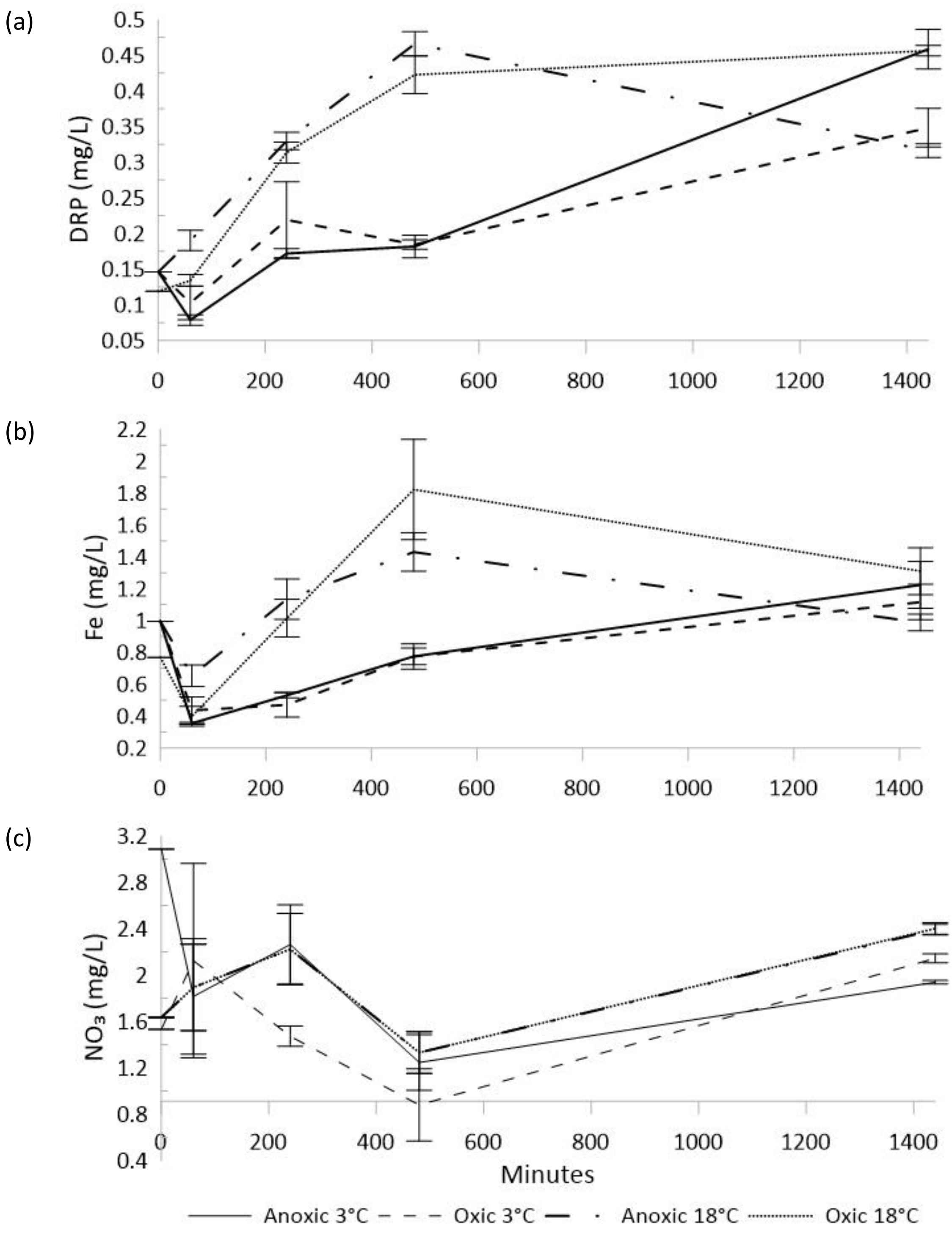

Figure 3.4 Example of the (a) dissolved reactive P (DRP), (b) dissolved iron (Fe), and (c) Nitrate-N ($NO_3^-$) concentrations detected over time under the various temperature and oxygen treatments for the silt loam receiving 20 kg ha$^{-1}$ yr$^{-1}$. Error bars represent the 95% confidence interval.

## 3.4 Discussion

### 3.4.1 Implications of Dithionite-P accumulation to depth

It is generally assumed and expected that soluble or available P does not increase with depth (van der Wal et al., 2007). However, the preliminary study indicated an enrichment of Dithionite-P with depth. As enrichment coincided with a depth where artificial drainage is commonly installed, these data suggested it may be important to take redox-sensitive P into account when considering P losses from periodically saturated soils. These data also begin to explain why soil tests conducted in aerobic conditions may not be representative of periodically saturated soils.

### 3.4.2 The effect of fertiliser, temperature and oxygen status on DRP release

The release of DRP from soil to solution depends on the quantity and strength of P sorbed to the soil relative to the capacity of the soil to sorb P, and physical conditions that control the kinetics of P release into solution (Dodd et al., 2013; McDowell, 2012). The following are possible controls:

a. In neutral to acidic soils the strength of P sorption increases with the quantity of P-sorbing Al and Fe hydrous oxides;

b. The exchange or potential release of P from sandier and young soils would be greater, as they are less likely to have soil constituents that would tightly hold soil P;

c. Finer textured soils have more surface area, so may have more stored P that could become available to loss; and

d. less P is sorbed and more desorbed as the quantity of added P increases relative to the number of P sorption sites in the soils (Dodd et al., 2013; McDowell, 2012; McDowell and Condron, 2004; Saunders, 1965; Simmonds et al., 2015).

In terms of the kinetics of P release, loosely sorbed and easily available P would be released before more strongly sorbed and recalcitrant P (Lair et al., 2009; Scalenghe et al., 2002; Toor and Bahl, 1999). No fertiliser effect was expected in the redox-sensitive parameters (Fe, Mn and $NO_3$) except for an increase in $NO_3^-$ in the silt loam (Table 2.8) where stock numbers, and therefore urine patches containing N in the New Zealand soils, were increased with fertiliser rates (McDowell and Smith, 2012).

Of the soils studied, the sandy loam released a majority if its total DRP in the first 60 minutes. Owing to its high sand content, it and other sandy soils have low concentrations of amorphous and crystalline Fe and Mn oxides (McCallister, 2015), which translates to a low ASC (viz. P sorption capacity). Coupled with a coarse texture, providing easy access to sorption sites, P desorbed easier than the other soils (Saunders, 1965). The high proportion of cumulative DRP release from the soil fertilised at 40 kg ha$^{-1}$ yr$^{-1}$ or 60 kg ha$^{-1}$ yr$^{-1}$ in the first 60 minutes suggests that the low number of sorption sites, reflecting the low ASC and coarse texture, were not only more saturated, but loosely bound than the other soils (McDowell and Sharpley, 2004).

In contrast to the other soils, the clay loam exhibited a delayed release of P. This has been observed in several studies (Ahmadi, 2018; Moazallahi et al., 2018; Toor and Bahl, 1999) and attributed to a two-phase reaction, where loosely-bound P is desorbed quickly before the dissolution of more tightly-held P occurs (Lair et al., 2009; Moazallahi et al., 2018). The influence of dissolution is supported by simultaneous flushes of DRP, Fe and Mn into solution. Coupled to this is a delay in reaction caused by aggregation whereby P is slowly diffused from the inside of aggregates under oxic or anoxic conditions (McDowell and Sharpley, 2003).

In the present study, temperature was consistently a significant factor controlling DRP desorption rate and solution concentration. Previous research has noted that warmer temperatures increase the rate of reaction. Overall, increased reactions rates are either caused by the temperature mineralising organic P, increasing reduction potential (Eh) in anoxic conditions, or by stimulating biological activity which utilises nutrients and oxygen under oxic and anoxic conditions (Gibbons, 2015; Sallade and Sims, 1997b; Schilling et al., 2019; Sparks, 2003). In this circumstance, rates were likely affected by stimulating biological activity (i.e. microbial Fe reduction).

Anoxic incubations on ditch sediments carried out by Sallade and Sims (1997b) demonstrated that a similar downward trend in Eh occurred in 7$^{o}$C and 35$^{o}$C incubations, but reduction potential decreased faster at 35$^{o}$C and more than doubled the soluble P concentrations after 21 days. Meanwhile, a study by Gibbons (2015) noted that sediments incubated at 10 and 20$^{o}$C had similar release rates, while the 30$^{o}$C incubation exhibited greater concentrations and release rates. The soils used in this study rarely reach above 20°C, and never in the late winter to early spring periods where waterlogging and anoxia are more likely to occur (Met Éireann, 2020; NIWA, 2019). The 18°C treatment only modestly increased concentrations in the averaged data, but the rationale was that this was more representative than the extreme temperature contrasts noted above. It is worth noting that the level of significance of the effect of temperature on DRP concentrations varied between soil types in the present study. The clay loam exhibited a muted effect (e.g. 0.04 mg $L^{-1}$ difference at 20 kg P $ha^{-1}$ $yr^{-1}$) compared to the other soil textural classes (e.g. 0.07-0.1 mg $L^{-1}$ difference at 20 kg P $ha^{-1}$ $yr^{-1}$), perhaps being buffered by a finer-texture and two-phase reaction process as noted above. Previous work on sediments highlighted how anoxic P release is inconsistent due to the fact that temperature influences a variety of factors (e.g. Eh, mineralisation, oxygen consumption, diffusion rates) (Gibbons, 2015).

The mean concentrations at each time point and over the length of the incubations suggested that anoxic conditions enriched P concentrations in solution across the soil groups. In theory, dissolution and diffusion should be aided by anaerobic conditions throughout the soil or in anaerobic microsites. Dissolution and diffusion enhance P release by the action of microbes (Hutchison and Hesterberg, 2004; Roden et al., 2000; Scalenghe et al., 2002). However, while the data presented herein suggested that anoxic conditions increased the rate of DRP release in the clay and sandy loam soils, no such conclusion could be made for the silt loam soil. The answer to this discrepancy may lie in the greater concentrations of TC and TN in the silt loam soil (Table 3.1) supporting microbial growth, which in turn would maintain anoxic conditions (Kölbl et al., 2017). It is also likely that $NO_3$ was formed via the mineralisation of organic N (a major proportion of TN in New Zealand pastoral soils) during soil disturbance (Kristensen et al., 2000; Ringuelet and Bachmeier, 2006). High $NO_3^-$ concentrations were also probably in solution sourced from urine and higher stocking rates used in the silt loam soil that was absent in the clay or sandy loam soils (18 stock units vs none for the clay and sandy soils respectively). Nitrate is a limiting factor in Fe-P release, as it will be preferentially used by microbes in redox reactions before Fe and Mn are acted upon (McMahon and Chapelle, 2008; Surridge et al., 2007b; Yuan et al., 2015). Nitrate concentrations in the silt loam were far greater than the clay or sandy loam and were hence inhibiting reductive dissolution (Figures 3.2-3.4). The lack of difference between DRP concentrations from the silt loam due to oxygen content suggests that 24 hours was not long enough to sufficiently remove enough

$NO_3^-$ in the silt loam system for metal oxides to be affected by reductive dissolution, or that the conditions were not reducing enough. Previous work has suggested that greater differences occur beyond a 24-hour time period – especially when $NO_3^-$ is present and there is a lack of OM – and that optimum reduction potential occurred after four days of incubation (Gibbons, 2015; Yuan et al., 2015). Conversely, the lower concentrations of TN in the clay and sandy loam textured soils (1.8 and 3.0 g $kg^{-1}$) likely buffered $NO_3^-$ concentrations, but not at a great enough concentration (0.5 mg $NO_3$ $L^{-1}$; McMahon and Chapelle, 2008) to prevent anoxic conditions from affecting DRP release.

### 3.4.3 Implications for Management

This experiment aimed to determine if over a 24-hour period, P release would be enhanced by increased temperature and anoxia. While the enhancement was true for two of the three soils, it is possible that this may be true for many soils if the soil contained a low soil N concentration. Furthermore, many of the effects were found within 60 minutes (Figures 3.2-3.4). Both findings are important for predicting how soils respond to saturated conditions. However, they more importantly highlight the need to refine the knowledge of local saturated areas. The present study also highlights the riskiest period of the year for losses due to these processes (i.e. late winter and spring). This is when soils are still moist and easily saturated with small rainfall events, temperatures are warmer, and most $NO_3^-$ had been leached from the soil. Soils would also likely stay saturated for more than 24 hours. Therefore, the there would be ample time for conditions to develop. Additionally, the difference between anoxic and oxic conditions align with previous work (Smith et al., 2021), and further suggests that normal oxic WEP tests are inaccurate for predicting P losses from soils that are often saturated.

General strategies like decreasing soil Olsen P to an agronomic optimum (Morton and Roberts, 1999) and/or switching to crops that produce well on lower Olsen P soils will be effective in decreasing P losses from these soils year-round (McDowell and Cosgrove, 2016). Provided the soil type and situation allows it, artificial drainage systems could be redesigned and improved to maximize drainage and avoid saturated conditions. However, such systems could end up losing the same load of P by draining a larger amount of diluting water. In order to decrease the load effectively systems could be designed to intercept and filter out P in drainage water by, for example, lowering the soil P through inversion tillage above the main perforated pipe or using a highly P-sorptive backfill (McDowell et al., 2008). Alternatively, where anthropogenically altering the land is untenable, saturated areas could be identified to inform management decisions, especially during high-risk periods of the year. For instance, strategies specific to springtime could include avoiding the grazing or the application of P fertiliser to wet paddocks (Smith et al., 2016). This includes delaying the grazing of forage crops in gullies to avoid animals grazing the base of gullies which are likely to be saturated (Monaghan et al., 2017).

Additionally, the results call into question the safety of accumulated P in riparian zones or buffer areas adjacent to water ways. If accumulated P is in a form that is vulnerable in the long-term (e.g. Anoxic WEP or Dithionite-P), the present study would suggest that buffer areas that have low $NO_3^-$ during risky periods (i.e. high temperature, low oxygen) may be a potential source of P to waterways. Another example where low $NO_3^-$ may pose a risk is in heavy-textured soils in Ireland. In these soils, where artificial land drainage is installed, there have been studies that recorded low $NO_3^-$ but high ammonium ($NH_4$). Soil N primarily being converted to the ammonium form would not provide the same buffering effect and may increase the potential for reductive dissolution of P, and its loss via artificial drainage (Clagnan et al., 2018a).

## 3.5 Conclusions

Over a 24-hour period the mean DRP concentration in water extracts increased with fertiliser application, temperature and in two soils, anoxic conditions - commensurate with the depletion of $NO_3$ and release of Fe and Mn via reductive dissolution. Fe-reducing conditions were not achieved due to the presence of $NO_3^-$, potentially due to enriched soil N concentrations at this location. Treatment effects on the kinetics of P release into water mirrored those of mean concentrations, except that for the clay loam soil which noted a distinct two-phase release attributed to its finer texture, greater surface area and potentially greater store of P held within soil aggregates than the silt or sandy loams. Importantly, treatment effects such as the enhanced release of P during anoxia were complete for the clay and sandy loam soils within 24 hours. Based on the results presented, late winter to spring would be the riskiest season for P losses due to this reaction, owing to moist soils that are easily saturated with small rainfall events, warmer temperatures, and low soil $NO_3$

concentrations. This knowledge highlights the necessity to consider and refine where in the landscape P losses are likely and what strategies can be used to mitigate losses.

# Chapter 4

# Reductive dissolution of phosphorus associated with iron-oxides during saturation in agricultural soil profiles

## 4.1 Introduction

Phosphorus (P) loading from agricultural land to surface water is a major cause of algal growth and declining water quality (Leinweber et al., 2018). Of P fractions, dissolved reactive P (DRP) is more available to algae than particulate P and many forms of dissolved unreactive P (Ekholm and Krogerus, 2003; Thompson and Cotner, 2018). Due to its high bioavailability, there has been significant interest in the transport of DRP to surface waters, especially in relation to where and when losses of DRP occur (Buda et al., 2009a; Dupas et al., 2017; Leinweber et al., 2018; Shore et al., 2016)

A considerable quantity of DRP comes from critical source areas (CSAs), where available DRP (a source) coincides with a means of transport and connectivity to surface waters (Thomas et al., 2016). Critical source areas can generate a disproportionately large amount of catchment DRP loss, despite only making up a small percentage of the landscape (Agnew et al., 2006; Dahlke et al., 2012). Although most attention is given to surface runoff in CSAs, subsurface flow losses of DRP can also be significant. These subsurface flow losses can contribute to surface runoff under saturated conditions such as in winter or spring, or in shallow or deep groundwater that may enrich DRP in the baseflow of streams, year-round. For instance, Smith et al. (2016) showed that with the installation of artificial drainage on a dairy-farm in Southland, New Zealand, P that was lost via surface runoff was lost in the same amount via subsurface flow.

Assessments of the risk of subsurface flow P losses currently rely on tools like the P index tool in the US, or maps of microtopography, or known artificial drainage networks (Sharpley et al., 2003; Thomas et al., 2017; Thomas et al., 2016). These tools identify CSAs using information on source P factors and transport data, based on parameters such as soil topographic indices, Light Detection and Digital Elevation Models and field data. However, models do not always account for subsurface impermeable layers (e.g. fragipans), shallow profiles, poorly-drained soils, or perched water tables, which are particularly vulnerable to increased soil solution, saturation, and increased surface runoff (Dahlke et al., 2012).

Along with increasing instances of runoff and drainage, saturation may increase DRP loss via anaerobic conditions, which can desorb DRP from soil particles due to pH changes and reductive dissolution via microbial respiration (Gu et al., 2019). Reductive dissolution involves the microbially-mediated release of DRP associated with redox-sensitive metal-oxides (Colombo et al., 2014; Gu et al., 2019). Microbial communities mediate reduction-oxidation (redox) reactions between soil components to make energy for respiration. Organic material is oxidised as an electron donor, and is coupled with an electron acceptor which is reduced during the reaction (Chacon et al., 2006). This is typically oxygen, as it is the most preferential and energetically favourable to reduce. However, there is an ecological succession of viable acceptors if oxygen is limiting. For instance, if oxygen is not easily available (i.e. anaerobic), $NO_3^-$ becomes the most energetically favourable. This is called the electron acceptor hierarchy or the redox cascade ($O_2 > NO_3^- > Mn(IV) > Fe(III)/SO_4^{2-} > CO_2$). When the electron acceptors are reduced, they are converted to their gaseous or dissolved forms and released into solution (McMahon and Chapelle, 2008). Therefore, if a soil profile becomes saturated and microbial communities deplete oxygen and $NO_3^-$ electron acceptors, Mn(IV) and Fe(III) could be dissolved into their Mn(II) and Fe(II) forms, and release their associated P in to solution (Gu et al., 2019). However, few data are available for soils with impermeable layers that are likely to exhibit periodic saturation at depth.

As $NO_3^-$ is the second most preferential acceptor, the presence of $NO_3^-$ would limit the solubilisation of P during wet periods. If not taken up by plants or leached during the growing season, residual soil N could inhibit DRP dissolution from soil above impermeable layers thereby decreasing P in sub-surface flow. However, no data are available that demonstrate this inhibitory effect. Moreover, this process can be microbially mediated, and declines with temperature. Greater temperature potentially stimulates biological activity or induces more negative redox potentials, which would both lead to greater reaction rates and a greater potential for reductive dissolution (Sallade and Sims, 1997a; Sparks, 2003). Therefore, cold temperatures at depth or during winter and spring may inhibit reductive dissolution. Given that much DRP is lost during winter and spring drainage (Ibrahim et al., 2013; Smith et al., 2016) there is a need to understand and characterise the conditions under which $NO_3^-$ may affect DRP release and potential transport to waterways.

This study determined the concentrations of DRP and key redox species (i.e. $NO_3^-$, Fe, Mn and $SO_4^{2-}$) in a soil with a slowly permeable layer (<4 mm $hr^{-1}$) over two drainage seasons. The hypothesis was that soil solution P peaks associated with wet periods were linked to the reductive dissolution of redox-sensitive Fe and Mn oxides and that dissolution would be inhibited by the presence of residual $NO_3^-$ in soil. Field monitoring was carried out to track changes in DRP and redox species over time and relate them to soil and climatic conditions. This was carried out in a small plot on a New Zealand dairy farm. The present study supplemented these field observations with additional laboratory and *in situ* experiments to artificially induce the saturated and reducing conditions that were hypothesised to cause an increase in dissolved P and metal oxides.

## 4.2 Materials and Methods

### 4.2.1 Study Site

The plot was established in a 10 $m^2$ area fenced-off within a 6.5 ha paddock of a Southland dairy farm near Mossburn, New Zealand (45°37'34.1"S 168°18'43.1"E). The plot was on grazed dairy pasture primarily sown with perennial ryegrass (*Lolium perenne* L), and remained fenced-off for the duration of the study (2017-2019). The area receives, on average, 1045 mm mean annual rainfall and has an average temperature of 9.5°C (NIWA, 2019). The soil is classified in the New Zealand soil classification system as a Melanic Orthic Gley soil (Hewitt, 2010), equivalent to an Aquept/Aquent in USDA soil taxonomy (Table 4.1). It is poorly drained with a slowly permeable profile (<4 mm $hr^{-1}$) at ~40 cm below ground level (bgl), which encourages lateral subsurface flow. Sixteen Teflon suction cups (MacroRhizon, Rhizosphere Research Products, Wageningen, The Netherlands) in total were installed in March, 2017. Eight were installed with 0.5 m spacing at 20 cm and eight installed at 80cm bgl, avoiding cups overlapping at a 45° angle (8 x 80 cm bgl, 8 x 20 cm bgl) using the method outlined in McDowell et al. (2016).

Rainfall and temperature (10 cm bgl) data was collected, and soil moisture (CS655 TDR sensor, Campbell Scientific, Logan, Utah; 0-30 cm depth) was monitored using *in situ* equipment, connected to a CR10 datalogger. Electrical conductivity (EC) and pH of samples were measured in the samples off-site using a probe (S20 SevenEasy pH, Mettler-Toledo GmbH, Hamilton, New Zealand).

Soil cores were taken in triplicate from the 0-20, 20-60 and 60-80 cm depths (Table 4.1) and analysed for: pH in water; Olsen P (Olsen et al., 1954); 1:300 soil to solution water extractable P (WEP) designed to mimic P loss in surface runoff (McDowell and Condron, 2004); calcium-chloride extractable P, designed to mimic P loss in subsurface flow (Koopmans et al., 2002; Self-Davis et al., 2009); sodium-dithionite-extractable P as an estimate of P available under reducing conditions (Dithionite-P); (Jensen and Thamdrup, 1993; Loeppert and Inskeep, 1996; Psenner and Pusckso, 1988; Smith et al., 2021); total nitrogen and total Carbon (TN and TC) by LECO C/N analyser; and anion sorption capacity (ASC) as a measure of P sorption capacity (Saunders, 1965).

### 4.2.2 Field site sampling and saturation treatment

Regular unsaturated zone pore water sampling occurred from late autumn to mid spring (May to September), 2017 and 2019 to coincide with soils wetting up and draining, respectively. In 2017, sampling occurred twice a week between the beginning of May and July to intercept the wetting front and coincide with drainage and rainfall events > 5 mm. Sampling then occurred weekly until the end of September 2017 to capture rainfall events at the tail end of the wet season. In 2019, sampling again followed rainfall events > 5 mm for the first couple of months, and then sampled at 7-to-10-day intervals for the remainder of the sample periods. Samples were taken by applying negative pressure to the Teflon suction cups with 50-mL syringes for 3 hours. The pore size of the suction cups is approximately 0.1 µm thereby negating the need for additional filtering in the field. All samples were also analysed for pH and electrical conductivity off-site, and for DRP, $Fe^{2+}$ and $Fe^{3+}$, $Mn^{2+}$, $Al^{3+}$, $Mg^{2+}$, $Ca^{2+}$, $Na^{+}$, $K^{+}$, $NO_3^-$ and $SO_4^2$ via Inductively Coupled Plasma (ICP-OES) and High-Performance Liquid Chromatography (HPLC). Where sample size allowed, total carbon (TC), total inorganic C (TIC) and total organic C (TOC) were measured using a Vario TOC Cube Analyzer.

In addition to the regular sampling, artificial saturation and $NO_3^-$ treatments were imposed at the end of the regular sampling period in September 2019. The experiment aimed to identify whether artificial saturation increased DRP concentrations, and if the presence of excess $NO_3^-$ would inhibit DRP release in these conditions. The injection of $NO_3^-$ and its sampling was based on a $NO_3^-$ push-pull test (Kim et al., 2005). At the site, a 0.4 m wide wooden border was installed to 0.2 m below ground level around the suction cups, to minimise surface spreading. The site was then flood irrigated to a depth of 100 mm with tap water (DRP < 0.002 mg $L^{-1}$) designed to saturate the soil profile to 80 cm depth. The required volume was calculated from real-time data of soil water-filled pore space (WFPS) and known soil physical characteristics. After equilibration for 16 hrs, a 30 mL treatment solution was injected into four cups per depth (half of cups per depth) followed by 5 mL of deionised water to flush the tubes. This treatment solution contained 10 mg $NO_3$-N $L^{-1}$ as $KNO_3$, 10 mg Br $L^{-1}$ as KBr, and 300 mg Glucose C $L^{-1}$ for an electron acceptor source, a tracer, and an substrate for microbes like carbon (*viz.* electron donor) for reduction, respectively (Collins et al., 2017). The remaining four cups per depth were injected with 30 mL of deionised water to act as a control. All cups were left for four hours (Clague, 2013; Kim et al., 2005; Rivas et al., 2014) before suction was re-applied to collect a fresh sample. Samples of tap water, the saturation and $NO_3^-$ treatments were analysed for $NO_3^-$, $Br^-$ metals (Fe, Mn), $SO_4^{2-}$ and DRP.

Daily rainfall and potential evapotranspiration (PET) were sourced from the National Institute of Water and Atmospheric Research climate database, from a monitoring site approximately 4.5 km away. These data were used to create a soil water balance that would estimate periods of saturation-excess likely to lead to surface runoff or drainage events. This method was applied to available data over 2015 to 2019 to identify common periods of saturation and deficit. The equations used in the balance were those explained by Scotter et al. (1979) and Woodward et al. (2001). This method also identified specific periods during 2017 and 2019 where saturation excess was generated, which was used as a supporting indicator that anaerobic conditions could be present.

### 4.2.3 Laboratory incubation experiment

An experiment was designed to replicate the treatments applied to the field site in September 2019, but more specifically to also determine if C was not limiting redox reactions. Six soil cores were taken at 20 cm and at 80 cm soil depths, 1 m away from the bordered plot. Soils were sieved (field moist) to 4 mm. A sub-sample was oven-dried overnight to help determine the amount of deionised water needed to make a 1:20 soil to solution ratio. Each field-moist sample was weighed and placed in a glove box, which was purged with helium (He). At the same time, deionised water was bubbled with He to bring it to <0.5 mg dissolved oxygen $L^{-1}$. Solutions of either deionised water, $NO_3^-$ (50 ppm), glucose-C (300 ppm) or $NO_3^-$ + glucose-C were added to make a soil to solution ratio of 1:20. The tubes were sealed and placed on an orbital shaker for four hours. Tubes were centrifuged (2000 rpm, 10 minutes) and the supernatant filtered to 0.45 µm. Extracts were analysed for $NO_3^-$ and $SO_4^{2-}$ (via HPLC) and DRP, Fe and Mn (ICP-OES).

### 4.2.4 Statistical and redox analysis

All data were checked for normality using a Shapiro-Wilk test and confirmed as either normally distributed or log-transformed if not. A two-way analysis of variance (ANOVA) was used to contrast mean DRP concentrations during the regular samplings of the field trial within and between depths. The same test was used to assess the differences between DRP, Fe and Mn concentrations in treatments during the artificial saturation experiment in 2019, within and across the two depths. The same was done in the laboratory trial between the four treatments, within and across depths. A contrast using a two-way ANOVA was also made of the $NO_3$+C and DI water treatments within and across depths in the lab trial as a comparison to the field treatments (i.e. without the other treatments). The output of a Tukey's Honestly Significant Difference (HSD) *post-hoc* test is given to contrast treatments.

Data for DRP, $Fe^{2+}$, $Mn^{2+}$, $SO_4^{2-}$ and $NO_3^-$ in the field and in the lab were used in the calculation of likely redox conditions using the method of McMahon and Chapelle (2008). A Pearson correlation matrix was created using concentrations of solution Fe, Mn, $NO_3^-$, $SO_4^{2-}$ and DRP from the laboratory experiment, to identify positive and negative correlations between the parameters after incubation.

## 4.3 Results

### 4.3.1 Site Chemical Characteristics

Soil physical and chemical characteristics at the start of the trial are given in Table 4.1. Concentrations of Olsen P, WEP, Dithionite-P and ASC at the 60-80 cm depth were approximately 25-50% of the amount that existed in samples taken from the 0-30 or 30-60 cm depth. Although total N and C concentrations were lower than in shallower depths, the C:N ratio was the same throughout the profile. The concentrations TN, TC and Dithionite-P in each depth were significantly different from one another. The mean ASC from 0-30 and 30-60 cm bgl were greater than typical values for other soils used for grazed grassland farming in New Zealand (McDowell and Condron, 2004). The mean ASC beyond 80 cm bgl was low compared to other soils. Mean Olsen P concentrations were enriched above the optimal range suggested for pasture production for drystock and dairy farming in New Zealand (20-40 mg $kg^{-1}$). This may explain why WEP and $CaCl_2$-P concentrations are high (Morton and Roberts, 2016; Roberts and Morton, 2009). The Dithionite-P was lower than other gley soils under pasture in

New Zealand (Smith et al., 2021). The soil pH was 5.5, which is the lower limit of the range considered optimal for pasture production (5.5-7.0) (Morton and Roberts, 2016).

Table 4.1 Mean (± standard error of the mean) soil profile physical and chemical parameters[1] for study site in Southland, New Zealand. Different lettering‡ show a significant difference in means by depth according to Tukey's Honestly Significant Difference (Tukey's HSD). The least significant difference § at the *P*<0.05 level is given for the contrast of parameters by depth (n = 3 per depth).

| Depth | Particle size[2] % | | | Permeability[2] | Soil pH | WEP | $CaCl_2$-P | Olsen P | Dithionite-P | ASC | TN | TC | C:N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | Clay | Sand | Stone | | | mg $L^{-1}$ | mg $L^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | % | g $kg^{-1}$ | g $kg^{-1}$ | |
| 0-30 | 25-30 | 15-25 | - | Moderate | 5.5 | $0.34^b$ | $0.49^b$ | 63 | $193^c$ | 43 | $4.5^c$ | $46^b$ | 10.4 |
| | | | | | (0.12) | (0.016) | (0.072) | (7.4) | (3.8) | (2.4) | (0.02) | (0.29) | (0.19) |
| 30-60 | 25-30 | 15-25 | 1-15 | Slow | 5.5 | $0.27^b$ | $0.17^a$ | 50 | $114^b$ | 51 | $3.5^b$ | $36^a$ | 10.2 |
| | | | | | (0.22) | (0.027) | (0.033) | (5.1) | (3.8) | (8.1) | (0.01) | (0.05) | (0.10) |
| 60-80 | 25-30 | 40-60 | 40-70 | Moderate | 5.5 | $0.09^a$ | $0.04^a$ | 41 | $54^a$ | 29 | $0.9^a$ | $9.6^c$ | 10.2 |
| | | | | | (0.02) | (0.003) | (0.010) | (1.6) | (7.3) | (5.5) | (0.01) | (0.11) | (0.29) |
| $LSD_{05\ depth}$§ | | | | | ns | <0.01 | <0.05 | ns | <0.001 | ns | <0.001 | <0.01 | ns |

[1] WEP = Water extractable P; Dithionite-P = Sodium-Bicarbonate-Dithionite extractable phosphorus; CBD-Fe = Citrate-Bicarbonate-Dithionite extractable Iron; ASC = Anion Sorption Capacity.

[2] Landcare Research (2019)

### 4.3.2 Field Site Sampling

Climatic data is presented in Figure 4.1. Data for regular sampling of DRP, Fe, Mn and $NO_3$ at the field site are presented by depth at 20 cm bgl and 80 cm bgl are presented in Figures 4.2 and 4.3, respectively. Concentrations of DRP in the suction cups at 20 cm bgl ranged from 0 to 0.49 mg DRP $L^{-1}$ over 2017 and 2019. The mean (± standard error of the mean, SE) concentration at 20 cm was 0.024 (±0.008) and 0.012 (±0.002) mg DRP $L^{-1}$ in 2017 and 2019, respectively. Concentrations of DRP at 80 cm bgl ranged from 0 to 0.30 mg DRP $L^{-1}$ over the two monitoring years. The mean concentration at 80 cm was 0.025 (±0.015) and 0.005 (±0.001) mg DRP $L^{-1}$ in 2017 and 2019, respectively.

In 2017, there were three notable DRP peaks at the 20 cm depth, but two coincided with Mn and Fe concentration increases. The first peak (0.1 DRP mg $L^{-1}$) occurred in July and did not coincide with a enough rainfall to cause saturation according to soil water balance calculations (Woodward et al., 2001). The second and third DRP peaks (both 0.1 mg DRP $L^{-1}$) occurred over two consecutive sampling events in September 2017 during and after a large rainfall event (63 mm) and increasing soil temperatures (5.7-9.1$^{o}$C) with the onset of spring. During these September 2017 events there was an increase in Fe concentration (0.1 mg Fe $L^{-1}$) compared to previous samplings (0-0.02 mg Fe $L^{-1}$), and a decrease in $NO_3^-$ in soil solution from 17 mg $NO_3$-N $L^{-1}$ to 6 mg $NO_3$-N $L^{-1}$. Using the redox assignment calculator (McMahon & Chapelle, 2008), most samples suggested the site was, at most, nitrate reducing, but not Fe or Mn reducing. The exception was for the two consecutive September 2017 events which suggested Fe and Mn reduction had occurred. Solution $SO_4$ remained unaffected.

In contrast to the 20 cm depth, DRP was enriched (0.30 mg DRP $L^{-1}$) at 80 cm depth only during the first of the two events in September 2017. Although Fe and Mn concentrations at the 20 cm depth suggested the soil was anoxic, concentrations at 80 cm were at most considered mixed anoxic ($NO_3$-Fe(III)/$SO_4$). This may be because the suction cups at 80 cm were below a slowly permeable layer at 40-60 cm below ground level. Therefore, the soil below this layer may not have been saturated.

Throughout the 2019 sample period, the greatest DRP concentrations occurred in July (0.024 mg DRP $L^{-1}$) and August (0.022 mg DRP $L^{-1}$). The July sampling coincided with a sustained period of light rainfall but no saturation excess generated. The August sample event occurred on the final day of a 7-day rainfall (46 mm) and drainage event, where the profile would have been saturated. Only the August event saw a commensurate increase in Fe concentration (0.02 mg Fe $L^{-1}$ and 0.06 mg $NO_3^-$ $L^{-1}$). The only other sample event that yielded similarly high DRP concentrations was during the artificial saturation experiment (0.025 mg $L^{-1}$).

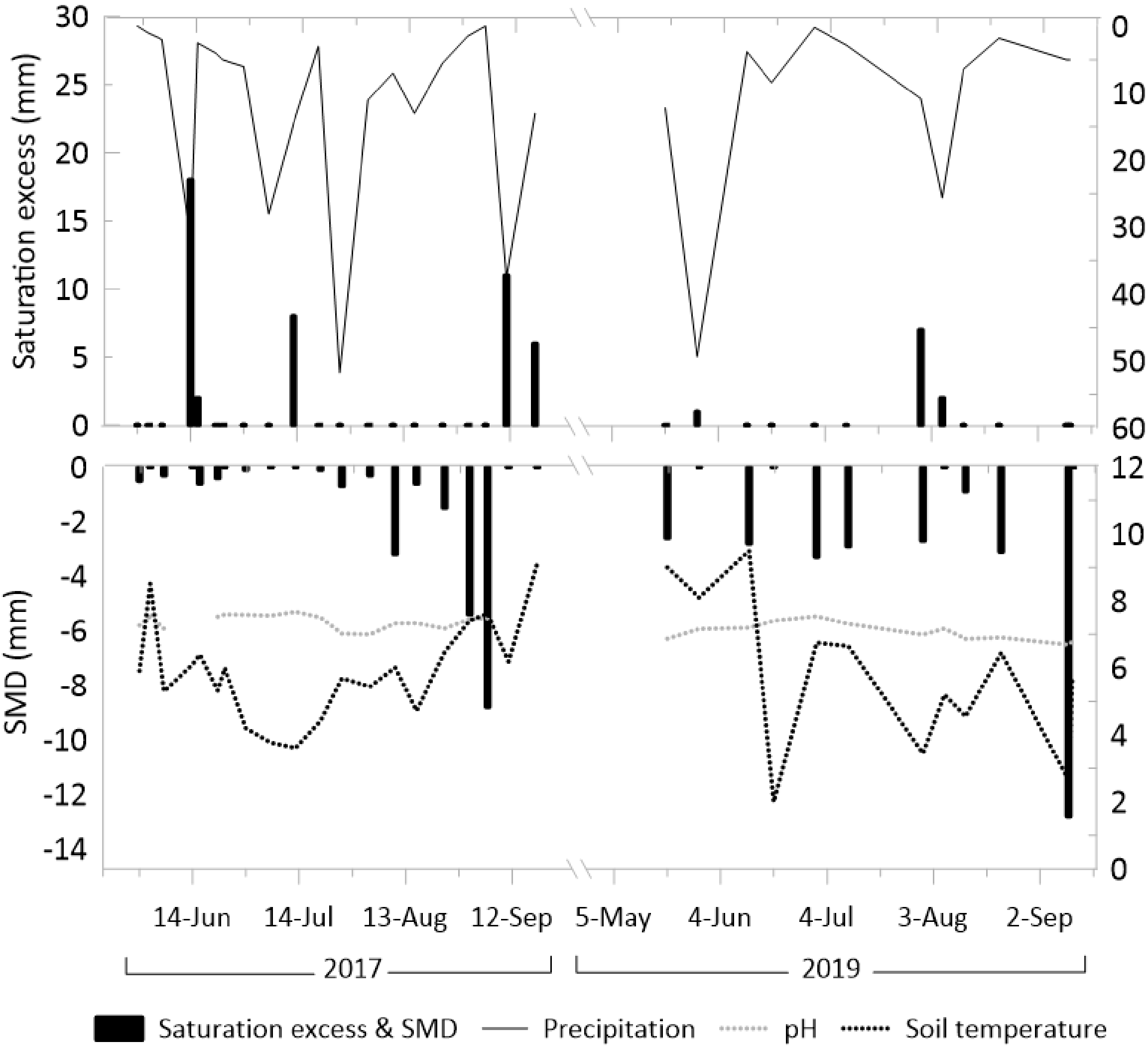

Figure 4.1 Data for climate and soil conditions between May 2017 to September 2017 and May 2019 to September 2019. Soil solution pH, soil temperature (10 cm), soil moisture deficit (SMD) and events that generated saturation excess (Excess) are shown. Excess was calculated using soil water balance equations (Woodward et al., 2001). Note a break in the x-axis.

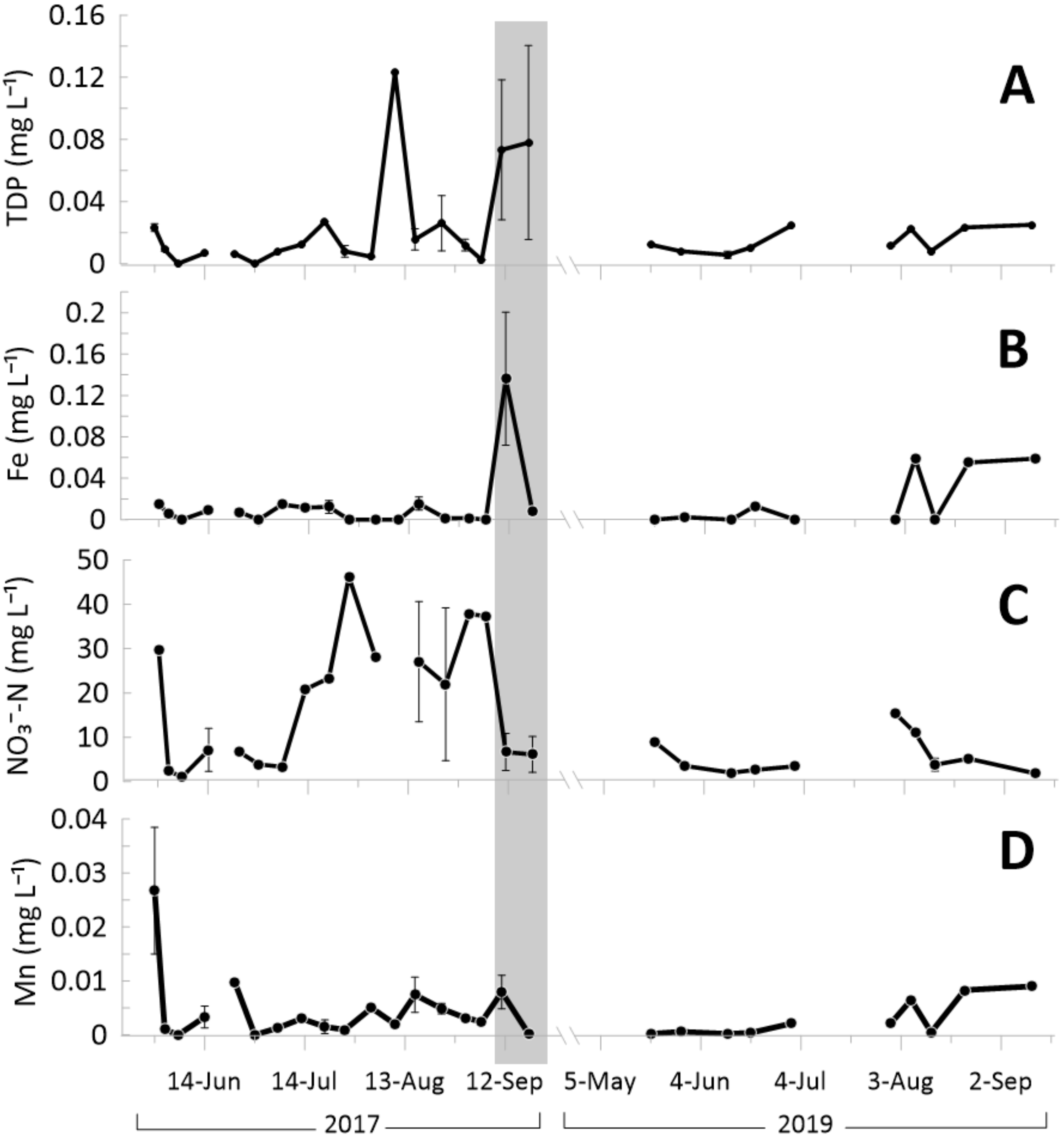

Figure 4.2 Mean solution concentrations at 20 cm below ground level (with error bars showing the standard error of the mean) between May 2017 to September 2017 and May 2019 to September 2019 for (A) total dissolved phosphorus (TDP), (B) iron (Fe), (C) nitrate-N ($NO_3^-$-N), and (D) manganese (Mn). Sample events shaded with a grey polygon indicate a reducing environment (McMahon & Chapelle, 2008). Note a break in the x-axis.

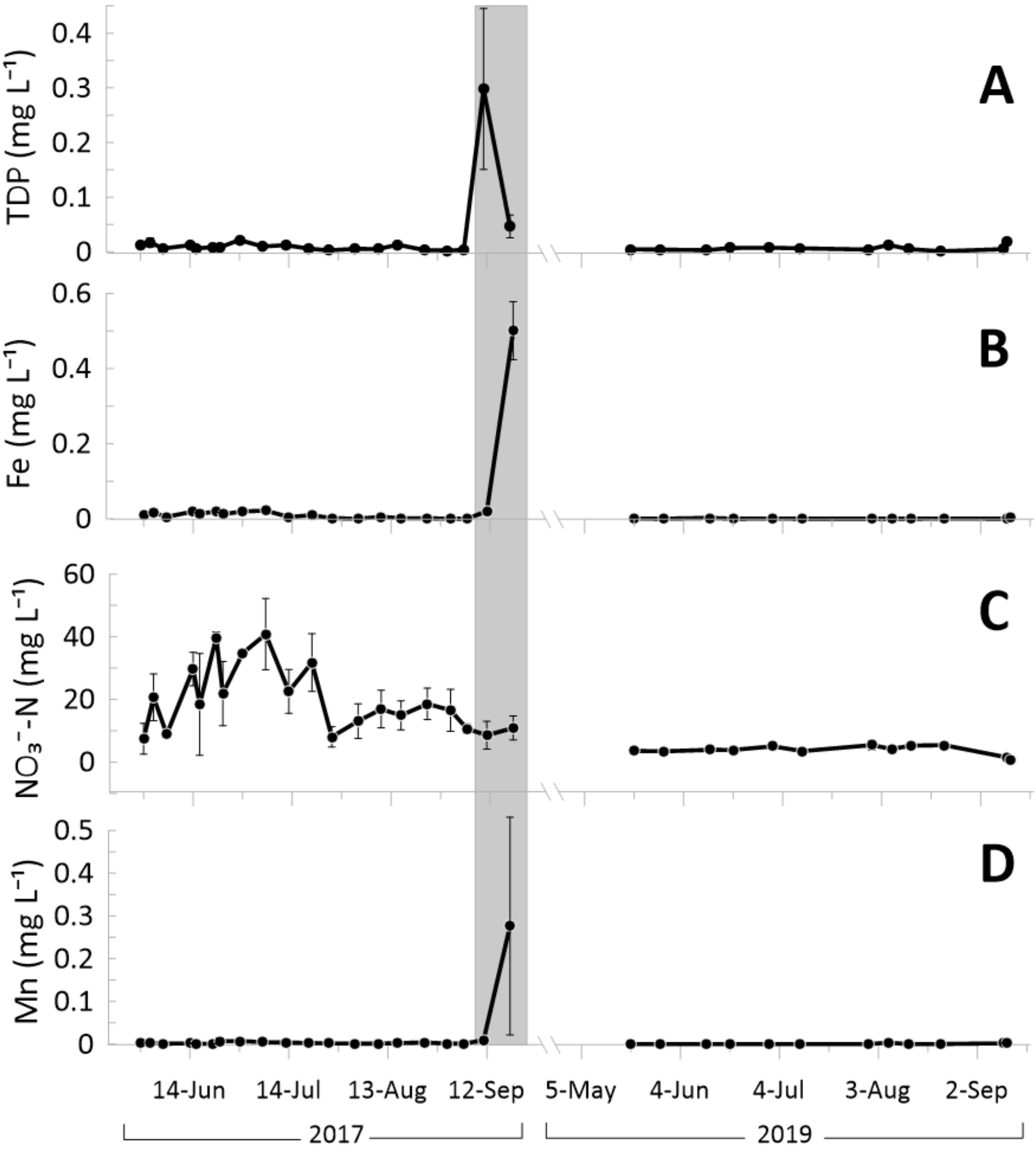

Figure 4.3 Data for May 2017 to September 2017 and May 2019 to September 2019 for mean solution concentrations at 80 cm below ground level (with error bars showing the standard error of the mean) of (A) total dissolved phosphorus (TDP), (B) iron (Fe), (C) nitrate-N ($NO_3^-$-N), and (D) manganese (Mn). Sample events shaded with a grey polygon indicate a reducing environment (McMahon & Chapelle, 2008).

### 4.3.3 Field and Laboratory Treatment

Data showing the response to the injection of treatments in the field at each depth is given in Table 4.2 and Figure 4.4. Average concentrations of DRP in solution was significantly greater in the deionised (DI) water treatment at both depths ($P < 0.01$ at 20 cm bgl, $P < 0.05$ at 80 cm bgl) compared to the $NO_3^-$ + C treatment. Concentrations of Fe were greater at 80 cm bgl ($P < 0.01$) in the DI water treatment than the $NO_3^-$ + C treatment but did not vary between treatments at 20 cm bgl. There was no interaction between treatment and depth for DRP, Fe or Mn. There was an interaction between treatment and depth for $NO_3^-$ ($P < 0.05$). Therefore, this suggests that depth played a part in the removal of N.

Concentrations of DRP in the laboratory experiment were greater than the field experiment, which may reflect different experimental conditions (Table 4.3 & Figure 4.5). The C treatment increased DRP at both depths compared to those treatments that contained $NO_3^-$, and the C treatment at 20 cm bgl was the only treatment to reach the redox category of 'Fe(III)/$SO_4$'. Iron concentrations from the soils treated with C were significantly greater than the soils with any $NO_3^-$ addition at 80 cm ($P < 0.001$), but not at 20 cm. While a similar pattern was seen for Mn concentrations, the differences in concentrations due to treatment were not statistically significant at either depth. When data were restricted to just the $NO_3^-$ + C and DI treatments (similar to the field trial experiment), concentrations of DRP were greater in the DI treatment in both depths (Table 4.4). Solution Fe was only significantly greater in the DI water treatment at 20 cm ($P < 0.05$).

There were significant differences in $NO_3^-$ between treatments ($P < 0.001$) and a significant interaction between treatment and depth ($P < 0.001$). Over 66% of the initial spike $NO_3^-$ was left in solution (66-76%), suggesting that the supply of $NO_3^-$ was not exhausted by redox reactions. However, the soil amended with $NO_3$-C at 20 cm had approximately 10% less mean $NO_3^-$ left in solution than the other soils with any $NO_3^-$ amendment (Table 4.3). These results would suggest that the absence of C was limiting redox reaction in this soil and that the lower C content at 80 cm bgl potentially compounded this (Table 4.1) (Kölbl et al., 2017; Yuan et al., 2015).

A Pearson correlation matrix (Table 4.5) showed that solution Fe, Mn and DRP amongst lab treatments were positively correlated with each other, while DRP was negatively correlated with $NO_3$, and $SO_4$ was negatively correlated with Fe and Mn.

Table 4.2 Mean (± standard error of the mean) dissolved reactive phosphorus (DRP), iron (Fe), manganese (Mn) and nitrate ($NO_3^-$) concentrations (mg $L^{-1}$) in soil solution samples at 20 and 80 cm depth following the injection of either deionised water (control), or 50 ppm $KNO_3$ and 300 ppm Glucose-C ($NO_3^-$ + C). Nitrate concentrations are also presented as the percentage of initial $NO_3$ spike left in solution after 4 hours[1], where applicable. The output (*P* values) of an analysis of variance is given to identify the significance differences in solution concentrations due to treatments within a depth and for the interaction of treatments by depth[2].

| Depth (cm) | Treatment | DRP | Fe | Mn | $SO_4$ | $NO_3$ | % $NO_3$[1] |
|---|---|---|---|---|---|---|---|
| 20 | $NO_3^-$ + C | 0.003<br>(0.0010) | 0.011<br>(0.0060) | 0.004<br>(0.0010) | 15.2<br>(8.96) | 16.7<br>(0.09) | 26.8 |
| | DI water | 0.022<br>(0.0020) | 0.053<br>(0.0060) | 0.007<br>(0.0020) | 10.6<br>(0.25) | 8.3<br>(0.12) | |
| 80 | $NO_3^-$ + C | 0.004<br>(0.0010) | 0.000<br>(0.0000) | 0.004<br>(0.0010) | 11.8<br>(0.70) | 26.3<br>(3.29) | 42.2 |
| | DI water | 0.014<br>(0.0030) | 0.048<br>(0.0190) | 0.003<br>(0.0020) | 28.3<br>(2.61) | 5.1<br>(2.28) | |
| *P* values | $\boldsymbol{P}_{\text{Treatments (20 cm)}}$ | <0.01 | ns | ns | ns | <0.001 | |
| | $\boldsymbol{P}_{\text{Treatments (80 cm)}}$ | <0.05 | <0.01 | ns | <0.01 | <0.01 | |
| | $\boldsymbol{P}_{\text{Treatments x depth}}$[2] | ns | ns | ns | <0.05 | <0.05 | |

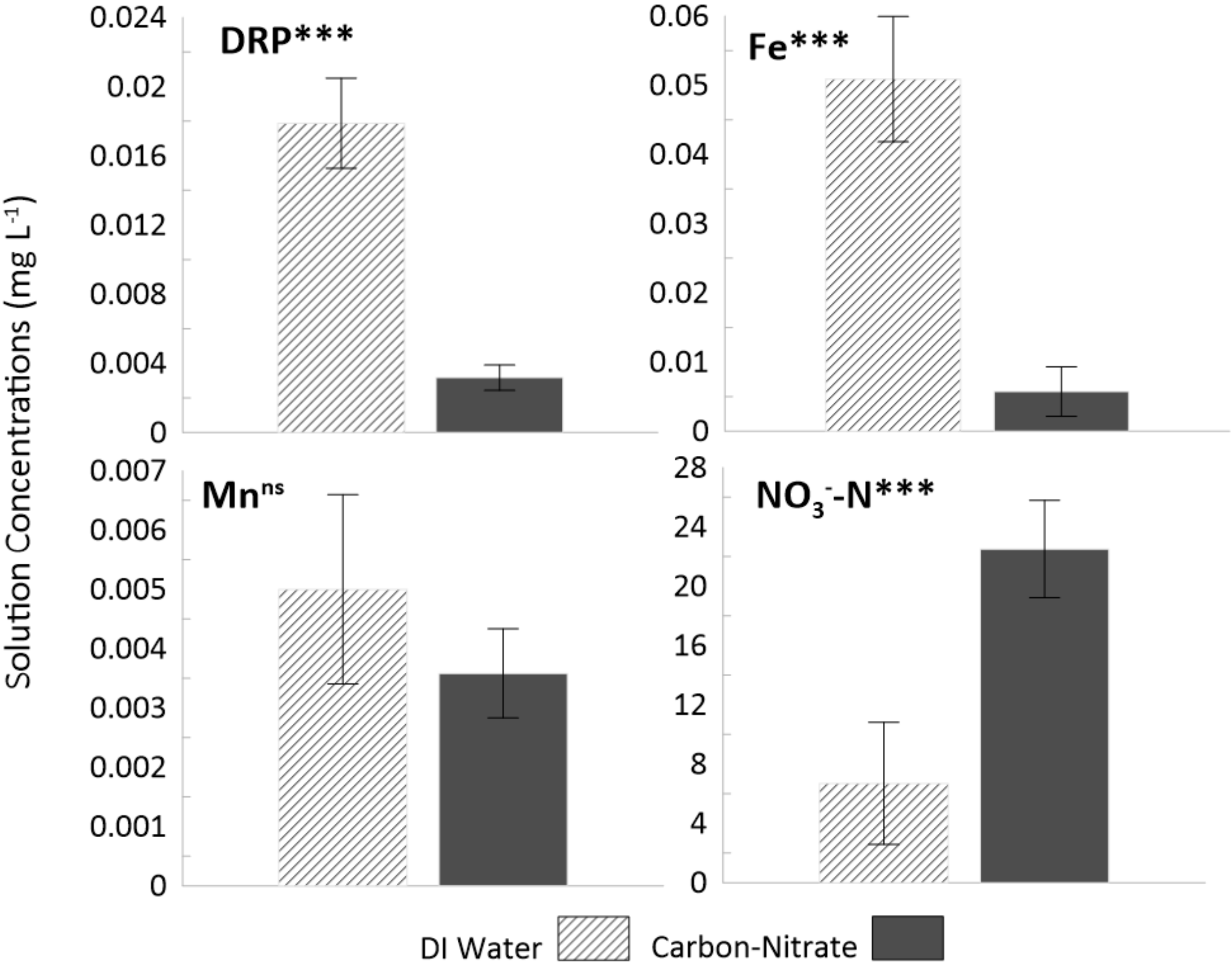

Figure 4.4 Field incubation mean (± standard error of the mean) total dissolved P (TDP), iron (Fe), manganese (Mn), and nitrate-N ($NO_3^-$-N) concentrations (mg $L^{-1}$) across both depths in response to treatments of deionized (DI) water or Nitrate + Carbon (50 ppm $NO_3^-$). Asterisks denote significant differences in means due to treatment, according to a one-way ANOVA (ns = not significant, * $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$) Note different y-axis scales.

Table 4.3 Laboratory incubation mean (± standard error of the mean) dissolved reactive P (DRP), iron (Fe), manganese (Mn), and nitrate ($NO_3^-$) concentrations (mg $L^{-1}$) at 20 and 80 cm depths in response to treatments of deionised (DI) water, glucose (C, 300 ppm), $NO_3^-$+C (50 ppm $NO_3^-$), and $NO_3^-$. The percentage of initial $NO_3$ spike left in solution after 4 hours are also presented, where applicable[1]. Also shown are the potential redox class, as per McMahon and Chapelle (2008). Analysis of variance *P* values are given to identify the significance differences in solution concentrations due to treatments within a depth and for the interaction of treatments by depth. Means within a depth are contrasted using Tukey's Honestly Significant Difference test[2].

| Depth cm | Treatment | DRP | Fe | Mn | $SO_4$ | $NO_3$ | $\%NO_3^1$ | Potential redox process |
|---|---|---|---|---|---|---|---|---|
| 20 | DI water | $0.37^{ab}$ ‡ (0.028) | $15.6^{a}$ (3.61) | $0.20^{a}$ (0.038) | $18.1^{c}$ (6.93) | $2.5^{b}$ (0.60) | | $NO_3$-Fe(III)/$SO_4$ |
| | C | $0.49^{b}$ (0.093) | $18.1^{a}$ (7.35) | $0.25^{a}$ (0.093) | $15.1^{bc}$ (7.70) | $0.8^{b}$ (0.20) | | Fe(III)/$SO_4$ |
| | $NO_3^-$ + C | $0.33^{ab}$ (0.020) | $13.5^{a}$ (3.34) | $0.13^{a}$ (0.020) | $10.8^{abc}$ (7.20) | $33.2^{a}$ (1.73) | 66.4 | $NO_3$-Fe(III)/$SO_4$ |
| | $NO_3^-$ | $0.26^{a}$ (0.024) | $7.2^{a}$ (0.71) | $0.19^{a}$ (0.024) | $13.0^{abc}$ (9.19) | $38.6^{a}$ (2.31) | 77.1 | $NO_3$-Fe(III)/$SO_4$ |
| 80 | DI water | $0.36^{b}$ (0.013) | $18.8^{ab}$ (0.86) | $0.27^{ab}$ (0.041) | $2.2^{a}$ (0.36) | $29.4^{a}$ (5.67) | | $NO_3$-Fe(III)/$SO_4$ |
| | C | $0.49^{c}$ (0.055) | $26.4^{b}$ (3.65) | $0.36^{b}$ (0.035) | $3.2^{ab}$ (0.16) | $7.7^{b}$ (6.25) | | $NO_3$-Fe(III)/$SO_4$ |
| | $NO_3^-$ + C | $0.29^{ba}$ (0.015) | $16.4^{a}$ (1.23) | $0.23^{ab}$ (0.029) | $3.7^{ab}$ (1.00) | $38.1^{a}$ (2.31) | 76.2 | $NO_3$-Fe(III)/$SO_4$ |
| | $NO_3^-$ | $0.26^{a}$ (0.008) | $14.1^{a}$ (0.82) | $0.21^{a}$ (0.032) | $2.8^{ab}$ (0.47) | $37.6^{a}$ (1.11) | 75.2 | $NO_3$-Fe(III)/$SO_4$ |
| *P* values | ***P*** Treatments (20 cm) | <0.05 | ns | ns | ns | <0.001 | | |
| | ***P*** Treatments (80 cm) | <0.001 | <0.001 | <0.05 | ns | <0.001 | | |
| | ***P*** Treatments (20 - and 80 cm) | <0.001 | <0.05 | ns | ns | <0.001 | | |

[2] Means of the same letter are not different

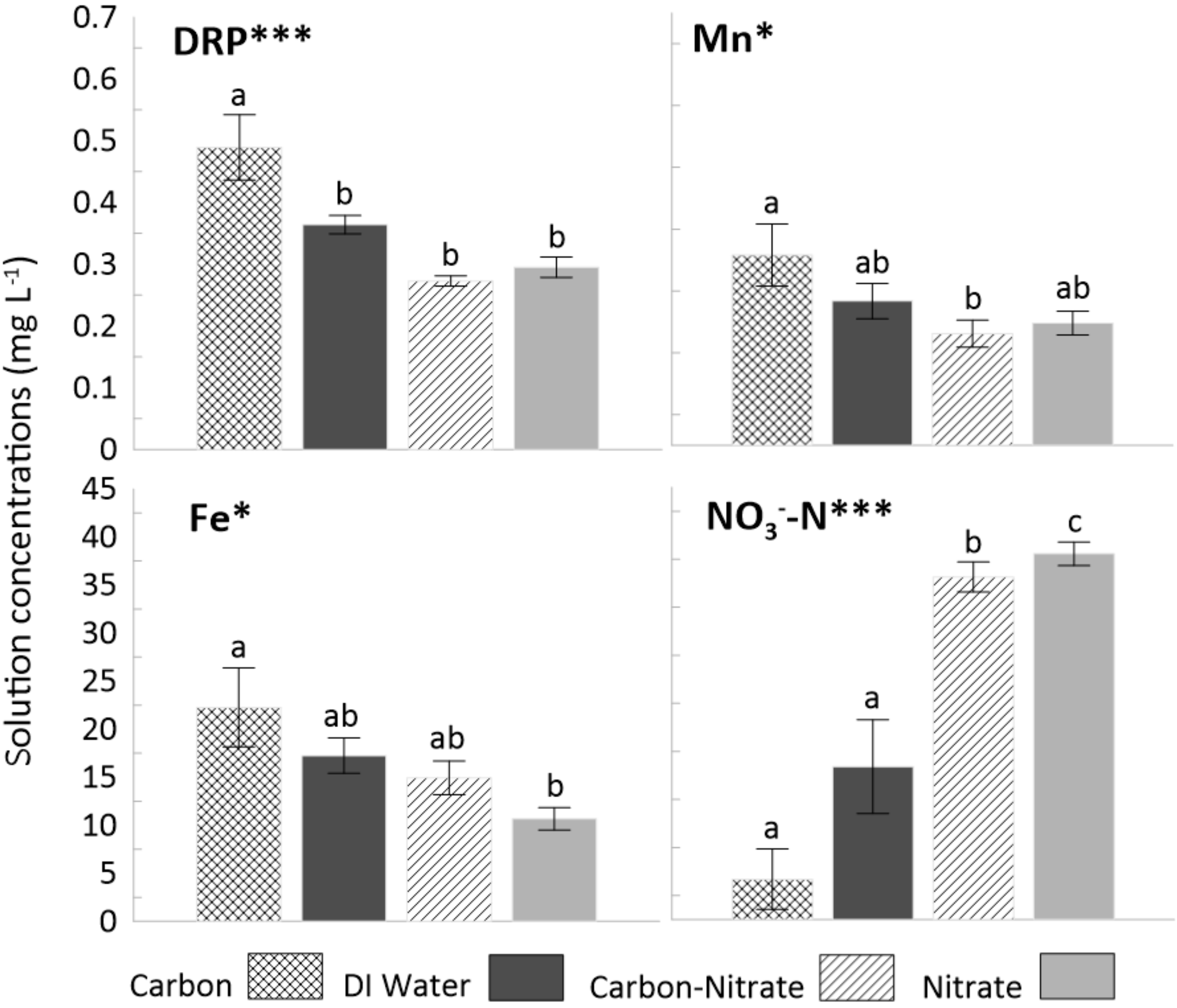

Figure 4.5 Laboratory incubation mean (± standard error of the mean) total dissolved P (TDP), iron (Fe), manganese (Mn), and nitrate-N ($NO_3^-$-N) concentrations (mg $L^{-1}$) across both depths in response to treatments of carbon, deionized (DI) water, nitrate + carbon (50 ppm $NO_3^-$), or only nitrate. Asterisks denote significant differences in means due to treatment, according to a one-way ANOVA (* $P < 0.05$, ** $P < 0.01$, *** $P < 0.001$) Differences via Tukey's Honestly Significant Difference (HSD) and are indicated by lettering. Note different y-axis scales.

Table 4.4 Laboratory incubation mean solution concentrations, isolated to the treatments used in the field incubation. Treatments were: deionised (DI) water (i.e. control); and, nitrate as $KNO_3$ with glucose-carbon ($NO_3^-$ + C). Significant differences between treatments within a depth and over both depths were calculated using a two-way ANOVA.

| Depth cm | Treatment | DRP | Fe | Mn | $NO_3$ | $SO_4$ |
|---|---|---|---|---|---|---|
| 20 | DI water | 0.37 | 15.6 | 0.20 | 2.5 | 18.1 |
| | $NO_3^-$ + C | 0.33 | 13.5 | 0.13 | 33.2 | 10.8 |
| 80 | DI water | 0.36 | 18.8 | 0.27 | 29.4 | 2.2 |
| | $NO_3^-$ + C | 0.29 | 16.4 | 0.23 | 38.1 | 3.7 |
| ***P* values** | ***P*** 20 cm | <0.01 | <0.05 | ns | <0.01 | ns |
| | ***P*** 80 cm | <0.01 | ns | ns | ns | ns |
| | ***P*** Over all depths | <0.00 | <0.05 | ns | <0.01 | <0.05 |

Table 4.5 Pearson correlation matrix of soil solution concentrations from an incubation of soils (n = 48) in laboratory conditions, across all depths. Values annotated with *, **, and *** mean *P* values at the 0.05, 0.01, and 0.001 level, respectively.

| | Fe | DRP | Mn | $SO_4$ |
|---|---|---|---|---|
| DRP | 0.512*** | | | |
| Mn | 0.583*** | 0.559*** | | |
| $SO_4$ | -0.441** | -0.065 | -0.359* | |
| $NO_3$ | -0.188 | -0.567*** | -0.172 | -0.323* |

## 4.4 Discussion

### 4.4.1 Field Monitoring

The concentration of DRP in samples taken in this study are relatively low, but never lower than the 80th percentile for DRP in streams in the area under reference conditions at 0.011 mg P $L^{-1}$ (McDowell et al., 2018). In samples where DRP concentrations were at their greatest (> 0.1 mg DRP $L^{-1}$), there are five potential explanations: 1) that there was an anthropogenic source; 2) that during rewetting after a dry period, microbial cell lysis occurred due to osmotic shock and released P (Turner et al., 2003); 3) that moist, warm conditions will induce organic matter decomposition, which would release P (USDA-NRCS Soil Quality Institute, 2001); 4) that under anoxic conditions, changes in solution pH cause P to desorb from soil particles (Gu et al., 2019); and 5) that reductive dissolution of P occurred under anoxic conditions (Gu et al., 2019; McDowell et al., 2019). No P fertiliser was supplied to the site. Additionally, the soil moisture data (Figure 4.1) suggests that the soil did not dry to the extent necessary (i.e. near permanent wilting point) that microbes would desiccate and release their P into soil solution (McDowell and Trudgill, 2000). In the September-2017 and August 2019 events, the increase in solution DRP was accompanied by an increase in Fe and Mn, and a decrease in $NO_3$. While we cannot discount the release of DRP, Fe and Mn from microbes, desiccation is also paired with a flush of N (Gordon et al., 2008; van Gestel et al., 1993). As the $NO_3^-$ in solution decreased in this situation, it would appear more likely that the increase in solution DRP is due to either desorption or dissolution.

Solution pH remained relatively stable during the trial (Figure 4.1). Although it is well known that changing pH can affect P availability and desorption in soils (Haynes, 1982), the magnitude of pH change (± 0.2 units) was small and near the limit of detection (0.1 unit) (Hendershot et al., 1993).

Increased soil temperature, and available C coupled with lower $NO_3^-$ concentrations may have influenced the occurrence and rate of the redox reactions releasing P, Fe and Mn into soil solution especially in the September, 2017 events; Figure 4.1 (Hossain et al., 2017; Scalenghe et al., 2002). Temperature increases the rate of reaction by stimulating more biological activity (Sallade and Sims, 1997a; Sparks, 2003). Reductive dissolution of Fe is stimulated by available C (Chacon et al., 2006). Total inorganic carbon (33 mg TIC $L^{-1}$) and total organic carbon (18 mg TOC $L^{-1}$) at 80 cm (insufficient sample volume was available for C analysis at 20 cm) were an order of magnitude greater in the September events than during the rest of the sample period. This may have been fuelled by increasing temperature and organic matter decomposition (Chacon et al., 2006; Hossain et al., 2017; Lindsay, 1979). Finally, $NO_3^-$ concentrations, which may have inhibited the reduction of Fe and Mn, were low. This was especially the case in the September 2017 events, compared to previous events, presumably caused by a combination of saturation, denitrification, and leaching of $NO_3^-$ over the winter period (Smith et al., 2016).

In contrast to the 20 cm depth, solution DRP, Fe and Mn enrichment in September-2017 appeared to be delayed at 80 cm bgl, which was below the depth where soil moisture was monitored (0-30 cm). This delay may be due to the poorly permeable layer at ~40 cm bgl, potentially inhibiting saturation of deeper soil layers. Another possibility is that there was a lack of bioavailable C in the subsoils. Smaller quantities of subsoil C occurred in the study by Kölbl et al. (2017), and using Carbon-13 Nuclear Magnetic Resonance (C-13 NMR) analysis could be used in future studies to explore this possibility further.

### 4.4.2 Field and Laboratory Incubation Experiments

Inundation and saturation of soils in the field and under controlled laboratory conditions appeared to confirm that anaerobically incubated samples resulted in Fe and Mn dissolution and P release. However, the presence of $NO_3^-$ appeared to buffer/inhibit the reduction and release of Fe and associated P. There are some instances where $NO_3^-$ can oxidise iron sulfide minerals, which would potentially increase dissolved Fe (Jørgensen et al., 20009), so it would have been beneficial to see the effects of only $NO_3^-$ on the soil chemistry. However, this was not viable due to space and the number of replicates. In the field and lab, the mean P released appeared to be greater in topsoil than subsoil – but only significantly so in the lab incubation – presumably reflecting the greater available fractions of WEP, $CaCl_2$-P and Dithionite-P in the topsoil (Table 4.1). As P is surface applied and usually well sorbed, P concentrations are well known to stratify, decreasing down the soil profile (Sharpley, 2003b).

If $NO_3^-$ is in ample supply there is no need for microbes to move onto less energetically favourable acceptors such as Fe- and Mn-oxides (McMahon and Chapelle, 2008), meaning P associated with these oxides will not be released. However, the activity of the microbial biomass will also be controlled by the limiting nutrient. In soil and water, much work has shown that this ratio hovers around a molar ratio of 106:16:1 C:N:P – somewhat dependant on the species involved (Cleveland and Liptzin, 2007). We supplied C (as glucose) to avoid C-limitation and studies have shown that the microbial biomass responds well to C additions. For instance, Iovieno and Bååth (2008) stated that adding glucose to moist soils caused five times greater bacterial respiration.

Adding C in the lab enhanced the dissolution of DRP, Fe and Mn suggesting that $NO_3^-$ was also used up. However, in those soils treated with artificial $NO_3^-$, at least 80% of the $NO_3^-$ added remained, meaning that the amount of $NO_3^-$ added was in excess of the soil's reductive capacity – with or without added C, and that a progression to the dissolution of Fe and Mn-oxides did not occur. Experiments on riparian wetlands such as those by Surridge et al. (2007a) in the United Kingdom and Lucassen et al. (2004) in the Netherlands identified $NO_3^-$ as a redox buffer. However, these are not on agricultural soils. In agricultural settings, studies have noted smaller P losses under increased N treatments (Dodd et al., 2014a; Gray et al., 2016b). However, these agricultural soils were not saturated or anoxic. Here, it is likely that a decrease in P had nothing to do with reductive dissolution, but that microbial growth was P-limited and therefore preferentially sequestered by microbes from the soil solution (N:P ratio > 16 molar basis or 7 on a mass basis).

### 4.4.3 Implications for Management

The enrichment of $NO_3^-$ in groundwater has been proposed as a potential cause for decreased P inputs to streams. A recent study of > 700 catchments in New Zealand by McDowell et al. (2019) found that only 4% of sites with enriched groundwater N had a decrease in surface water P concentrations. However, the present study suggests that agricultural systems that have low N inputs paired with significant P stores could be more vulnerable to P loss in saturated conditions. Without the buffering influence of $NO_3^-$ in a soil profile, anaerobic conditions caused by inundation could cause a soil profile to become Fe- and Mn-reducing and release associated P. Hence, different rates of N and its influence on reductive dissolution of P should be explored in more detail to determine and avoid situations where N concentrations are so low that P becomes enriched and potentially lost to P-limited surface waters. It is also necessary to study the influence of the presence of N on DRP in a variety of settings, as the results may vary depending on the soil type, climate and local practices. As one of many possible examples of how locale and soils could affect the relationship between $NO_3^-$ and P; heavy textured soils in the south of Ireland are known to convert $NO_3^-$ to ammonium ($NH_4^+$) (Clagnan et al., 2018a). Therefore, the resulting low $NO_3^-$ concentrations and the influence of

$NH_4^+$ on pH may affect DRP release differently. The outcomes of this could improve knowledge of knock-on consequences of changing N management and surpluses and their influence on N stores available to buffer reducible P.

## 4.5 Conclusions

The results of this study indicates that reducing conditions in agricultural soils may increase metal-oxide and associated P dissolution. Through a combination of field monitoring, *in* situ incubations and laboratory incubations, the present study shows that soil saturation excess resulted in the reductive dissolution of P. Additionally, $NO_3^-$ is a key buffer for the reaction. Therefore, an area that is prone to saturation excess and lateral flow could induce P loss and its transport downslope to waterways, particularly if it is a low $NO_3^-$ system. It is important to identify these high P/low N systems, particularly in sites that are prone to saturation events (e.g. hydrologically sensitive areas or riparian zones) as they may exacerbate P release into waterways in the future and should be managed as CSAs and incorporated into the P risk indices.

# Chapter 5

# Phosphorus and metal-oxide transport from a hydrologically isolated grassland slope

## 5.1 Introduction

Agricultural intensification can have negative implications for water quality (Leinweber et al., 2018). In particular, phosphorus (P) loss from agricultural soil to water is linked to degradation of surface water quality and eutrophication (McDowell et al., 2020). Due to its high bioavailability, there has been significant interest in the transport of dissolved reactive P (DRP) to surface waters (Buda et al., 2009a; Dupas et al., 2017; Leinweber et al., 2018; Shore et al., 2016). In the European Union, the Water Framework Directive (WFD) outlines regulations and thresholds to avoid degradation of water. These regulations stipulate that concentrations of filtered molybdate-reactive P (viz. DRP) should not exceed 30 µg P $L^{-1}$in Irish rivers (Cleneghan et al., 2005). However, to reduce or maintain DRP concentrations below this threshold, the mechanisms and pathways (surface and subsurface) of DRP loss from agricultural land must be fully understood.

The primary transport pathways for DRP from agricultural land to waterways are surface runoff, near-surface lateral flow, and artificial drainage conduits. Surface runoff and lateral flow can provide a transport pathway for DRP in the upper soil horizons and soil surface, while drainage and deeper lateral flow provide a subsurface pathway (McDowell and Monaghan, 2014; Monaghan et al., 2016). The proportion of DRP transported via surface or subsurface pathways depends on climatic and soil conditions. The number of studies that have examined DRP loss in drainage is increasing but those examining grassland systems are rare compared to those examining DRP losses from croplands (Christianson et al., 2016; Dupas et al., 2015; Grant et al., 1996; Ibrahim et al., 2013; Kronvang et al., 2005; Moore, 2016; Peyton et al., 2016). Owing to their suitability to cooler and wetter climates, grasslands tend to exhibit a greater proportion of drainage resulting from saturation-excess conditions than cropping systems (Cassidy et al., 2016; Doody et al., 2010; Monaghan et al., 2016; Thompson et al., 2012). The frequency and length of time a soil is waterlogged is known to influence DRP dissolution into soil solution (Gu et al., 2019; Warrinnier et al., 2020) Hence, it is important to know the mechanisms responsible and when such conditions occur, to avoid inappropriate management (such as intensive grazing) that could exacerbate DRP losses.

In soils, a combination of poor drainage and inundation can lead to waterlogging, whereby the soil profile can quickly become anaerobic due to microbial respiration. During respiration, microbes gain energy by mediating oxidative-reductive (redox) reactions between an electron donor (usually carbon, C) and an electron acceptor. The most energetically preferable electron acceptor is oxygen. When this is depleted, $NO_3^-$ becomes preferable, then Mn, Fe, sulphate ($SO_4^{2-}$), and carbon dioxide ($CO_2$) (McMahon and Chapelle, 2008). The reductive dissolution of P-sorbing iron (oxy)hydroxides (i.e. Fe oxides) and Mn oxides (Colombo et al., 2014; Smith, 2020; Warrinnier et al., 2020) releases P into the soil solution, which in turn could be lost in drainage (Heiberg et al., 2012; Martynova, 2010). In grazed grasslands where most $NO_3^-$ leaching occurs via urine patches, appropriate timing of grazing and stocking rate may influence DRP loss under waterlogged conditions. Additionally, movement of $NO_3^-$ in groundwater may flow downgradient into an area with a shallow water table (Clagnan et al., 2018b).

Although studies have examined the availability of P under reducing conditions, these have largely been in: river and lake sediments (Heiberg et al., 2012); wetland systems (Moustafa et al., 2011; Reddy et al., 1998b); or in wetted fields in China’s vegetable production systems (Wang et al., 2020; Yan et al., 2013), which all maintain anaerobic conditions for long periods and have defined wetting and drying phases. Far fewer studies have been undertaken in a soil profile (Prem et al., 2014; Warrinnier et al., 2020) or at the drainage outlet. Recent work has shown that anaerobic conditions can increase DRP availability in soil solution quickly, particularly in warmer conditions (Heiberg et al., 2012; Jenkinson and Franzmeier, 2005; Smith, 2020). Depending on the efficiency of the drainage network and climate, and the timing of grazing and stocking rate of the farm, this raises the likelihood of P losses in drainage events, with wide variation throughout the year. While there is evidence of anaerobic conditions affecting P release into soil solution, further research into the effects of this release at the drainage outlet is required, as the relative importance of the mode of P release depends on its connectivity to a receiving water body (Thomas et al., 2016). Additionally, the released P may be attenuated during transport by precipitation, undissolved Fe oxides, aluminium (Al) oxides that are impervious to redox, or grass uptake (Prem et al., 2014). Therefore, it is important to identify if redox-sensitive phosphorus is represented at the drainage outlet.

The aim of this study was to investigate the processes controlling intra- and inter-event and seasonal DRP losses from a poorly drained grassland hillslope. Surface runoff and artificial drainage P losses were examined and related to the likelihood of anaerobic conditions and redoximorphic species including $NO_3^-$. The study was conducted in Ireland where half of agricultural soils fall into poorly or imperfectly drained categories (O'Sullivan et al., 2015).

## 5.2 Method

### 5.2.1 Site description and sampling

The ungrazed silage study site was located on a 4.2 ha study area on a beef farm at Teagasc, Johnstown Castle, Co. Wexford, SE Ireland (52°17'36"N, 6°31'6"W). Mean annual precipitation is 1002 mm. The soil is a Stagnic Brown soil (Irish Soil Classification) or a Cambisol (WRB Soil group). The site is derived from mixed drift of shale quartzite and Irish sea muds and has soils from the Rathangan (poorly drained) and Crosstown (variable drainage) associations. Previous work at the site has identified the particle size fractions as 45% sand, 20% silt, and 34% clay (Fenton et al., 2009; Ibrahim et al., 2013). The bulk density to 100 mm depth was 1.35 Mg $m^{-3}$. Within the monitoring periods: N fertiliser was applied in 2009 as urea to all plots on the 23rd March (118 kg N $ha^{-1}$), and as calcium ammonium nitrate (101.8 kg N $ha^{-1}$) 31st May; phosphorus fertiliser was applied on the 21st March (37 kg P $ha^{-1}$). Approximately 98 kg N $ha^{-1}$ was applied as cattle slurry on the 30th October 2018. A full description of the management of the site is found elsewhere, including fertiliser management outside of the relevant monitoring periods (Ibrahim et al., 2013).

The study area contained six hydrologically isolated plots (Figure 5.1) on a uniform slope (2% slope), that were installed in 2005. Four of the plots were utilised which had similar saturated hydraulic conductivities ($K_{sat}$) as there is a correlation between $K_{sat}$ and $NO_3^-$ (Fenton et al., 2009). Previous work at the site (Clagnan et al., 2018b) noted groundwater (> 3 m below ground level) at the site had $NO_3^-$-N concentrations between 4.7-8.1 mg $L^{-1}$. The previous study also noted that $NO_3^-$ was transferred to the slope via groundwater from a free-draining upgradient site. Subsurface drainage was installed to 1 m below ground level (bgl) using pipes and gravel, with 10 m spacing between drains. Surface runoff from each plot collected into a pipe at the bottom of the slope. The surface and subsurface pipes transported water to dedicated v-notch weirs at a downslope monitoring station. The weirs were connected to Sigma 900 Max autosamplers (Sigma, Hach Company, USA) which were calibrated using pressure transducers and the angle of the receiving weir's v-notch. The autosamplers took samples of every 500 L of runoff or discharge from January to October 2009, and from January 2018 to April 2019. The 2009 data were obtained from a previous, unpublished study. The site had piezometers installed previously at the top, middle, and bottom of the slope in each plot, to sample groundwater >3 m bgl. Water table depths were recorded daily in these piezometers using a water diver (MiniDiver, Schlumberger Water Services, Delft, Netherlands).

All sampling and analytical procedures for the 2018 and 2019 sampling years, were consistent with those of 2009. Runoff and drainage rates were automatically recorded to enable the calculation of flow-weighted concentrations of DRP (fwc-DRP) and other nutrients. Samples were filtered (0.45 µm) and analysed for DRP, $NO_3^-$, $Fe^{2+}$ and $Fe^{3+}$, $Mn^{2+}$, and $SO_4^{2-}$ using standard methods (APHA-AWWA-WEF, 2005). A synoptic national weather station was located on site measuring daily to hourly rainfall, soil moisture deficit (SMD) to 1 m, air temperature, soil temperature, and solar radiation from 2009-2019. The nearest receptor of flow was the Kildavin River, which was approximately 70 m from the drainage pipe outlets and 100-200 m from the plots themselves.

Soil topsoil samples (0-10 mm depth) were taken from spatially distributed points across the study site and analysed for: 1:300 soil to solution water extractable P designed to mimic P loss in surface runoff (McDowell and Condron, 2004); sodium-dithionite-extractable P as an estimate of P available under reducing conditions (Dithionite-P); (Jensen and Thamdrup, 1993; Loeppert and Inskeep, 1996; Psenner and Pusckso, 1988); P in Morgan's extractant (Morgan, 1941; Smith, 2020); and, Mehlich-Fe, -Mn and -P (Sims, 2009).

### 5.2.2 Data analysis

A soil-water balance was calculated using climate and soil moisture data (to 1 m bgl) using the method of Horne and Scotter (2016). This, combined with the SMD data from the weather station, indicates when soils are saturated with water past their storage capacity (*viz.* 'Saturation-excess') and runoff (including drainage) is generated. Water level data were used to show when drainage was occurring when the water table had risen to within 1 m of the soil surface. In addition to this, Clagnan et al. (2018b) clarified the net provenance of N at the site previously and showed that the artificial drainage network is connected to the field surface and is not disturbed by upwelling groundwater. Additionally, the signal of $NO_3^-$ in artificial drainage is different to that at 3 m groundwater depth. Therefore, the present study is justified in examining SMD, $NO_3^-$ concentrations, soil test P and water samples from the soil profile to approximately 1 m bgl.

The redox status of every event sampled was calculated using the method of McMahon and Chapelle (2008). Periods where $NO_3^-$ concentrations were too low to buffer the redox reaction ($NO_3^-$-N < 0.5 mg $L^{-1}$) were identified. Previous work at the site (Clagnan et al., 2018b) demonstrated that $NO_3^-$ attenuation is occurring, attributed to reduction and denitrification.

Each plot exhibited differences in runoff and drainage volumes. Therefore, to avoid these volumes skewing the data, concentrations were presented rather than yields (i.e. kg $ha^{-1}$). Flow-weighted mean concentrations were produced by dividing the sum of the product of each event-based concentration and discharge by the sum discharge of all events. Mean data for the plots were contrasted by season via an analysis of variance and post-hoc test (Tukey's Honestly Significant Difference). Correlation matrices were produced to identify significant ($p < 0.05$) associations between flow-weighted mean concentrations and climatic conditions across all events and plots.

## 5.3 Results

### 5.3.1 Site and soil characteristics

Soil chemical characteristics of the site are given in Table 5.1. The soil pH (6.0) was within range of other grazed Irish soils studied (Daly et al., 2017). The Mehlich-Fe (269 mg $kg^{-1}$) extracted from the topsoil at this site was approximately half of that from similarly poorly-drained grazed sites, but had similar or greater Mehlich-3 P and Morgan-s P concentrations (Daly et al., 2017). The degree of Mehlich-P saturation relative to P sorbing Mehlich-Fe and -Mn was 16.0%, which according to Kleinman and Sharpley (2002) was indicative of a soil that was not strongly saturated with P. However, there was a moderate amount of reducible soil Dithionite-P (38.3 mg $kg^{-1}$) in the soil compared to other Irish soils of similar Morgan- or Mehlich-3 P concentrations (Smith, 2020).

Rainfall totals in the three years of sampling were 1453 mm, 1147 mm, and 1060 mm for 2009, 2018 and 2019, respectively. Climate data from 2009 to 2019 showed mean daily rainfall was greatest in autumn (Table 5.2). The daily mean air temperature and soil temperature to 10 cm bgl were both lowest in winter and greatest in summer (Table 5.2). There were small SMDs (to 1 m bgl) in summer, autumn, and spring, but on average saturation-excess conditions (SMD >0 mm) prevailed over winter (Table 5.2, Figure 5.1). In general, over 60% of days showed saturation excess (SMD ≤0 mm) across the seasons (Table 5.2). A large SMD of > 80 mm occurred in the summer of 2018. Runoff discharge was much smaller after this than in 2009 and early 2018, and there was not consistent saturation excess until mid-October 2018 (Figure 5.2).

As stated, Clagnan et al. (2018b) showed artificial drainage to 1 m was relatively uninfluenced by groundwater. In the present study the water table in the piezometers at the top, middle and bottom of the four slopes was generally below 2 m. However, the middle and bottom slope location in plot 1 occasionally reached within 1 m of the surface between November and May each year. This plot may have been influenced by groundwater.

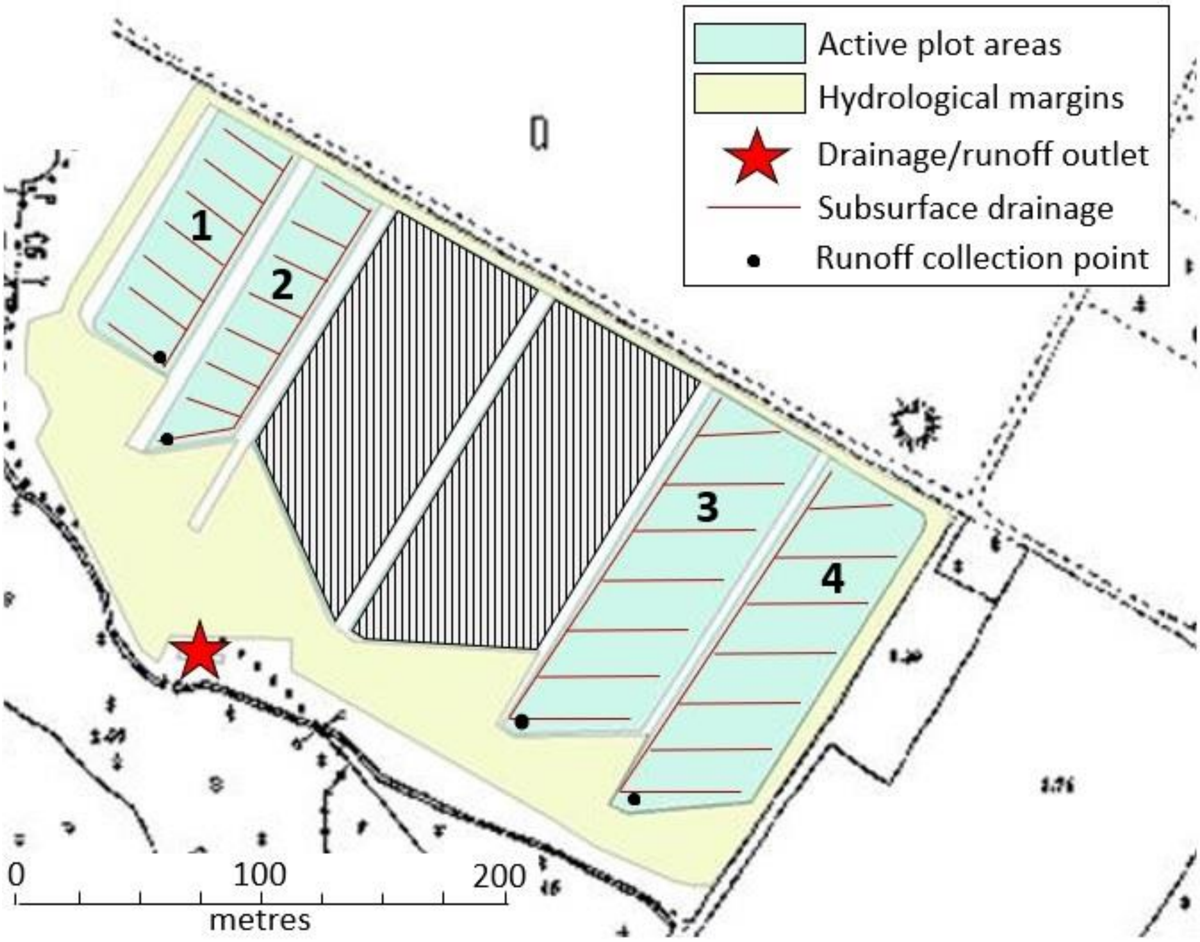

Figure 5.1 Map of the study slope in Wexford, Ireland, adapted from Ibrahim et al. (2013) Grey hashed areas indicate plots that were not monitored.

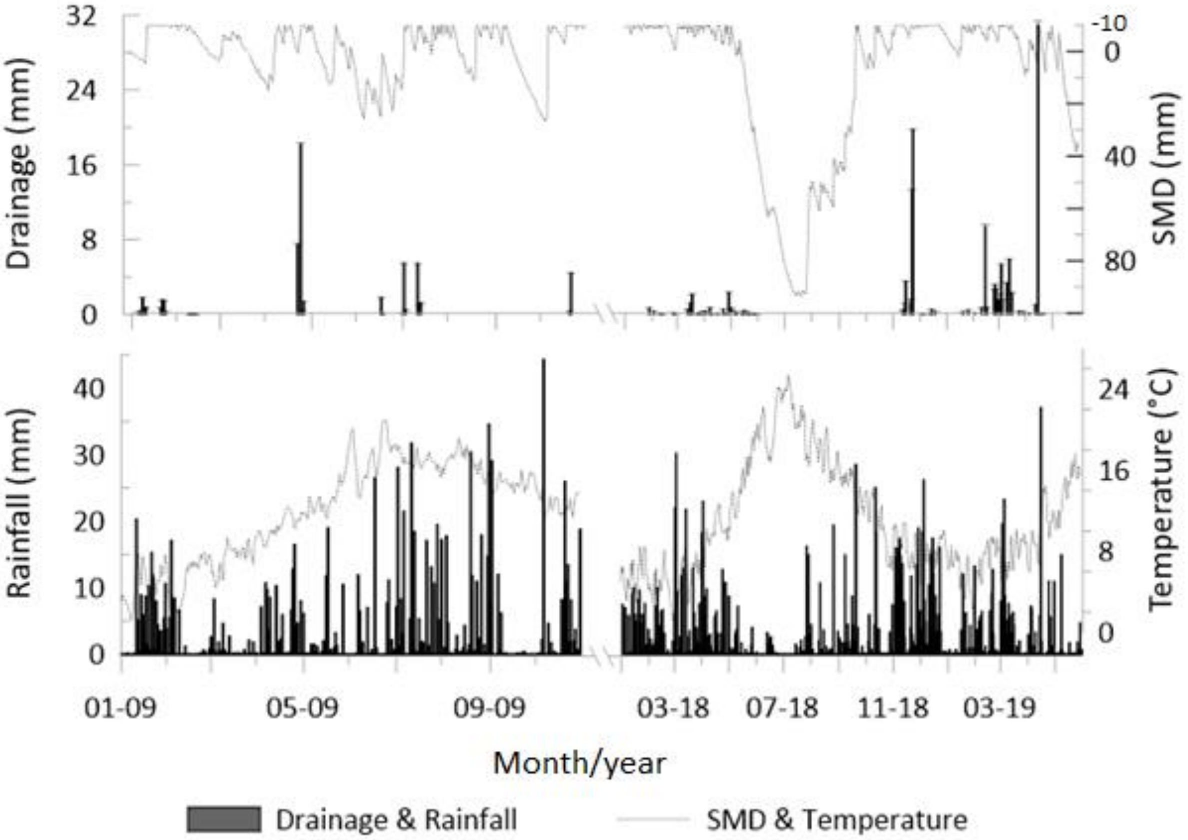

Figure 5.2 Daily data for soil moisture deficit (SMD, mm), rainfall (mm), soil temperature (°C, top 10 cm), and mean daily subsurface drainage (mm) from January to October 2009, and January 2018 to May 2019. Periods where SMD < 0 show site field capacity and saturation-excess potential. Note the x-axis break and inverted y-axis for SMD.

Table 5.1 Selected soil and farm characteristics for the experimental slope, mean (± standard error of the mean). Soil samples were from topsoil (0-75 mm depth), spatially distributed across trial site.

| Soil fertility properties | Mean |
|---|---|
| $pH_{water}$ | 6.0 (0.02) |
| WEP, mg $L^{-1}$ | 0.009 (0.0012) |
| Morgan's P, mg $L^{-1}$ | 1.75 (0.362) |
| Mehlich P, mg $kg^{-1}$ | 26.3 (2.201) |
| DPS[1], % | 16.0 (0.76) |
| Dithionite-P, mg $kg^{-1}$ | 38.3 (3.41) |
| Mehlich Mn, mg $kg^{-1}$ | 55.1 (9.97) |
| Mehlich Fe, mg $kg^{-1}$ | 269.2 (20.62) |

[1] DPS = Degree of phosphorus saturation = Mehlich-P/α(Mehlich-Fe + Mehlich-Mn) (Kleinman and Sharpley, 2002).

Table 5.2 Mean daily rainfall, soil and air temperature and soil moisture deficit (SMD) at the site (± standard error) from January 2009 to December 2019. Differences between seasons were established via an analysis of variance. Lettering indicates significant differences in means due to season, according to Tukey's Honestly Significant Difference (Tukey HSD) post hoc test.

| Season | Months | Rainfall | Soil temp | Air temp | SMD[1] | days SMD≤0 |
|---|---|---|---|---|---|---|
| | | mm | °C | °C | mm | % (n) |
| Summer | Jun-Aug | 2.7 (0.18)$^{ab}$ | 17.6 (0.07)$^{d}$ | 14.8 (0.06)$^{d}$ | 25.7 (0.75)$^{d}$ | 61 (276) |
| Autumn | Sept-Nov | 3.4 (0.21)$^{c}$ | 11.7 (0.11)$^{c}$ | 11.0 (0.11)$^{c}$ | 6.3 (0.45)$^{b}$ | 62 (283) |
| Winter | Dec-Feb | 3.3 (0.18)$^{bc}$ | 5.7 (0.07)$^{a}$ | 6.0 (0.09)$^{a}$ | -1.3 (0.14)$^{a}$ | 65 (511) |
| Spring | Mar-May | 2.2 (0.14)$^{a}$ | 10.3 (0.11)$^{b}$ | 8.8 (0.09)$^{b}$ | 9.9 (0.38)$^{c}$ | 63 (520) |
| $\boldsymbol{P}$ value | | <0.001 | <0.001 | <0.001 | <0.001 | ns |

[1] SMD<0 indicates saturation excess/waterlogging

Table 5.3 A correlation matrix for mean daily concentration (mg L$^{-1}$) and climatic data in surface runoff samples from all plots, showing the relationship between parameters[1] over the 2009, and 2018 to 2019 events.

| | Flow | DRP | Fe | Mn | $NO_3^-$-N | TP | PP | Rain | Soil temp |
|---|---|---|---|---|---|---|---|---|---|
| DRP | 0.287*** | | | | | | | | |
| Fe | -0.006 | -0.089** | | | | | | | |
| Mn | -0.120 | -0.084** | -0.005 | | | | | | |
| $NO_3^-$-N | -0.020 | -0.205*** | 0.369*** | -0.092*** | | | | | |
| TP | 0.412* | 0.932*** | -0.096* | -0.272*** | 0.053 | | | | |
| PP | 0.395* | 0.247*** | -0.001 | -0.250*** | -0.092* | 0.584*** | | | |
| Rain | 0.445*** | 0.232*** | -0.004 | -0.173*** | -0.097*** | 0.343*** | 0.319*** | | |
| Soil Temp | 0.146 | 0.148*** | 0.161*** | 0.003 | -0.150*** | 0.191*** | 0.342*** | 0.365*** | |
| SMD | -0.336* | -0.271*** | -0.089** | -0.021 | 0.250*** | -0.268*** | -0.235*** | -0.541*** | -0.324*** |

[1] DRP = Dissolved reactive phosphorus, Fe = Iron, Mn = Manganese, $NO_3$ = Nitrate, TP = Total phosphorus, PP = Particulate phosphorus, SMD = Soil moisture deficit (mm), Flow = surface runoff discharge (mm)

[2] *** < 0.001, ** < 0.01, * < 0.05

### 5.3.2 Loss of nutrients in runoff and drainage

Runoff volumes from the plots during storm events were not significantly different between seasons (Table 5.2). Mean DRP concentrations in spring and summer were an order of magnitude greater in runoff compared to drainage concentrations. Runoff DRP was significantly greater in spring ($p < 0.001$) compared to the other seasons, but this did not align with mean concentrations of redox-sensitive analytes. Mean Fe was greatest in summer, Mn was greatest in autumn and winter, and $NO_3^-$ was greatest in autumn and winter ($p < 0.001$). Particularly in summer and autumn, more than half the samples collected from each season contained nutrient concentrations indicative of a low redox potential to reduce and dissolve Mn and Fe into solution ($NO_3^-$-N <0.5 mg $L^{-1}$, Table 5.5). In instances like this where solutions appear to have enriched Mn and Fe and depleted $NO_3^-$ from reductive dissolution, events will be described as 'metal-reducing'. Events that have elevated $NO_3^-$ concentrations and minimal Mn and Fe will be described as '$NO_3^-$-reducing'. Periods of metal-reduction were paired with sustained saturation excess (SMD <0 mm), no recent N addition, and potentially minimal interaction with N-rich groundwater. In a correlation matrix of runoff nutrient concentrations, flow and climatic conditions, DRP was not positively correlated with any of the redox-sensitive nutrients, and Fe was positively correlated with $NO_3^-$-N (Table 5.3).

Mean drainage DRP concentrations were 0.01 mg $L^{-1}$ in summer and winter, 0.04 mg $L^{-1}$ in autumn, and 0.08 mg $L^{-1}$ in spring. The greatest mean Fe, Mn and $NO_3^-$ concentrations in drainage were measured in autumn (Table 5.2). In contrast, the greatest mean concentration of DRP occurred in spring, when $NO_3^-$ concentration was moderate. In a correlation matrix of all drainage data (Table 5.6), DRP concentrations were positively and significantly correlated with dissolved Fe in artificial drainage, but negatively and significantly correlated with $NO_3^-$-N. Concentrations of Fe were negatively correlated with $NO_3^-$-N and SMD.

In contrast to the runoff data, artificial drainage data suggests that, on average, there is a connection between DRP and Fe released from a waterlogged soil profile, especially when $NO_3^-$ is depleted. The seasonal patterns of Fe, Mn and $NO_3^-$ in DRP loss is supported by the proportion of artificial drainage samples that classified as likely to be metal-reducing in summer (Table 5.2), whereas the leaching and greater concentration of $NO_3^-$ in autumn, winter and spring led to them being more often classified as $NO_3^-$-reducing. This may be because the water table level at the site never reaches within 1 m bgl outside of November to

May. Therefore, in the summer to autumn period, there would be no upgradient groundwater source of $NO_3^-$-N to replenish the N supply and continue to buffer the redox reaction. However, in the winter to spring months, there may be some interaction from groundwater that could introduce new N.

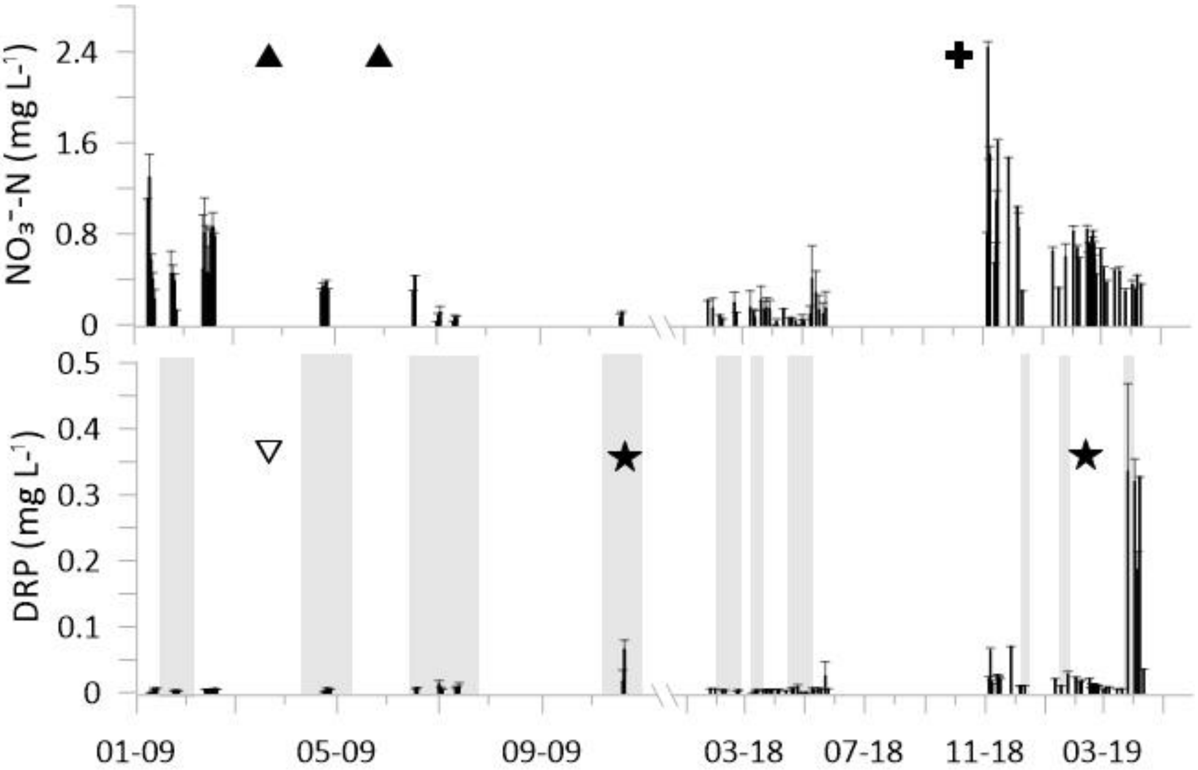

Figure 5.3 Averaged daily data for dissolved reactive phosphorus (DRP, mg $L^{-1}$) and nitrate ($NO_3^-$, mg $L^{-1}$) in drainage from January to October 2009, and January 2018 to May 2019. Note the x-axis break. Sample events that occurred under iron- and manganese-reducing conditions ($NO_3 < 0.5$ mg $L^{-1}$) are shaded in grey. Specific events (★) are explored in Figures 5.6 and 5.7 for Fe(III)-$SO_4$-reducing (Oct 2009) and $NO_3$-reducing (Feb 2019) conditions. Symbols ▲, ▽, and ✚ indicate nitrogen fertiliser, phosphorus, and slurry addition, respectively.

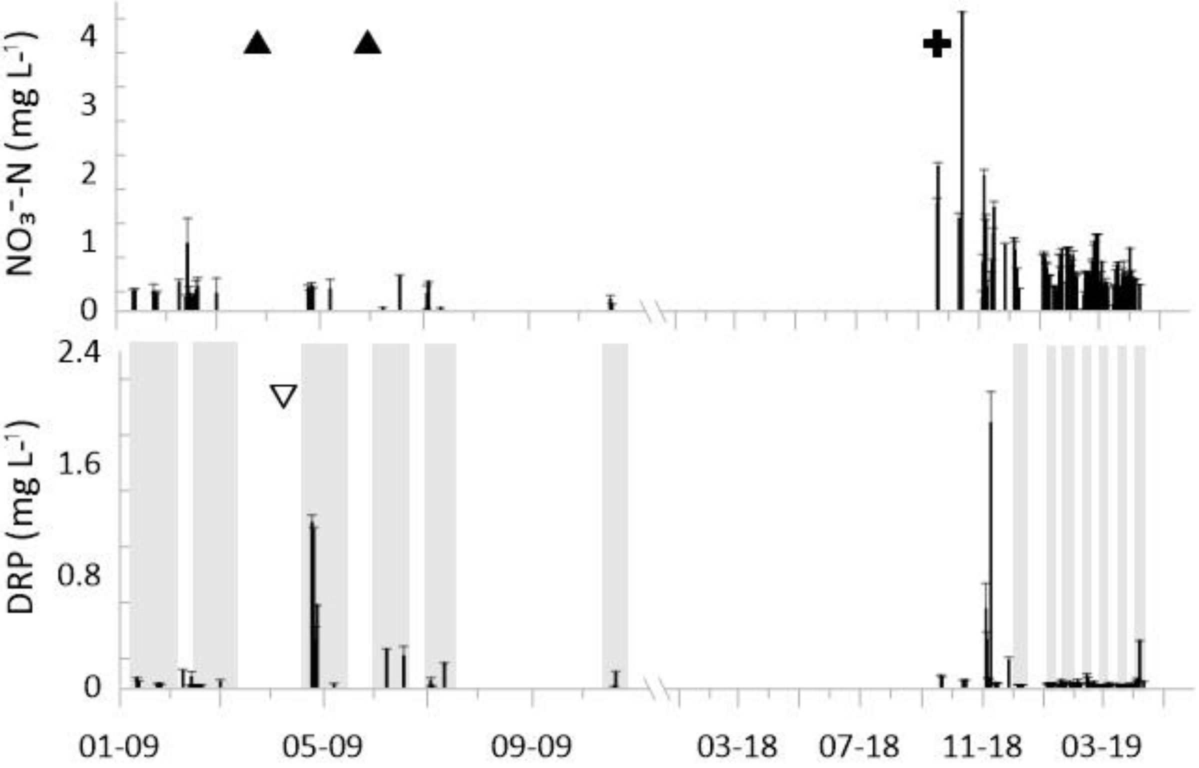

Figure 5.4 Averaged daily data for dissolved reactive phosphorus (DRP, mg L$^{-1}$) and nitrate (NO$_3^-$, mg L$^{-1}$) in surface runoff from January to October 2009, and January 2018 to May 2019. Note the x-axis break. Sample events that occurred under iron- and manganese-reducing conditions (NO$_3$ < 0.5 mg L$^{-1}$) are shaded in grey. Specific events (★) are explored in Figures 5.6 and 5.7 for Fe(III)-SO$_4$-reducing (Oct 2009) and NO$_3$-reducing (Feb 2019) conditions. Symbols ▲, ▽, and ✚ indicate nitrogen fertiliser, phosphorus, and slurry addition, respectively.

Table 5.4 Mean runoff (mm) and drainage (mm) and flow-weighted concentrations (mg L$^{-1}$, ± standard error) in surface runoff and drainage events of dissolved reactive P (DRP), iron (Fe), Manganese (Mn) and nitrate-N (NO$_3^-$-N), across all plots by season from 2009, 2018 and 2019. Differences between seasons were established via an analysis of variance. Lettering indicates significant differences in means due to season, according to Tukey's Honestly Significant Difference (Tukey HSD) post hoc test.

| Flow path/ Season | n[1] | Volume | DRP | Fe | Mn | NO$_3^-$-N |
|---|---|---|---|---|---|---|
| Surface runoff | | | | | | |
| Summer | 7 | 16.5<br>(9.55) | 0.19<br>(0.007)$^{b}$ | 0.46<br>(0.033)$^{a}$ | 0.03<br>(0.014)$^{b}$ | 0.04<br>(0.010)$^{c}$ |
| Autumn | 6 | 6.0<br>(5.92) | 0.09<br>(0.018)$^{b}$ | 0.35<br>(0.040)$^{b}$ | 0.61<br>(0.106)$^{a}$ | 0.59<br>(0.076)$^{a}$ |
| Winter | 47 | 7.8<br>(4.97) | 0.03<br>(0.003)$^{c}$ | 0.27<br>(0.022)$^{bc}$ | 0.50<br>(0.101)$^{a}$ | 0.61<br>(0.029)$^{a}$ |
| Spring | 64 | 14.0<br>(11.1) | 0.35<br>(0.030)$^{a}$ | 0.21<br>(0.014)$^{c}$ | 0.18<br>(0.060)$^{b}$ | 0.37<br>(0.001)$^{b}$ |
| ***P*** value | | ns | <0.001 | <0.001 | <0.001 | <0.001 |
| Drainage | | | | | | |
| Summer | 8 | 2.4<br>(0.64) | 0.01<br>(0.001)$^{a}$ | 0.87<br>(0.050)$^{b}$ | 0.04<br>(0.017)$^{ab}$ | 0.10<br>(0.013)$^{a}$ |
| Autumn | 11 | 4.0<br>(1.95) | 0.04<br>(0.005)$^{a}$ | 1.60<br>(0.091)$^{c}$ | 0.14<br>(0.023)$^{b}$ | 0.77<br>(0.053)$^{d}$ |
| Winter | 42 | 1.7<br>(0.34) | 0.01<br>(0.000)$^{a}$ | 0.33<br>(0.019)$^{a}$ | 0.04<br>(0.005)$^{ab}$ | 0.60<br>(0.018)$^{c}$ |
| Spring | 37 | 2.8<br>(1.24) | 0.08<br>(0.014)$^{b}$ | 0.33<br>(0.029)$^{a}$ | 0.04<br>(0.031)$^{a}$ | 0.37<br>(0.011)$^{b}$ |
| ***P*** value | | ns | <0.05 | <0.001 | <0.001 | <0.001 |

[1] n = Number of events across four plots that were averaged

Table 5.5 The number and percentage (in parentheses) of samples categorised by the concentration of redox-sensitive analytes in solution. Samples were divided between those with increased nitrate concentrations ($NO_3^-$ > 0.5 mg $L^{-1}$), and those that had low $NO_3^-$ (<0.5 mg $L^{-1}$) and increased iron (Fe) and manganese (Mn) oxides.

| Season | Samples with $NO_3^-$-N > 0.5 mg $L^{-1}$ | Samples with $NO_3^-$-N < 0.5 mg $L^{-1}$, Fe/Mn > 0.1 mg $L^{-1}$ * | Number of samples per season |
|---|---|---|---|
| Drainage | | | |
| Summer | 0 (0) | 98 (100) | 98 |
| Autumn | 120 (48) | 131 (52) | 251 |
| Winter | 234 (56) | 185 (44) | 419 |
| Spring | 499 (60) | 337 (40) | 836 |
| Runoff | | | |
| Summer | 31 (7) | 400 (93) | 431 |
| Autumn | 39 (14) | 230 (86) | 269 |
| Winter | 171 (23) | 566 (77) | 737 |
| Spring | 231 (31) | 521 (69) | 752 |

*Thresholds indicated by McMahon and Chapelle (2008)

Table 5.6 A correlation matrix for mean daily concentration (mg $L^{-1}$) and climatic data in drainage samples from all plots, showing the relationship between parameters[1] over the 2009, and 2018 to 2019 events

| | Flow | DRP | Fe | Mn | $NO_3^-$-N | TP | PP | Rain | Soil temp |
|---|---|---|---|---|---|---|---|---|---|
| DRP | -0.067 | | | | | | | | |
| Fe | 0.142 | 0.215*** | | | | | | | |
| Mn | -0.111 | -0.005 | -0.125* | | | | | | |
| $NO_3^-$-N | 0.082* | -0.111*** | -0.361*** | -0.140*** | | | | | |
| TP | 0.915*** | -0.057 | 0.306 | -0.134 | -0.007 | | | | |
| PP | 0.912*** | -0.069 | 0.299 | -0.146 | -0.004 | 0.999*** | | | |
| Rain | 0.146 | -0.080 | 0.255* | -0.098 | -0.311*** | 0.217 | 0.208 | | |
| Soil Temp | 0.094 | -0.041 | 0.241* | 0.295** | -0.297*** | 0.139 | 0.136 | 0.382*** | |
| SMD | -0.158 | 0.171*** | -0.302** | 0.425*** | 0.075* | -0.289 | -0.277 | -0.617*** | 0.147 |

[1] DRP = Dissolved reactive phosphorus, Fe = Iron, Mn = Manganese, $NO_3$-N = Nitrate-nitrogen, TP = Total phosphorus, PP = Particulate phosphorus, SMD = Soil moisture deficit (mm), Flow = surface runoff discharge (mm)

[2] *** < 0.001, ** < 0.01, * < 0.05

### 5.3.3 Concentrations in specific storm events

Concentrations of DRP determined in runoff and drainage over 2009, 2018 and 2019 show no clear pattern alongside site climatic data (Figures 5.4-5.5), which aligns with the lack of significant seasonal differences in runoff, drainage and % SMD days (Table 5.2-5.3). However, more valuable information is gained for drainage when events are examined individually relative to management and soil redox conditions. Applications of P and nitrogen (N) fertiliser are indicated by an up and down triangle, respectively (Fig. 5.4 and 5.5). An increase in DRP concentration in surface runoff occurred following the application of P fertiliser in May 2009. No increases were evident following the application of slurry in drainage or surface runoff until the slurry-N was depleted (Figure 5.5). Concentrations of $NO_3^-$ followed a general pattern of leaching and potential $NO_3^-$ attenuation via denitrification (Clagnan et al., 2018b) during the winter and spring drainage events. Nitrate concentrations appeared to be depleted during significant DRP drainage losses, and all DRP concentrations greater than 0.1 mg $L^{-1}$ in drainage occurred when concentrations were less than 1 mg $NO_3^-$-N $L^{-1}$. This warranted further investigation on an event-by-event basis.

Two drainage sample events were isolated to identify the behaviour of DRP, Fe, Mn and $NO_3^-$ concentrations over the course of the events. The first occurred in an event classed as metal-reducing (Figure 5.6), while the second had excess $NO_3^-$-N in drainage (> 0.5 mg $L^{-1}$) (Figure 5.7). Fire 5.6 demonstrates an initial Mn-reducing process and an increase in solution Fe as the storm event progresses. Solution DRP increases as solution Fe increases. At the end of the rainfall event, $NO_3^-$ begins to increase, but still remains < 0.5 mg $L^{-1}$, below the $NO_3^-$ buffer threshold. In the second event (Figure 5.7), $NO_3^-$ is consistently > 0.5 mg $L^{-1}$, and the only period where there is a large change in DRP, Fe and Mn is when $NO_3^-$ concentrations in solution are halved towards the end of the event. Concentrations of Fe are approximately half and DRP an order of magnitude smaller in this event than in the metal-reducing event.

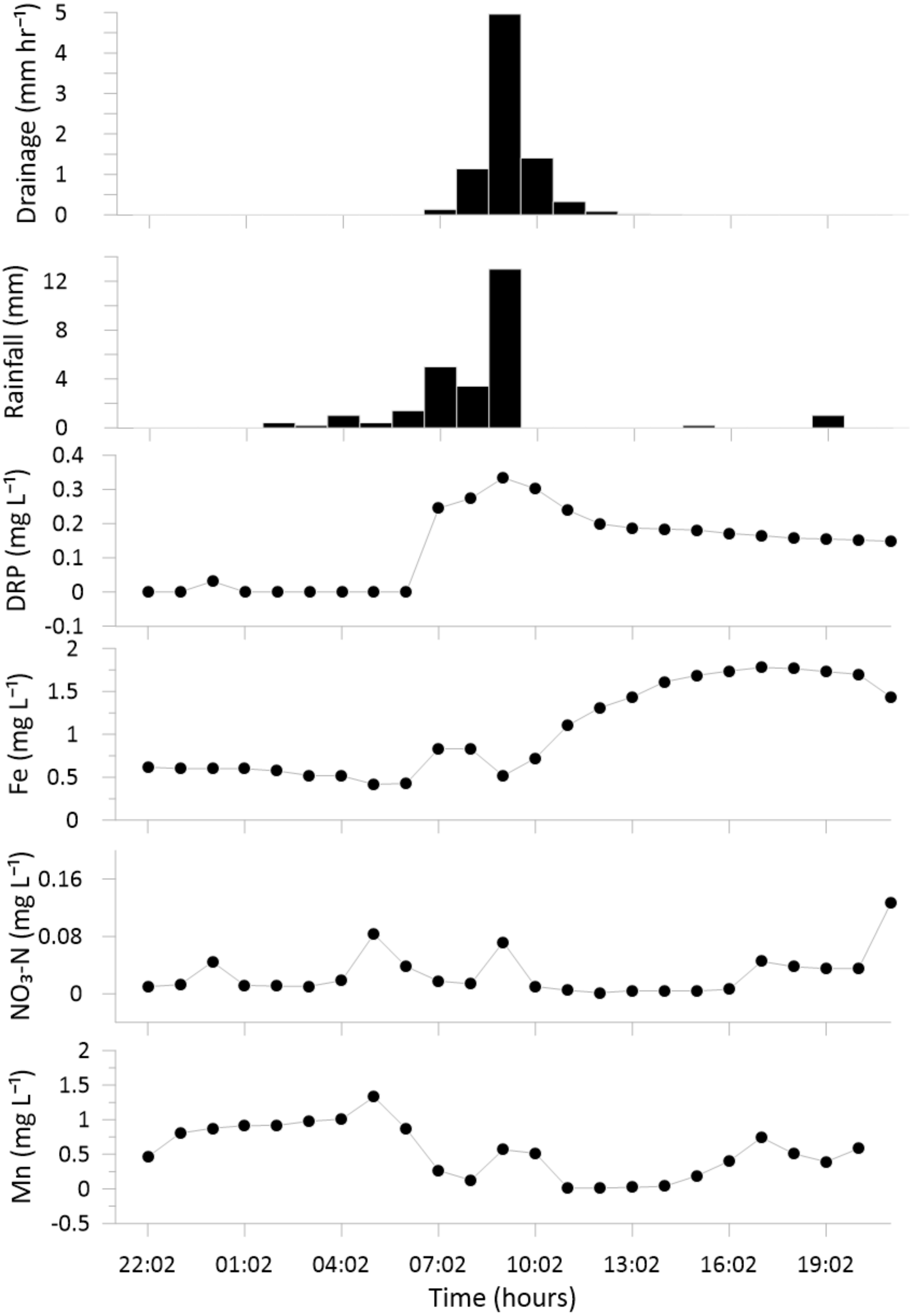

Figure 5.4 An intensively sampled event from Plot 2 in October 2009, where redox-sensitive components were characterised as 'metal-reducing' (McMahon and Chapelle, 2008).

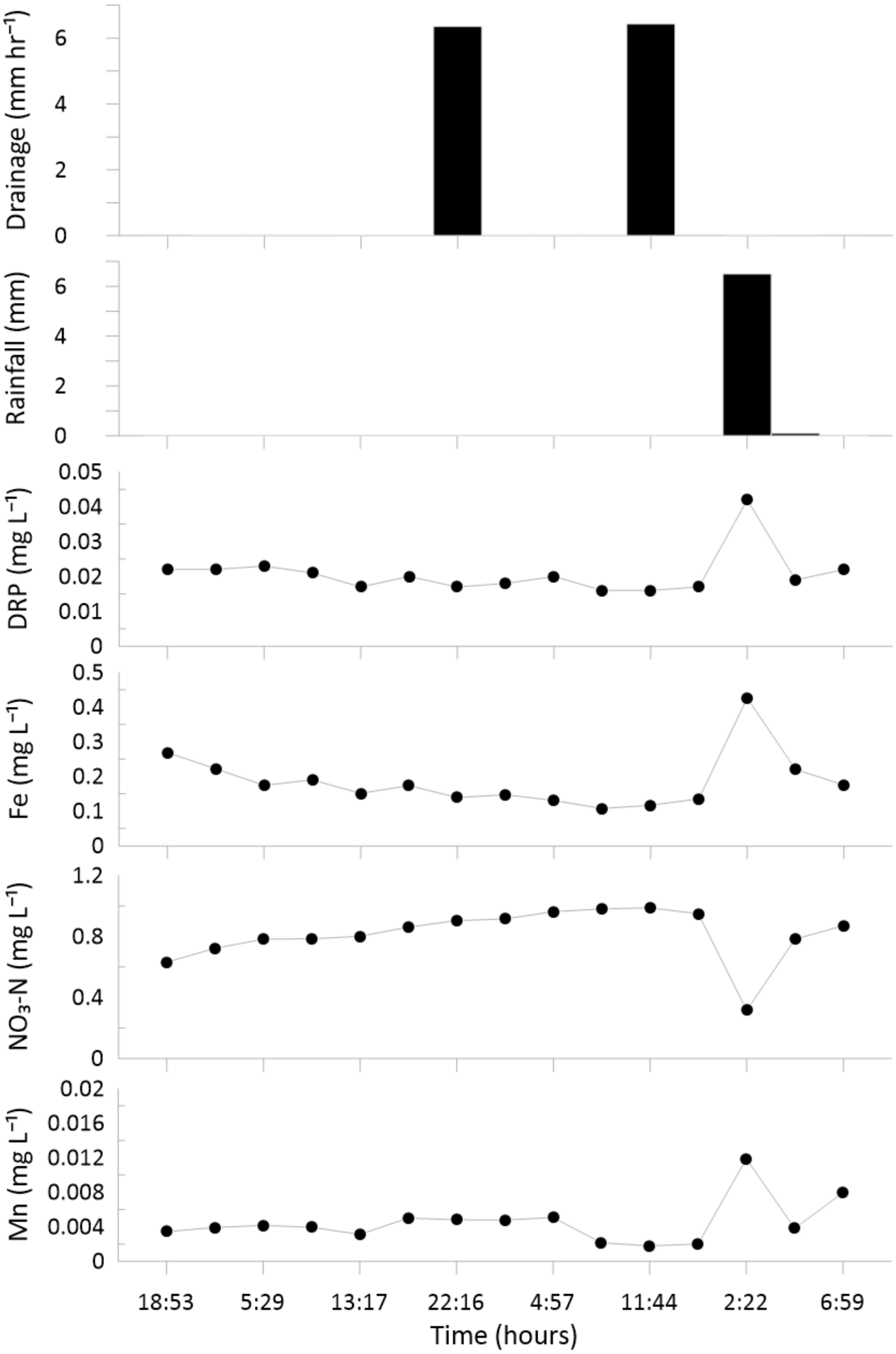

Figure 5.5 An intensively sampled event from Plot 1 in February 2019, where redox-sensitive components were characterised as ‘$NO_3$-reducing’ (McMahon and Chapelle, 2008).

## 5.4 Discussion

### 5.4.1 Nutrient characteristics in surface runoff

Concentrations of DRP in surface runoff were an order of magnitude greater soon after P fertiliser and slurry application than in other events. This coincides with a period of high P solubility, where recently applied P could be lost in surface runoff before it is adsorbed to the soil (McDowell and Catto, 2005). The relationships between DRP, Fe and Mn in surface runoff were contrary to the trend demonstrated in drainage. While apparent metal-reduction was seen in a greater proportion of surface runoff samples, those samples also showed a negative correlation between DRP, Fe and Mn, even during periods of sustained waterlogging and where events were classed as metal-reducing by their chemical make-up. Thus, it is likely that the increase in Fe and Mn in surface runoff during saturation-excess generated runoff periods may be connected to soil profile reductive dissolution, but the additional topsoil P released into surface runoff may mask this relationship. This is not unexpected, as runoff constitutes a mix of older water that may carry a metal-reducing chemical signature, but also new oxic water that has interacted and derived P from chemical and physical processes by interaction with a thin layer of topsoil (Ahuja and Lehman, 1983). Another explanation is that colloidal P and Fe could be resulting in an overestimation of solution Fe and P in the present study. A study by Zhang and Oldham (2001) showed that particles are mobilised, and colloidal Fe and P are seen in increased concentrations, which affects final estimates. A method to identify the source of P and Fe in runoff would be necessary to explain the effects of reductive dissolution and on saturation-excess generated runoff.

### 5.4.2 Nutrient characteristics in artificial drainage output

Drainage DRP concentrations from the present site in summer and winter (0.01 mg DRP $L^{-1}$) were comparable to another grazed Irish site with similar Mehlich-P concentrations (Daly et al., 2017). However, the mean drainage concentration seen in autumn (0.04 mg $L^{-1}$) was enhanced and comparable to losses from another Irish site with high legacy P (Valbuena-Parralejo et al., 2019). This implies that waterlogging and redox processes induce DRP losses that are greater than indicated by simple soil tests. Although as mentioned above, Dithionite-P, designed to assess reducible-P was enriched in this soil.

The relationship between DRP and Fe release into drainage was positive and significant, and both were negatively correlated with $NO_3^-$ (Table 5.6). This concurs with other studies (Ann et al., 2000; Surridge et al., 2007b; Zak and Gelbrecht, 2007). There was no significant relationship with Mn, which is likely because Mn can begin to reduce in the presence of $NO_3^-$ (Grybos et al., 2007). Events collected after fertiliser-N addition did not generally meet the requirements for metal-reduction until $NO_3^-$ contributions to solution were depleted. This may have been due to fertiliser-derived N becoming depleted via denitrification - which was not measured in the present study, but was proven in previous work (Clagnan et al., 2018b) - or its removal via surface runoff or drainage. After this point, concentrations of Fe and DRP increased (Figures 5.4-5.7). Previous work at the site has shown that the soils have a significant denitrification capacity above the drainage system, or potentially dissimilatory $NO_3^-$-reduction to ammonium (Clagnan et al., 2018b). However, this process was overwhelmed and disrupted by N fertiliser applications inputs in March and May 2009 that led to increases in $NO_3^-$ in drainage (> 0.5 mg $L^{-1}$) that buffered reduction until July 2009 (Grybos et al., 2007; Surridge et al., 2007b; Young and Ross, 2018). A similar buffer mechanism was likely after the slurry spreading in late October 2018, which was only sufficiently depleted the next month.

There was a significant correlation between decreasing soil moisture deficit (i.e. becoming more waterlogged) and Fe, and increasing moisture deficit and $NO_3^-$, which indicated that the state of DRP and the redox-sensitive components in drainage were related to the level of waterlogging and frequency of the soil. As this site was waterlogged for at least half of every season, its propensity to become metal-reducing, provided $NO_3^-$ is depleted, is high. However, the soil profile experienced an unusually high moisture deficit in the summer of 2018 (Fig. 5.4). The persistence of $NO_3^-$ at the site for a month could have been caused by drought impairing the capacity of soil microbial biomass to utilise N (Gu et al., 2018) or because more oxygen was penetrating into the soil profile (Stirling et al., 2020). Additionally, P was released in larger quantities during this month, but was greater relative to Fe release than after the first waterlogging event and was accompanied by high levels of $NO_3^-$. This could be explained by P released from microbial cell lysis during drying, osmotic shock and rewetting, especially as biomass may not have adapted to drought conditions at this site (Blackwell et al., 2009; Butterly et al., 2009; Gu et al., 2018).

### 5.4.3 Implications for management and the environment

The mean concentration of DRP over all samples (0.04 ± 0.005 mg DRP $L^{-1}$), particularly during autumn and spring were greater than a commonly reported eutrophication threshold of 0.03

mg DRP $L^{-1}$ (Trodd and O'Boyle, 2018). This was despite low soil P concentrations (Table 5.1) and P fertiliser inputs. Since previous work has shown that P desorption increases with increasing P saturation (Pal, 2011), it is clear that in this system with low nutrient inputs, other properties such as redox potential need to be taken into account to minimise P loss.

In terms of influencing DRP losses, the data showed that the combination of waterlogging and low $NO_3^-$ were more important than seasonality. Without the buffering influence of $NO_3^-$ in a soil profile, waterlogging could lower redox potential and release DRP from Fe and Mn (Surridge et al., 2007b). The present study suggests that there is a point at which $NO_3^-$ is too low and DRP loss to waterways increases as a result. All DRP concentrations > 0.1 mg $L^{-1}$ in drainage occurred when $NO_3^-$-N concentrations were < 0.5 mg $L^{-1}$. Finding this point in a range of P saturation, waterlogging vulnerability, soil textures, organic carbon availability, and temperature will improve the ability to restrict N and P loss (Heiberg et al., 2010; Lair et al., 2009; Plach et al., 2019; Prem et al., 2014).

The sites experience frequent waterlogging year-round, results may differ in sites with more defined seasonal differences. The knowledge of local management practices, weather, and the likelihood of waterlogging is therefore critical to mitigating DRP losses. Common strategies for minimising P losses from soils include decreasing soil Olsen P and/or utilising crops that grow well on low P levels (Morton and Roberts, 1999). However, the study site was already below soil test P concentrations considered optimal for pasture production (Wall and Plunkett, 2016) and according to Kleinman and Sharpley (2002) had a low degree of P saturation (Table 5.1). Therefore, the focus should be on improving the efficiency of artificial drainage, provided this does not increase P losses (Monaghan et al., 2016). Alternative methods of interrupting the connectivity between the waterlogged paddock and receiving water bodies could also be explored. For instance, controlled drainage can lower P losses by encouraging sediment to deposit, but can also increase DRP losses via reductive dissolution (Sunohara et al., 2015). Some work has also looked at routing drainage water through P-sorbing material, but those containing Fe will be discounted in favour of those containing less P-sorptive Ca-materials (Ballantine and Tanner, 2010). Failing this, if a site is deemed particularly wet and P leaky, it may be better to retire the area than continue to farm it.

## 5.5 Conclusions

This study highlighted that soil profile waterlogging and low $NO_3^-$ increase P loss from the soil and into drainage, potentially via reductive dissolution. Areas that are prone to frequent waterlogging and lateral flow could exhibit increased P loss to receiving waterways under reducing conditions. If such areas have moderate P levels and are managed to keep N losses very low, P losses may be exacerbated. The present study highlights the importance of having local knowledge of soil behaviour and waterlogging throughout the year, in order to minimise the potential for P loss via fertiliser and grazing management. Otherwise, it highlights a need to introduce or improvement of artificial drainage systems to minimise the likelihood of saturation events in a soil profile.

# Chapter 6

# General Discussion & Conclusions

## 6.1 Summary of results and implications for P loss management

The overall hypothesis for this research was that anaerobic conditions in soils will contribute significantly to total annual phosphorus (P) loads in a catchment. Following a literature review, four main areas were highlighted as being necessary to investigate in-depth regarding the influence of anaerobia and reduction on P release. The main aim of the thesis was to investigate and ascertain the importance of P release associated with the reductive dissolution of Mn- and Fe-oxides in the soil, and how this might affect overall loads of P being lost to waterways. Specific objectives were prepared to individually study this process in three areas: in laboratory conditions; in the field at the plot scale; and from the field in discharge. These were intended to confirm that the hypothesis that reducing/anaerobic conditions increase P release, should be integrated into current critical source area models and used to inform develop potential mitigation strategies.

Objective 1: Quantify the potentially reducible-P component in the lab for a range of stored soils

Models and management to decrease losses increasingly focus on P that is available and transported from areas in the landscape that are regularly saturated – and periodically anaerobic. However, current models use soil tests conducted in oxic conditions, which may not represent anaerobic conditions. The water extractable P (WEP) and sodium-bicarbonate-dithionite extractable P (Dithionite-P) tests were developed to predict P that is available in the short- and long-term, respectively. Using archived soils from New Zealand and Ireland, it was confirmed that Anoxic WEP and Dithionite-P varied by soil order and land use, and that Anoxic WEP was greater than Oxic WEP, which showed the short-term impact of soil anoxia on P release. Fluvisols, Gleysols and Luvisols were found to be particularly enriched in Anoxic WEP and Dithionite owing to their periodic saturation. Models predicting Anoxic WEP and Dithionite-P at the 1:50,000 scale in New Zealand found relatively small proportions of agricultural land predicted to have Dithionite-P >85 mg $kg^{-1}$ (31%) or Anoxic WEP > 0.291 mg $L^{-1}$ (3%).

Objective 2: Determine if redox reflects changes in P with attention to the time of inundation and temperature

Samples from soil cores taken to approximately 2.5 m depth were analysed for Anoxic WEP and Dithionite-P. Vertical distributions of WEP and Dithionite-P concentrations showed that the former remained the same with depth, but the latter increased with depth. Therefore, this demonstrated disparity between the behaviour of normal WEP and the more potentially-reducible P represented by Dithionite-P. Three grassland soils (clay, silt and sandy loam textures) were saturated and incubated for 24 hours to determine if the mean concentration and release rate of dissolved reactive P (DRP) into water was exacerbated by superphosphate fertiliser (varying from 10 to 60 kg P ha-$^{1}$ yr-$^{1}$), warming temperatures (3 v 18 $^{o}$C) and anoxia. The mean DRP concentration and its rate of release increased with fertiliser application, temperature and in two soils, anoxic conditions - commensurate with the depletion of $NO_3^-$ and the reductive dissolution of Fe and Mn. The enhanced release of P during anoxia was complete within 24 hours. The results identify late-winter to spring as the riskiest season for P losses owing to wet soil conditions, warmer temperatures, and low soil $NO_3^-$ concentrations.

Objective 3: Observe trends of P  and Fe loss in saturated field conditions through different seasons and storm events, and assess the role of redox in loss

It was hypothesized that single rainfall events in wet winter-spring conditions could cause saturation over a fragipan or in a poorly drained soil and cause subsurface P concentrations to increase via reductive dissolution. Also, dissolution – being microbially-mediated – would be buffered by the presence of $NO_3^-$. Unsaturated zone monitoring from May to September, in the years 2017 and 2019, showed that events in July and August in 2017 and 2019 resulted in reducing conditions (Fe(III)/sulphate-reducing) and up to 77% and 96% greater P and Fe release, respectively. In an additional experiment in 2019, 100-mm of flood irrigation was applied, together with 10 mg $NO_3^{-}$–nitrogen (N) as potassium $NO_3^-$ and carbon as glucose was injected into half the cups at the site. The other cups received no N. Cups treated with N yielded up to 0.02 mg L-1 DRP and 0.05 mg L-1 less Fe than the no-N cups. A laboratory incubation of soils from the site confirmed that $NO_3^-$inhibited P release.

Objective 4: Determine the role of redox in connecting P and Fe release in soil water, to drainage and runoff through different seasons and storm events.

Dissolved reactive phosphorus (DRP) loss from agricultural soil can degrade surface water quality. Shallow subsurface pathways can dominate P losses in grassland soils especially in wetter months when waterlogging can be common. Subsurface drainage at 1 m and surface runoff was collected from four hydrologically isolated plots. Artificial drainage accounted for 89% of discharge. Water samples were analysed for DRP and redox-sensitive parameters (i.e. Fe, Mn, and $NO_3^-$). Simple linear regression and correlation matrices showed positive relationships between DRP, Fe and soil moisture excess, and negative relationships between these three factors and $NO_3^-$ concentrations in drainage. The data indicate that waterlogging and low $NO_3^-$ dictate the release of P in drainage, potentially via reductive dissolution. The relationship between DRP and metal release was less obvious in surface runoff, as nutrients gathered from P-rich topsoil camoflaged redox reactions. Having a high P/low nitrogen system, particularly in sites that are prone to waterlogging may exacerbate P release into waterways in the future.

## 6.2 Implications for P loss management

### 6.2.1 Predicting redox-sensitive P loss

The difference between P released from anoxic and oxic conditions in Chapters 4 and 5 show that normal oxic WEP tests are inaccurate for predicting P losses from soils that are often saturated. Data from Chapter 4 indicates that there may be a short-term store of redox-sensitive P (i.e. Anoxic WEP) that is immediately affected by saturation, and a long-term store of P (i.e. Dithionite-P) that would be slowly affected by cyclical saturation. Therefore, a better estimate of risk may incorporate P availability via Anoxic WEP in the short-term and Dithionite-P in the long-term. The models presented in Chapter 4 could be used to inform future modelling and decision support tools designed to aid management at a catchment scale, whether by predicting concentrations using proxy soil tests with moderate confidence ($R^2 >$ 50%), or by conducting the proposed soil tests at the location for better accuracy.

As the accumulation of Anoxic WEP and Dithionite-P appears to generally relate to soil drainage class, it would be important for farm managers to have in-depth knowledge of saturated areas and their behaviour throughout the year. However, if management requires detailed knowledge of saturated areas it may be worth the additional time and resources to measure Anoxic WEP than predict it. Conducting the proposed soil tests is recommended to calibrate the model to the specific location to overcome error, if robust data is lacking, or the scale of the exercise is small/fine (e.g. at the farm scale). Having finer scale data will help to improve the isolation of critical source areas of P loss due to saturated conditions and the targeting of strategies to mitigate loss.

### 6.2.2 Rapidity of reduction reaction

The incubation experiment in Chapter 5 and 6 shows that an aerobic and anaerobic environment can cause differences in DRP release into solution. In the laboratory incubation in Chapter 5, the reaction could occur within 60 minutes, and reaction rates plateaued within 24 hours. In the field experiment in Chapter 6, saturation also caused a significant difference in DRP release within 24 hours. Therefore, this suggests that a single rainfall event that saturates the soil could cause a reductive dissolution reaction and significant P release into solution. Therefore, P loss could occur relatively soon after saturation is reached, and anticipated periods of saturation that occur at certain times of year could be highlighted as periods of expected P vulnerability.

### 6.2.3 Risky periods for P loss

The findings of this study indicate that high soil profile saturation, low $NO_3^-$, and increased temperature induce P release, potentially via reductive dissolution. Without the buffering influence of $NO_3^-$ in a soil profile, anaerobic conditions caused by inundation could cause a soil profile to become Fe- and Mn-reducing and release associated P. Based on the results of the incubation (Chapter 5) and field studies (Chapters 6 and 7), the period of greatest risk is likely to be when saturation (i.e. anaerobia and reduction) overlaps with increasing temperatures.

These conclusions identify late winter to spring as risky periods for P loss, due to the combination of: existing moisture; warmer temperatures; minimal rainfall quantities required to saturate the soil profile; and, $NO_3^-$ is likely to be depleted via leaching from the soil. This again highlights why it is important to understand where saturation occurs on-site. For instance: in typically poorly-drained soils; in low-lying areas where flow from upslope would accumulate; or on soils over poorly-permeable layers (e.g. the site used in Chapter 6).

Additionally, as redox-sensitive P release is connected to $NO_3$ and saturation, the results call into question the safety of accumulated P in riparian zones or buffer areas adjacent to water ways. If accumulated P is in a form that is vulnerable in the short term or the long-term (e.g. Dithionite-P), this thesis would suggest that buffer areas that have low $NO_3^-$ during risky periods (i.e. high temperature, low oxygen) may be a potential source of P to waterways.

## 6.3 Mitigation

A year-round strategy to reduce P losses via reductive dissolution would be to decrease Olsen P (Morton and Roberts, 1999) and/or switch to a land use or crop types that produces well on reduced P availability, such as certain ryegrass cultivars (McDowell and Cosgrove, 2016).

The results of Chapters 5 and 6 show that P release may relate to soil N concentrations, and that $NO_3^-$ can be a buffer for the reductive dissolution of P in a normal agricultural system. However, this may not be a reliable mitigation strategy, as the costs of introducing excessive N could outweigh the benefits of reducing P. However, future research could involve investigating whether there is a N/P ratio optimum to minimise losses overall.

As spring has been highlighted as a high-risk period, mitigation methods specific to this period could also be used to minimise P losses. For instance, land managers could avoid grazing or P fertiliser application to saturated soil (Smith et al., 2016), or specifically avoid areas that are known to become saturated during this time (e.g. low lying areas or gullies). However, this would require good knowledge of the landscape and good farm management. For instance, if it is decided animals are to be grazed on a less obviously saturated paddock, it is important to know whether this paddock may have direct connectivity to surface water or other such characteristics that may represent another conduit for P loss. If the proposed equations were developed further and integrated into critical source area models, the models would be useful to identify hotspots in the landscape that can be targeted with mitigation measures, and areas that are not as risky and could be used during the late-winter to spring period.

If it is viable or economical to do so, artificial drainage systems could be redesigned and improved to maximise drainage and avoid saturated conditions. However, such systems could end up losing the same load of P by draining a larger amount of dilute water. In order to decrease the load effectively systems could be designed to intercept and filter out P in drainage water by, for example, lowering the soil P through inversion tillage above the main perforated pipe or using a highly P-sorptive backfill (McDowell et al., 2008).

## 6.4 Future Research Priorities

Based on the presented findings and potential changes, the following future steps are recommended;

### 6.4.1 Model refinement

The model presented in Chapter 4 contains errors, and it is recommended that manual testing should be conducted using the soil tests presented in that study in order to overcome to error or to calibrate the model for better accuracy. It would be beneficial to develop the models for Dithionite-P and Anoxic WEP further in order to integrate them into current critical source area management models. From this, it would be necessary to establish whether these two new tests improve the accuracy of such models.

### 6.4.2 Relevance of Dithionite-P and Anoxic WEP

The importance of Dithionite-P and Anoxic WEP to predictions and losses needs to be explored in a range of environments and settings, in order to decrease error and better identify problem areas. The importance of soil type on the prediction of Dithionite-P in Chapter 4 and the incubations in Chapter 5 showed that soil type, texture and soil chemistry play an important role in P vulnerability and Dithionite-P accumulation. Therefore, it would be beneficial to expand the investigation to areas such as riparian zones and monitor their release of P at different times of the year, and their influence on surface water concentrations.

### 6.4.3 Nitrate buffering

The behaviour of Fe and Mn in relation to N and P fluctuations are not often monitored, so it cannot be said whether these studies are examples of $NO_3^-$ buffering reductive dissolution. Therefore, it is necessary to carry out future experiments using different rates of N, and monitor its influence on the reductive dissolution of metal-oxides and associated P. This would help to understand and avoid the point at which low N and P enrichment causes saturation, reductive dissolution, and loss to P-limited surface waters. Additionally, it would be necessary to study the relationship between N and DRP release under a range of soil types, management conditions, and environments. This is necessary, as the incubation experiment in Chapter 5 showed that not all soil textures and chemistries react at the same rate to anaerobic conditions. The outcomes of this could improve knowledge on the consequences of changing N management and surpluses and their influence on biogeochemical N cycling.

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