Phosphorus Responses to Soil Moisture in Southern Ontario Agricultural Soil

by

Stephanie Mary-Lynne Higgins

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Agricultural landscapes are known to increase phosphorus (P) losses to waterways, contributing to the eutrophication of freshwater surface water bodies. In cold agricultural regions, the nongrowing season drives annual P transport and discharge. Previous research has focused on discharge from fields and watersheds to understand P dynamics in response to hydroclimatic events such as snowmelt and rain storms. Although P supply in soils has been considered a dominant mechanism driving P runoff, the dynamic nature of this supply on an annual basis in response to climate drivers is poorly understood. The goal of this thesis is to determine climatic (seasonal, moisture and temperature) controls on the supply of soluble P in agricultural soils. Two experiments were set up: one in a field setting and the other in a lab setting. The field study involved a snow-manipulation experiment in an agricultural field, in which soil P pools and net transformation rates were quantified under snow and limited-snow conditions. The lab experiment explored the impacts of frost severity, frost duration, frost cycle number and moisture addition on soil concentrations of water-extractable soluble reactive P (SRP), total dissolved P (TDP) and Olsen P, microbial biomass P, aggregate stability, and concentrations of SRP, TDP and TP (total phosphorus) in leachate draining from cores. In both studies, frost magnitude did not significantly impact soil P fractions or supply. Although soil water extractable P (WEP) was greater during the non-growing season than summer, this was not impacted by increased frost due to the removal of snow cover. The lab study also showed that frost magnitude did not impact P supply; however, both frost duration and moisture additions appeared to affect P supply. Water extractable P was positively related to moisture content in both experiments. An improved understanding of climate drivers on P cycling is needed in light of climate change. This thesis suggests that the supply of P may be impacted by a changing climate, but more due to moisture shifts rather than temperature.

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Chapter 1
Introduction and Problem Statement

Eutrophic conditions in freshwater are defined by the high concentration of nutrients, particularly phosphorus (P) and nitrogen (N) (Dodds & Smith, 2016; Wurtsbaugh et al., 2019; Withers et al., 2014) causing increased algal blooms and hypoxic conditions (Scavia et al., 2014; Watson et al., 2016). Ultimately, eutrophic conditions cause changes to ecosystem productivity, which changes predator-prey body-mass ratios, which leads to instability in the food web and extinctions (Binzer et al., 2015) due to the 'paradox of enrichment' (Rosenzweig, 1971; Binzer et al., 2015, Rip & McCann, 2011). Phosphorus has long been connected to algal blooms in freshwater with strong evidence that reduction in P alone can reduce eutrophic conditions (Schindler et al., 2016). While Lake Erie has historically found success lowering total P (TP), presently Lake Erie is facing increased external soluble reactive P (SRP) loading from nonpoint sources (Baker et al., 2017). As SRP is more bioavailable, there has been increased algal blooms despite the fact that TP decreased for a period (Baker et al., 2014). Consequently, reductions in SRP entering Lake Erie are necessary.

The framework for understanding nutrient dynamics is shifting to better synthesize our previous conceptual understanding of nutrient mobilization. Elevated rates of nutrient movement or cycling have been linked to "hot spots" and "hot moments" (McClain et al., 2002); however, the ecosystem control point (Bernhardt et al., 2017) framework enables the consideration of both spatial and temporal processes as a singularity and might grant a holistic understanding of nutrient dynamics. When dominant mechanisms for P flow in a system are understood, BMPs can address control points within ecosystems and prevent eutrophication.
Given that nutrient mobilization is linked to both *supply* and *transport* processes, an improved understanding of P dynamics in soil and runoff (both small- and large-scale) is one component that is essential to reducing P in runoff. Soil test P has been found to correlate to runoff P in small-scale core studies (Pote et al. 1996, Dougherty et al., 2011; Sharpley & Kleinman, 2003), but also at the field scale (Plach et al., 2018a; Pease et al., 2018; Duncan et al., 2017). Greater soil test P (STP) has been linked to agricultural landuse, (Kim et al., 2016; Irvine et al., 2019; Smil, 2000) considering soil test P (STP) concentrations increase in time when P is added in

surplus to crop needs leading to legacy P concentrations (Bennett et al., 2001, Kleinman et al., 2011; Sharpley et al., 2013). To reduce P concentrations, best management practices (BMPs) and farmer involvement are needed (Scavia et al., 2014; Watson et al., 2016); however, the specific environmental controls of soil P to runoff P are less well-understood.

With regards to transport processes, soil moisture plays a dominant role in TP and SRP export. The consistent time for TP and SRP transport is connected to snowmelt in midlatitude areas (Irvine et al., 2019; Lam et al., 2016). Large storm events and snowmelt have been shown to have elevated concentrations of TP and SRP compared to baseflow conditions (Long et al., 2014), and P losses are elevated with wetter antecedent conditions (Macrae et al., 2010). Lam et al., (2016) found a clear moisture threshold for runoff generation and a significant relationship between TP and SRP loads with discharge volume; however, concentrations of P in runoff were not correlated to discharge. Discharge-concentration relationships for P in runoff are inconsistent due to non-linear responses during periods of high flow (Macrae et al., 2010). Very wet antecedent conditions are typically associated with the nongrowing season (NGS), when evapotranspiration is suppressed and soils are at or near field capacity (Lam et al., 2016; Van Esbroeck et al., 2017; Macrae et al., 2010).

Climate change is anticipated to have impacts on both precipitation patterns, melt patterns and temperature, which have the potential to impact the mobilization of P to runoff in agricultural areas, worsening water quality issues. This may be due to changes in both hydrology (transport) but also supply (i.e., availability of P to runoff from soils). Phosphorus transformation rate (P_{trans}; defined as the water-extracted phosphorus soluble reactive fraction from a paired soil core held in an incubation bag for three weeks subtracted against the paired soil core from the beginning of the three weeks) was used as a metric to describe the net effect of change in the soil caused through the time period, unaffected by changes in moisture. Most previous studies have explored the impacts of climate drivers on runoff processes (e.g., Van Esbroeck et al., 2017; Lam et al, 2016; Macrae et al., 2010); however, less is known regarding the impacts of climate drivers on P supply, particularly during the NGS. This thesis explores the impacts of winter hydroclimatic conditions on soil P dynamics in a cold agricultural region.

Chapter 2

Literature Review

2.1 Soil Phosphorus Dynamics

2.1.1 Inorganic Soil Phosphorus Fractions and Exchange Between Pools

Soil P is divided into different fractions and varies in concentration, understanding these fractions and concentrations over time is essential to understanding P export in runoff. Phosphorus content and form in soil is related to stage of soil development (Walker & Syers, 1976; Yang & Post, 2011). Soil P cycling centers around more readily available orthophosphate [$H_2PO_4^-$, HPO_4^{2-}] in soil solution as it cycles inorganically and organically in soil (Sims & Pierzynski, 2005). Simply, inorganic P in solution can be adsorbed onto soil colloids, precipitated, or taken up organically (Smil, 2000). Soil P fractions (or "pools") are commonly divided by the extraction process of P, and are simplified to the readily soluble fraction of P, the isotopically exchangeable or anion resin-extractable labile P, primary mineral P apatites, secondary mineral P which can be adsorbed onto the surface of minerals or clays, and secondary mineral P can be absorbed to form crystalline minerals which contain P in their structure, referred to as occluded P (i.e., Al phosphate, Fe phosphate, Mn phosphate, and carbonate phosphates) (Holtan et al., 1988; Smeck, 1985). Direct measures of the chemical form, such as using nuclear magnetic resonance spectroscopy can determine the molecules and functional groups of compounds (Turner et al., 2003; Cade-Menun, 2017), however time and cost make categorizations by extraction process more feasible for broader application. Dissolution of P from primary minerals can occur, secondary minerals can precipitate, and secondary minerals can go back into solution (Sims & Pierzynski, 2005). While some secondary minerals are physically encapsulated by minerals with no P in their structure and need to be released from being encapsulated before being directly available to react with the environment or in a laboratory setting (Smeck, 1985).

Phosphorus forms exchange between pools over time. When soil develops in natural environments over time, total P declines and becomes primarily occluded P and organic P (Walker & Syers, 1976; Yang & Post, 2011). Inorganic P input is limited to particulate atmospheric deposition and is estimated to range between 0.07-1.7 kg ha^{-1} $year^{-1}$ (Newman 1995), which is considered minimal. Inorganic P in solution moves by diffusion in the soil along a concentration gradient through soil pores (Sims & Pierzynski, 2005). The turnover times between P pools have been recorded as being as rapid as seconds for dissolved (soluble) P, minutes to hours for resin-extractable P, days to months for NaOH-extractable inorganic (primary or secondary mineral) P, and years to millennia for HCl extractable (residual) P (Helfenstein et al., 2018; Helfenstein et al., 2020). Pools of P in soil A and B horizons were tested in relation to moisture on the Kohala climate gradient on the Island of Hawaii, where soil age and parent material are constant, however rainfall ranges from 280 to 3100 mm over 12 km. With higher annual precipitation, microbial P increased, resin-P decreased, HCl-P decreased, and NaOH-extractable inorganic P (P_i) and P in organic molecules (P_o) pools increased (Helfenstein et al., 2018). Therefore, the factors that impact the soluble P pool (i.e., precipitation), occur and impact the P pools in the soil very quickly.

Phosphorus exchanges between inorganic pools if the soils are saturated. Moisture impacts the redox potential of the soil (E_h), a measure that describes the environments likelihood that substrates will be oxidized or reduced (Pepper & Gentry, 2015). Positive E_h occurs in aerobic conditions and a molecule will more likely be oxidized, while anaerobic conditions have a negative E_h and a molecule will likely be reduced (Pepper & Gentry, 2015). Phosphorus solubility increases with negative E_h conditions (Shaheen et al., 2021). The anaerobic conditions encourage the reduction of Fe-Mn-oxhydr)oxides and sulfate (Shaheen et al., 2021), with strongest relationships with Fe, then Mn.

2.1.2 Organic Soil Phosphorus Fractions and Exchange Between Pools

Phosphorus is immobilized in organic growth and is stored in soil. In organic molecules, P is an essential nutrient for growth used in photosynthesis, in skeletons, DNA and cell walls (Filippelli, 2008), and therefore is immobilized in plants or soil biomass. Phosphorus can be mobilized from organic matter to soluble organic P, humus or available P (Sims & Pierzynski, 2005). Input in the soil of P includes plant litter, but that depends on the quality and quantity of plant litter supplied (Damon et al., 2014). The majority of soil organic P is phosphate esters on inositols, phospholipids and nucleic acids (Cosgrove, 1977). Organic P has higher concentrations in surface layers of the soil (Walker & Syers, 1976). Moisture is an important factor for P pool turnover as more humid climates cycle P more quickly biologically than in arid areas (Helfenstein et al., 2018). Organic P immobilization occurs in soils and can cause P to remain latent in the soil (Walker & Syers, 1976).

Microorganisms mineralize organic P sources, as well as mediate redox reactions mineralizing previously inorganically bound P, and microorganisms immobilize soluble P. Incubated soils had organic matter added of varying organic quality (had a wide range of C:N ratios), and tested for acid-extractable P 8 times within 12 weeks. As plant residues and manure decomposed, P was lost from the initial organics (Jalali & Ranjbar, 2009). The amount of P mineralized was related to the P concentration of initial organics, and there was a negative correlation between C:P ratios in the residues and the P released (Jalali & Ranjbar, 2009). In another incubation experiment, Baggie et al. (2004) incubated 5 plants with varying inorganic P fertilizer concentrations. The P loss from organics is related to decomposition rate, which was not impacted by the inorganic P fertilizer concentration, but was impacted by the initial quality of the organics. Isotopic dilution of ^{32}P- or ^{33}P-labeled soils enable quantification of mineralization rates (Bünemann, 2015). Bünemann found that microbial immobilization and remineralization (microbial turnover), was most of the organic P mineralization flux, compared to non-living organic P in arable soils under grasslands and forest. Microorganisms are an essential link in the soil ecosystem that mineralize organic P sources, as well as can become P sources themselves after death through mineralization of organically bound P to mineral P.

2.2 Spatiotemporal Variability in Soil Phosphorus Dynamics

2.2.1 Soil Characteristics and Their Importance to Phosphorus Availability

The pH and mineralogy of soil is important when considering P solubility. Phosphate fixates to iron at very low pH (<4.5), to aluminum at low pH (4.5-6.5), and to calcium at mid to alkaline pH (>6.5), therefore phosphorus solubility is typically considered around 4.5 and 6.5 (Penn & Camberato, 2019). However, soil texture is known to affect this (Gustafsson et al., 2012), considering clays have more negative sorption sites than silt and sand. Low P solubility was found between 6 and 7 for clay soils, while similar solubility of P for sandy soils was found regardless of pH, and low solubility of P at pH 5.9 was found for intermediate soil texture (Gustafsson et al., 2012). Soil acidification naturally occurs over time due to additions of acidic precipitation. In calcareous soils phosphate is more soluble with acidic additions (Gustafsson et al., 2012). Increasing the pH of an acidic soil with lime facilitates P solubility, however if too much lime is added then Ca-P will precipitate so a balance must be found if the purpose of lime addition is to increase soluble P, although this reaction can take weeks (Penn & Camberato, 2019). Subsequently, mineralogy has an important impact on soil P solubility, as the initial concentrations of Fe, Mn, Al, Ca and P naturally occurring in the soil will determine what P is bound to. For example, it has been found that when there is more Al, there is more phosphate sorbed (Moazed et al., 2010). Mineralogy of soil and additions also impact P sorption, it was found salt leaching of exchangeable Al by adding Na, K or Ca causes less P to sorb to soils in a montmorillonite (Coleman et al., 1960). However, soils with high Fe, and Al oxides, that were saturated with the same ions were not affected by salt-leaching, and thus P sorption was not impacted. The pH and mineralogy of soil are important characteristics as they give a clear indicator on how available P will be in soil.

Buffering capacity (BC) and sorption capacity of the soil are related parameters that inform soluble P in the soil. The P buffering capacity of the soil is an important measurement as it describes the desorption and diffusion of labile P (Holford, 1997). Plant uptake of soil P and the concentration of labile P is dependent upon the BC, which in turn is controlled by the P sorption capacity and the sorption strength of the soil (Holford, 1997). Ultimately, this is an important P characteristic in the soil because when the maximum P sorption is known, it can guide maximum limit of P application in soil (Daly et al., 2001), or be used a measurement of the likely risk of P loss (Ige et al., 2005; Leclerc et al., 2001). The sorption capacity of P can be negatively related to high organic content in peat soils (Daly et al., 2001), but has also been reported as positively related to organic content (Ige et al., 2005). A clear relationship between P sorption capacity and soil texture exists as P sorption capacity is positively related to clay content and negatively related to sand content due to more sorption sites being available on clay particles than sand due to the surface area of the particles (Ige et al., 2005; Leclerc et al., 2001; Moazed et al., 2010). As there are more sorption sites, or compounds that adsorb P, there will be a greater capacity for soils to hold P in the soil, and release labile P. Therefore, fixation of P is greatest in acid clayey soils with high Fe and Al content, and relatively less fixation will occur in soils that are sandy soils with a near neutral pH (Smil 2000), although more fixation will occur for more alkaline soils than at neutral pH due to Ca content being able to sorb P. Overall, buffering capacity of P and P sorption capacity are indices that might be valuable to consider in future work to estimate soluble P concentrations in soils with moisture.

2.2.2 Changes in Soil Phosphorus Availability

Soil P concentration is impacted by anthropogenic inputs and crop yields. As STP declines in soils over time, P can become a nutrient limiting growth. However, agricultural soil management practices can increase soil test P through inorganic (mineral fertilizer) or organic (plant or animal origin) additions (Gustafsson et al., 2012; Kleinman et al., 2011; Sharpley, 1995). These additions in surplus of agricultural needs have led an accumulation of P in agricultural soils named legacy P (Bennett et al., 2001, Kleinman et al., 2011; Sharpley et al., 2013). There is evidence significant phosphorus accumulation in soil is occurring on livestock operations (Reid et al., 2019; Bouwman et al., 2011; Kleinman et al., 2011), while deficiency is predicted in about 61% of Canadian agricultural land from 1981 to 2011 (Reid et al., 2019), therefore there is a need correct these imbalances to better reduce pollution of P. Drawdown of legacy soil P can be as simple as no further additions, with promising field results showing crop yields are unchanged, money is saved on purchasing P amendments, and P reduced linearly with crop production each year (J. Liu et al., 2019; Zhang et al., 2020). Therefore, there is evidence that there is spatial variability in legacy P which can be targeted for reduction.

2.2.3 Moisture Impacts on Soil Phosphorus Fractions

Soil P pools vary with moisture in field and lab experiments, however the standard method to determine soil test P concentration is to use dried soils. It is vital to accurately portray real-world phenomenon in experimentation and for this reason field-moist samples are utilized in this thesis. In sandy grasslands, Magid & Nielsen (1992) found a strong negative relationship between soil moisture on the day of sampling and inorganic P concentration, and resin-extractable P was negatively related to soil moisture in another grassland as well (Liebisch et al., 2013). Magid & Nielson (1992), Liebisch et al., (2013) both use field moist samples when they tested P, although Olsen P and water-extractable P (WEP, easily soluble pool) methods are operationally defined, and typically dried. Dried soils are considered better when analysis cannot be done immediately so they are stored and then extracted (Schoenau & O'Halloran, 2008; Sharpley et al., 2008; Sims, 2000). Completely air-drying samples for analysis on average increased water-extractable P (Turner & Haygarth, 2001), bicarbonate-extractable inorganic and organically bound P (Turner & Haygarth, 2003). With the majority of this additional P being released related well to microbial biomass P, therefore air-drying could cause cell lysis (Turner & Haygarth, 2001; Turner & Haygarth 2003). And Microbial P was found to be negatively related to soil moisture (Liebisch et al., 2013). Therefore, drying soils has an impact on soil P fractions, although this is practical for storing soil, it is not appropriate when considering climate impacts on soil phosphorus, as microbial biomass P is impacted and influences labile and soluble soil P.

2.2.4 Freeze-Thaw Impacts on Soil Phosphorus Fractions

Freeze thaw cycles (FTCs) in soil impact several factors that ultimately impact P including the soil structure, soil microbiology, and plants. FTCs can have a negative impact on soil microorganisms, with evidence showing that four successive FTCs from -13°C to 4°C reduced microbial biomass to 40% (Yanai et al., 2004). It was found by Rosinger & Bonkowski (2021), that microbial biomass loss is greatest after the first FTC, and continues to decline in following FTCs, with less and less metabolic activity occurring with FTCs as well. This agrees with Gao et al., (2021) who found microbial biomass and enzymatic activity declines with FTCs. Soils can be aggregated or fragmented with FTCs, however, reach a state of equilibrium largely between 10-50 FTCs (Zhai et al., 2021). This depends on the initial state of the sample but ultimately, FTCs change the grain-size distribution of sand, silt and clay and can change the soil texture (Zhai et al, 2021). Sand can be changed to silt, and silt to clay particles, ultimately FTCs on soil aggregates and mineral particles will allow for more sorption sites of P. Cover crop species can have P loss (likely from cell lysis) after FTCs, although amount released depends on cover crop species (Cober et al., 2019). Therefore, FTCs do impact several factors that could have a variable impact on soluble P. By better understanding the net effect and individual effects of these factors, we can better understand how these work in tandem and what the controlling mechanisms are for soluble P in soil with FTCs.

2.3 Spatiotemporal Drivers of Phosphorus Concentrations in Runoff

2.3.1 Forms of Runoff Phosphorus

Water samples in streams, from tile drains and in drainage basins are treated similarly when testing for P. Phosphorus form in water samples is operationally defined depending on the size of filter the sample is passed through. Forms of P are known as soluble (or dissolved) if the sample passes through 0.45μm filter, and is further divided by reactive P and unreactive P by whether it reacts to Murphy-Riley molybdate reaction readily or needs to be digested first and then reacts (Haygarth & Sharpley, 2000; Murphy & Riley, 1962). To calculate particulate P (PP), soluble reactive P (i.e., SRP) and dissolved unreactive P (i.e., NRP) is found (i.e., TDP) and then subtracted from total P (i.e., TP), leaving the P concentration that is greater than 0.45μm (Haygarth & Sharpley, 2000). Phosphorus in water is calculated as a concentration, and when volume over time (discharge) is known when the sample was taken, the load (amount) of P can be calculated.

2.3.2 Soil Characteristics and Their Importance For Runoff Phosphorus

Aggregate stability is an important characteristic for soil phosphorus when considering P export on sediments. Aggregate stability of the surface soil has been found to be closely negatively related to soil susceptibility to runoff and erosion across scales, landscapes, and soil types (universally) (Barthès & Roose, 2002). As P can co-transport on sediments (Steegan et al., 2001; Stone et al., 1995), and there is the potential for P desorption from sediments once in aquatic environments (Stone et al., 1995), aggregate stability plays an important role in P erosion and export to aquatic environments. Furthermore, it has been found that P can be exported on fine sediments that are eroded (McDowell & Sharpley, 2002; Wang et al., 2012), although aggregate stability of the soil was not tested in these studies. Although there are sediment-producing and depositional areas of sediment for a specific site, and as such should be considered and managed (Steegan et al., 2001). Aggregate stability is impacted by antecedent moisture, decreasing in stability with more antecedent moisture (Vermang et al., 2009). Physical erosion can occur from raindrops and decrease aggregates when precipitation occurs directly on the soil (Glanville & Smith, 1988). Aggregate slaking occurs with wetting and drying of aggregates, and has been correlated to the rate or wetting (Glanville & Smith, 1988). Furthermore, swelling clays have been shown to increase aggregate breakdown from wetting even more (Burroughs et al., 1992). Therefore, aggregate stability is an important factor when considering the soil P characteristics which lay soil susceptible to erosion and P export.

Soil characteristics such as soil test P, sorption capacity, and drainage capacity influence runoff P. The soil test P concentration relates to runoff P concentrations (J. Liu et al., 2019; Pote et al., 1996; Sharpley, 1995). Runoff P concentrations were linearly related to P sorption saturation percentage for ten surface soils tested from Oklahoma (Sharpley, 1995). Andersson et al. (2013), found P leaching reduced from soils that had low P saturation in the subsoil, even if the topsoil had high P saturation, suggesting that lower P saturation at depth decreases the P losses from a field as subsurface soils have the capacity to sorb P. Across the Lake Erie basin, the sorption maximum is greater with soil depth (Plach et al., 2018a). Although the stratification of P in soil depth has been found to increase P export from agricultural soils in the Lake Erie Basin (Baker et al., 2017; Daloğlu et al., 2012). Surface runoff decreases in soils that have greater drainage capacity (Kleinman et al., 2006), as drainage capacity is increased when there are more air spaces in the soil, more macropores and therefore more water can move freely into the soil as opposed to runoff the surface. Although tile drained systems remove excess soil water that could be damaging to plants, tile drained systems create more direct pathways to irrigation ditches without the possibility for P to be intercepted before leaving the site. There is evidence that supports peak tile discharge occurs at the same time as peak surface runoff so macropore flow from the surface is evident in the Lake Erie Basin (Smith et al., 2015). Phosphorus from tile drains have been found to be more supply limited whereas surface runoff was transport limited (Plach et al., 2019), so tile drains, when active, have been shown to readily transport P. This speaks to the importance of knowing how soil characteristics at depth will interact with P in the soil and potentially export P in field losses.

2.3.3 Effects of Antecedent Moisture on Runoff Phosphorus Mobilization

Antecedent soil moisture is an important variable for P export that deserves further research. Increasing antecedent moisture conditions of soil have been found to increase runoff from a basin, soil in plots and homogenized soil boxes (Kleinman et al., 2006; Macrae et al., 2010; McDowell & Sharpley, 2002; Wang et al., 2012). Wang et al. (2012) determined that high antecedent moisture increased P runoff, and that with 25% antecedent soil moisture, the runoff P concentration was high at the beginning of runoff and declined rapidly with time, eventually stabilizing. Macrae et al., (2010) found increases in SRP and TP concentrations in streams with increased antecedent moisture, however this relationship was highly variable. Soil antecedent moisture plays an important role in runoff P, although this has been variable, so a better understanding of soil moisture dynamic and P would be beneficial.

Precipitation and subsequent discharge influences P concentration, and annual P load, however variability in the concentrations of P at peak concentrations modelling or estimation efforts difficult. Macrae et al., (2007) found in a headwater agricultural watershed in southern Ontario, that event flow (precipitation or snowmelt) was responsible for the majority of TP export (75%), and SRP export (80%), although discharge values could predict nutrient export for small events, larger events were more variable for nutrient export, and so predictions were not accurate. This speaks to the need to sample event flow, specifically large events (Macrae et al., 2007). Supporting this finding, in an agricultural headwater catchment of eastern England Outram et al., (2016) found high TP concentrations during peak summer storms and large winter flows compared to lower flow conditions. Total phosphorus concentrations did not relate directly to fertilizer application in that study either, pointing to the importance of point source loading of TP. Furthermore, Daloğlu et al., (2012) found that SRP export to Lake Erie was increased due to the precipitation pattern. An increased frequency of extreme events (over the 85th percentile for the study period) occurred near the end of the study period (1970-2010, attributed to climate change), with more SRP exported related to these extreme events. Large precipitation events are difficult to estimate P loads or concentrations from due to the variable nature of P release, so a greater understanding of P availability in the soil to be lost in export might enhance our modelling capabilities at these higher flow conditions.

In regions that experience snow, agricultural snowmelt is dominant for P export. The spring has a large percentage of annual discharge (75%) and annual total P loss (71%) in Manitoba agricultural fields in South Tobacco Creek watershed (J. Liu et al., 2019). Van Esbroeck et al., (2016) in southern Ontario also found similar results, with 83-97% of annual runoff from tile drains and surface runoff, 84-100% of SRP loss occurring, and 67-98% of TP loss occurring in the nongrowing season. Seasonal patterns for agricultural SRP and TP concentrations show peaks of SRP and TP concentrations at spring and summer, as SRP and TP concentrations increased with increased snowmelt discharge, then during dry conditions, lower discharge and consistent release of SRP and TP increased concentrations (Van Meter et al., 2020). Seasonal P losses relate to annual hydrological processes, thus an understanding of seasonal soil P dynamics are imperative for a holistic understanding of P available for loss.

2.4 Effects of Climate Change on Phosphorus Losses in Runoff

2.4.1 Temperature and Moisture Regime Differences Expected with Climate Change

Climate change is expected to impact the NGS temperature and moisture significantly in areas which experience snow. In the Great Lakes Region of North America, climate change is anticipated to make the NGS warmer, have more melt events, and more extreme runoff events. Temperatures are expected to increase by 3.7-4.5 °C for the City of Toronto by 2070 (Berardi & Jafarpur, 2020), and has already changed from climate zone 5 to climate zone 4 since 1989 to 2014 according to the Hadley Regional Model 3 (HRM3) and Hadley Climate Model 3 (HadCM3) (Berardi & Jafarpur, 2020). The warmer temperatures are expected to warm the NGS, creating greater uncertainty for NGS weather patterns as more rain-on-snow and winter heat wave events are already taking place and are significantly increasing daily stream flow data on a watershed scale in Hubbard Brook Experimental Forest in New Hampshire, USA (Casson et al., 2019). Potential freeze-thaw cycles with warmer winter air-temperatures can occur due to decreasing snowpack (Reinmann & Templer, 2018).

Climate change is expected to change the nongrowing season which can impact nutrient export. Principally, climate change will continue to warm air temperatures, with air temperatures in Canada warming at more than double the global rate, less snow cover, earlier spring peak streamflow, increased precipitation with less snowfall and more rainfall, with more winter precipitation (Bush & Lemmen, 2019). Furthermore, climate change will increase the likelihood of large precipitation events, increase FTCs and cause several melt events in the winter.

Although much work has been done on understanding the impacts of a variable climate on runoff processes (Eimers, 2019; Van Esbroeck et al., 2017), less is understood regarding the impacts of climate change on the supply of nutrients in soils. It is unclear if and how changing temperatures and moisture regimes may impact the P supply in soils. An improved understanding of these processes may provide insight into the high P concentrations exported with large storms and snowmelt events; and could provide additional metrics for environmental models, which can provide better projections of the impacts of climate change on water quality.

2.5 Thesis Objectives

The objectives of this thesis were to:

1) quantify seasonal variation in soil WEP and P_{trans},
2) determine the impacts of reduced snow cover on soil temperatures, soil WEP and P_{trans} during the non-growing season,
3) relate temporal differences in soil WEP to environmental drivers such as soil moisture and temperature,
4) to quantify the effects of freezing magnitude and duration on soil P availability (i.e., water-extractable soluble reactive (WEP), total dissolved P (WEPT) and nonreactive P (WEPN) forms and Olsen P),
5) to relate differences in soil P availability and speciation under the variable climatic conditions to biotic and abiotic drivers, and
6) to quantify differences in the magnitude and speciation of P in leachate (soluble reactive P (SRP), dissolved nonreactive P (NRP), total dissolved P (TDP), particulate P (PP), and total P (TP)) under the variable climate conditions.

Objectives 1, 2 and 3 are addressed in “Seasonal variability and moisture controls in water extractable phosphorus concentrations from agricultural soil in a cold, temperate region” (Chapter 3 of this thesis) and objectives 4, 5, and 6 are addressed in “Impacts of moisture, freeze-thaw cycle duration and magnitude and potential phosphorus mobilization from agricultural soil” (Chapter 4 of this thesis).

Chapter 3

Seasonal Variability and Moisture Controls in Water Extractable Phosphorus Concentrations From Agricultural Soil in a Cold, Temperate Region

3.1 Abstract

Agricultural soils are a source of phosphorus (P) to runoff, and can contribute to impaired water quality. Little is known regarding the potential P supply in soil throughout the non-growing season (NGS), which is a critical period for runoff in humid, temperate regions, or how soil P supply may change with anticipated climate variability. This study employed a field experiment in a silt-loam cropped field to i) quantify seasonal variation in soil water extractable P concentrations (WEP) and net P transformation rates (P_{trans}: the difference of WEP over three weeks for a soil core, where half was tested initially and half was incubated in a bag in the field); ii) determine the impacts of reduced snow cover on temperatures, moisture, WEP and P_{trans} in soil; and iii) relate temporal differences in soil WEP to environmental drivers such as moisture and temperature. Both WEP and P_{trans} were more variable during the NGS relative to the growing season. Soil WEP was greater during the NGS, whereas P_{trans} did not differ between the seasons. Reduced snow cover led to more variability in soil temperatures and more freeze-thaw cycles relative to snow-covered soil, which experienced little soil frost; however, this did not lead to differences in soil WEP or P_{trans}. In general, positive relationships were found between WEP and soil moisture ($p < 0.05$), which may explain the variability between the seasons. It is hypothesized this relationship is caused by loosely sorbed phosphate desorbing, as part of the buffering capacity of the soil when more acidic rain or melt-water enters the calcareous soil of this study site. Much attention has been given to the potential impacts of climate change on both soil P supply and hydrology; however, this study suggests that little variability in soil P dynamics will occur with temperature changes alone.

Keywords: winter, snowmelt, silt loam, no-till, fertilizer application, soil frost

3.2 Introduction

Eutrophication is problematic to aquatic ecosystem health and is widely connected to nonpoint additions of phosphorus (P) and nitrogen from agricultural runoff (Carpenter et al., 1998), with P being the limiting nutrient in freshwater (Schindler & Hecky, 2008). Harmful and nuisance algal blooms negatively impact ecosystem health, tourism, recreational users, commercial fisheries, public health, property values, and drinking water treatment efficiency (Dodds et al., 2009; Smith et al., 2019). Such blooms are pervasive throughout North America, (Bianchi et al., 2010; Scavia et al., 2014; Schindler et al., 2012; Smith et al., 2019), with much of the P originating from nonpoint agricultural landscapes. Existing water quality challenges are likely to be exacerbated by climate changes, with temperature and moisture regime shifts expected in the Great Lakes region of North America. Thus, there is a need to understand if and how climate change may impact P dynamics.

Phosphorus concentrations in runoff are strongly related to water-extractable P (WEP) (the soluble P fraction) concentrations in soil (Hooda et al., 2000; Pote et al., 1999; Schroeder et al., 2004; Wang et al., 2010; Vadas et al., 2005). Several studies reported that agricultural P losses in runoff are often transport-limited due to the elevated soil P levels in these systems (Bowes et al., 2005; Bowes et al., 2015; Hanrahan et al., 2021). However, in agricultural fields with lower soil P concentrations, subsequent P concentrations in subsurface runoff can be supply limited (Plach et al., 2018b). Although agronomic soil P (e.g., Olsen P) is a strong predictor of P concentrations in runoff (e.g. Sharpley & Syers, 1979), there is considerable variability in these relationships (Duncan et al., 2017; Pease et al., 2018). Soil test P and soil WEP are often correlated; however, soil test P concentrations do not vary significantly over short time periods whereas WEP can be more temporally dynamic (Pote et al., 1996).

The availability of soluble P may vary temporally in response to climate drivers such as moisture and temperature, which may impact the mobilization of P in runoff across different seasons. The occurrence of frost and freeze-thaw cycles (FTC) in particular, may increase the supply of soil P. This is hypothesized to occur because of both biological and physical mechanisms. Biologically, FTC can increase the supply of P through microbial cell lysis (Feng et al., 2007), plant cell lysis (Bechmann et al., 2005; Cober et al., 2019) including in fine roots

(Reinmann & Templer, 2018; Tierney et al., 2001). FTCs have also been shown to disrupt microbial cycling in soils by leading to a shift in microbial species and reducing the decomposition of lignin (Feng et al., 2007). Physically, FTC can either degrade soil aggregates (Cheng et al., 2018) or they may aggregate the soil, depending on the initial soil aggregate composition, the soil moisture content, soil texture, and organic matter content (Kværnø & Øygarden, 2006; Lehrsch & Jolley, 1992). Sometimes, even the same soils may show aggregation and degradation after different numbers of FTCs (Oztas & Fayetorbay, 2003). Changes in soil aggregation can impact P exchange between soil and water by changing the exposure of sorption sites. For example, depending on soil type, FTCs can promote P adsorption (Özgül et al., 2012) or P availability due to decreased adsorption capacity (Wang et al., 2017). In turn, sorbed P concentrations contribute to variability in soil P supply (Chen et al., 2021). As such, an improved understanding of the net impact of moisture and temperature (including FTC) on soil WEP and net P transformation rates (Ptrans: i.e., net mobilization versus net immobilization) is needed, particularly in light of climate change.

In humid, temperate regions, the majority of annual P losses occur during peak-flow conditions (Duan et al., 2012; Jordan et al., 2007; Macrae et al., 2007; Banner et al., 2009), particularly with the spring snowmelt period. In the Great Lakes Region of North America, studies have shown that the majority of annual P losses occur during the non-growing season (NGS) (84-98% of P losses between October and April (King et al., 2016; Lam, et al. 2016; Van Esbroeck et al., 2016). This is largely driven by increased runoff (Macrae et al., 2010; King et al., 2016), but may also be related to differences in P supply from soil, as high soil moisture content can elevate soil WEP (Pote et al., 1999) and can increase P mineralization (Whalen et al., 2001). In addition, management practices (including the type of organic and inorganic amendments, and timing since application) are known to be factors contributing to soil WEP (Kashem et al., 2004), and may impact seasonal variability in soil P supply. Although many studies have examined seasonal differences in P concentrations and loads in runoff, few have quantified seasonal variability in WEP and P_{trans} in the soil. This information is relevant to the prediction of runoff P concentrations and modelling efforts and may inform the use of conservation practices.

Agricultural landscapes throughout the Great Lakes Region will be impacted by climate change (Brown & Mote, 2009). Although air temperatures are typically below freezing during the winter months (December-March), the region has historically experienced prolonged snowpack development as a result of lake-effect snowfall that insulates the soil and impedes significant soil frost development. The Great Lakes Region is anticipated to have higher air temperatures, more frequent melt events, and reduced snowpack depth and duration because of climate change (Brown & Braaten, 1998; Fischer & Knutti, 2015; Vincent et al., 2012; Brown & Mote, 2009; Wang et al., 2015), as well as more instances of heavier precipitation in winter months (Fischer & Knutti, 2015; Vincent et al., 2012; Brown & Mote, 2009). Considering the potential impacts of soil temperature and FTCs on soil P supply, the anticipated changes in climate have the potential to impact P losses to waterways.

To understand the impacts of seasonality and the potential impacts of climate change during the NGS on soil P dynamics, this study characterized patterns in WEP (soluble P fraction) and net P transformation rates (P_{trans}; in this study defined as the difference between incubated soil (soil held in clean polyethylene bag for three weeks) WEP and the WEP of a paired core from the beginning of the incubation period) in an agricultural silt-loam soil in Ontario, Canada under both natural and experimental (i.e., snowpack removed) conditions. Changes in soluble P concentration is impacted by pH (Penn & Camberato, 2019), plant uptake (Ping et al., 2020), desorption-mineralization processes which are impacted by soil sorption capacity and water content (Yadav et al., 2012). Furthermore, the annual changes of soluble P concentrations in the Great Lakes Region has not been studied as far as this author is aware. The specific objectives of the study were to i) quantify seasonal variation in soil WEP and P_{trans}; ii) determine the impacts of reduced snow cover on soil temperatures and soil WEP and P_{trans} during the NGS; and iii) relate temporal differences in soil WEP to environmental drivers such as soil moisture and temperature.

3.3 Materials and Methods

3.3.1 Study Site

This study was conducted in an agricultural field in St. Mary's, Ontario (Figure 3.1). The region has a humid, continental climate (Dfa, Koppen) and receives 916.5 mm of precipitation annually, 159.7 cm as snowfall between the months of October and May (ECCC, 2020). The mean annual temperature is 7°C, with annual mean daily minima in January (-10.3 °C) and maxima in July (14 °C) (ECCC, 2020). The nearest ECCC weather station with averages from 1981 to 2010 available was Waterloo, and for consistency with the averages, Kitchener weather station was used to determine average air temperatures and precipitation for the study period. Soils are classified as Perth silt loam, Brookston silt loam, have a silt-loam texture and are luvisolic (AAFC, 2021). The field has a slope of 0.63%.

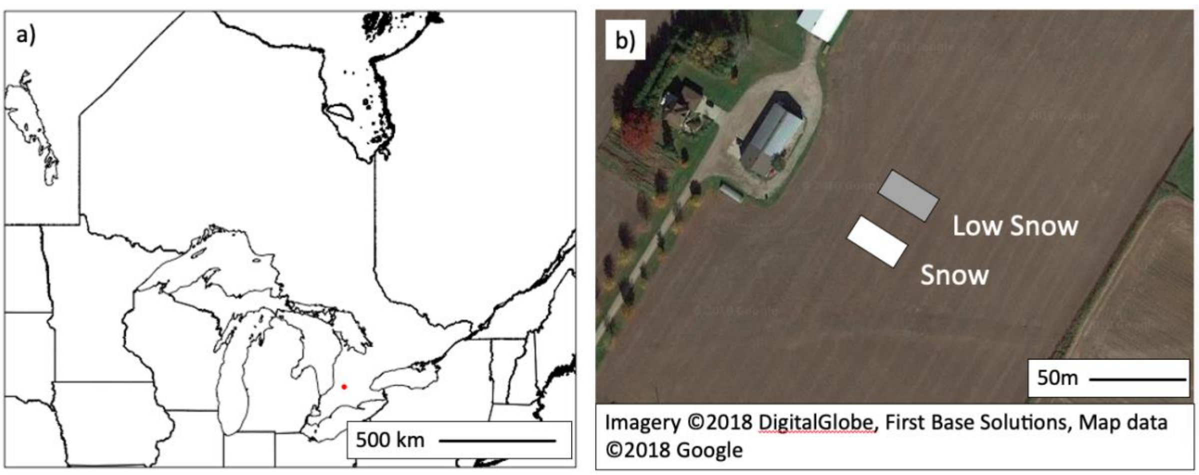


Figure 3.1. Field site location in St. Mary's, Ontario (a) and experimental plot outlines (snow covered plot in white and low snow cover plot in grey) shown on an aerial photograph of the field site (b).

The field is tile drained systematically at a depth of 0.9 m with 10 cm perforated pipe laterals spaced at 18 m. Rotational, conservation tillage (vertical tillage to 5 cm depth) has been practiced on this field for more than a decade. Crops grown on the field are a corn-soy-winter wheat rotation. Winter wheat was grown the summer prior to the experiment (2017), with cover crops of ryegrass and crimson clover that were terminated in the late autumn. In September

2017, liquid dairy manure consisting of 15.6 kg nitrogen (N) ha^{-1}, 17.4 P ha^{-1} and 75.8 kg potassium (K) ha^{-1} was applied. The following season (2018), corn was planted on May 8th. At that time, 88.5 kg N ha^{-1} and 57.2 kg P ha^{-1} were placed in the subsurface with the corn seed, and subsequently supplemented with 95.3 kg N ha^{-1}on May 30th. Initially, the N fertilizer was approximately 28% liquid and P fertilizer was approximately half dry formulation and half liquid from the product ammonium polyphosphate 10-34-0 (Table 3.1).

Table 3.1. The agricultural methods applied on the field site for the three years prior to the study.

Management	Year	Decision or Fertilizer Concentration
Crop	2017	Wheat
	2018	Corn
Tillage	2017	Rotational conservation till disc 5cm (September)
	2018	None during the study period
P Application Rate (P_2O_5 kg ha^{-1})	2017	17.42 (liquid dairy manure)
	2018	57.15 May 8 (mono-ammonium phosphate, granular)
N Application (kg ha^{-1})	2017	15.60
	2018	88.45 May 8, 95.25 May 30
Application method	2017	Surface dragline then incorporated, disked 2-3 inches
	2018	Band applied with planting, liquid mid-season sidedress
Cover crops	2017	Crimson clover, ryegrass
	2018	Not applicable during the study period

3.3.2 Soil Sampling For P Availability and Net P Transformation Rates

Soil samples were collected for the determination of WEP at the beginning and end of each three-week time period. As well, a paired core sample from the beginning of the time period was incubated in a clean polyethylene bag that was loosely twisted to enable air flow and prevent moisture exchange. This incubation core was placed back in the same hole that it was retrieved from and incubated in the field for three weeks. The WEP concentration from the buried bag incubation was subtracted from the initial WEP concentration from the time period resulting in net P transformation rates (P_{trans}) (Binkley & Hart, 1989). Fresh WEP samples were taken 12 times and P_{trans} were taken 8 times within a year (December 2017 – October 2018) from plots in an agricultural field. At each sampling period, 10 paired soil cores were collected on each of the two plots. Each paired core was separated by depth (surface: 0-2 cm, middle: 2-5 cm, and bottom: 5-10 cm) with vegetation from the surface was left in the 0-2 cm samples, same with roots in lower depths. In the late spring, summer, and fall, samples were taken from, and incubation samples were placed between corn rows.

3.3.3 Snow Removal Field Experimental Design

In the nongrowing season (December 18th-April 6th), one plot remained snow covered, whereas snow was removed from the low-snow plot to simulate a reduced snow-cover treatment expected with climate change. Two field plots 24 feet by 12 feet in length were delineated and marked with stakes on the corners (Figure 3.1 b). The topography of the field was such that the low-snow plot was slightly higher in elevation than the snow-covered plot, with the north-west side of the plots slightly higher in elevation than the north-east side. Of the two plots, the low-snow plot consistently had its snow removed manually with a shovel within 24h of snowfall and routinely between snowfall events (following the redistribution of blowing snow) whereas the snow-covered plot was not touched. Although snow was removed from the low-snow plot, ~ 1-2 cm of snow remained on the plot to avoid disturbing the soil. For sampling periods during which snow was present on the snow-covered plot, snow was gently removed prior to core collection and subsequently replaced above the buried bags for the incubations.

In the NGS, the snow-covered plot and the low-snow plot each had their own EM50 logger with a Decagon ECT Sensor measuring the air temperature and relative humidity at the surface and Decagon 5TM probes at 2 cm, 5 cm, and 10 cm depth measuring soil temperature and volumetric water content (VWC) at half hour intervals. One EM50 logger with ECT Sensor and 5TM probes at the same depths were used in the growing season (GS).

3.3.4 Laboratory Analysis

Samples were homogenized prior to extraction and pieces of vegetation were not included in weighed soils. Approximately 5 grams of field moist sample was shaken with 50 mL of distilled water for 1 hour on a reciprocating shaker within 48 hours of collection from the field. The samples were filtered with Whatman No. 42 filter papers, and then syringe filtered to < 0.45 μm (sodium acetate filters) into conical polypropylene tubes (Pierzynski, 2000). Filter samples were stored at 4°C prior to P analysis, or frozen if analysis did not occur within 24 hours of extraction. Soluble reactive phosphorus (SRP) in the extracts were measured using colorimetric analysis in the Biogeochemistry Lab at the University of Waterloo (Bran Luebbe AA3, Seal Analytical Ltd., Seattle, USA, Method G-103-93). To express the P pools per unit of dry soil, the gravimetric water content for each soil sample was determined by weighing approximately 5 grams of field moist samples into a weigh tin and drying at 105°C for 24 hours, weighing the dry sample and calculating the amount of moisture for each sample (Reynolds, 1970). More moist soils had less soil in the sample with the dry soil over water ratio in the samples ranged from 12.00 to 0.71.

Soil texture of this plot has been previously described by Plach et al. (2018a) as the top 0-5cm classified as a loam and the 5-15 cm depth classified as a clay loam. This data was taken at different depth scales than this study, therefore 0-5 cm spans both surface and middle depths, with the bottom depth only 5-10 cm. Loss on ignition (Rowell, 1995) was performed to estimate organic content and carbonate content percentages by first drying the soil at 105°C for one day, then burning soil at 550°C for two hours and 950°C for two hours, weighing the samples after each drying. The percentages were calculated from the formulas in Heiri et al. (2001), with the average values presented by depth in Table 3.2.

Table 3.2. The organic content and carbonate contents by depth, samples taken at the beginning of the study. Sand, silt and clay percentages are from analysis by Plach et al. (2018a).

Soil Depth	Organic Content %	Carbonate Content %	Sand %	Silt %	Clay %
Surface (0-2cm)	7.9	0.86	28	46	26
Middle (2-5cm)	6.4	0.89			

Bottom (5-10cm)	5.8	0.86	24	47	30

3.3.5 Data Analysis

Observed changes in WEP (mg kg^{-1}) were determined by subtracting the WEP at the end of the time period from the WEP at the beginning of the time period for each core. Thus, a negative change in WEP indicates that a decline in WEP was observed. Net P transformations were calculated by subtracting the transformed (incubated) sample from the fresh sample collected three weeks prior. Rarely samples were lost in the field, however there were always at least n=9 for all time periods by depth, condition, and time period. It was not possible to collect new fresh samples on February 22nd (T_2) due to the presence of saturated frozen ground that prevented sampling. Consequently, when observed change in WEP for T_2 was determined, there was a six-week delay between sampling, however P_{trans} bags were removed from the soil after three weeks only. As a result, the T2 observed change in WEP rates were divided by two, to match the amount of time the P_{trans} samples were in the soil, as P_{trans} bags were in the soil half the amount of time that occurred between the samplings of fresh WEP.

Observed changes in WEP and P_{trans} were plotted against each other to determine whether the P_{trans} could account for the observed changes in WEP in the field. Where samples fell along the 1:1 line, it was assumed that P_{trans} accounted for the observed changes in WEP. If the observed change in WEP was greater than the P_{trans} rate, then WEP increased over the time period more in the soil or decreased in the incubation bags. While, if the observed change in WEP was less than the P_{trans} rate, WEP increased in the incubation bag more than in the soil or decreased in the soil more than the incubation bag.

3.3.6 Statistical Tests

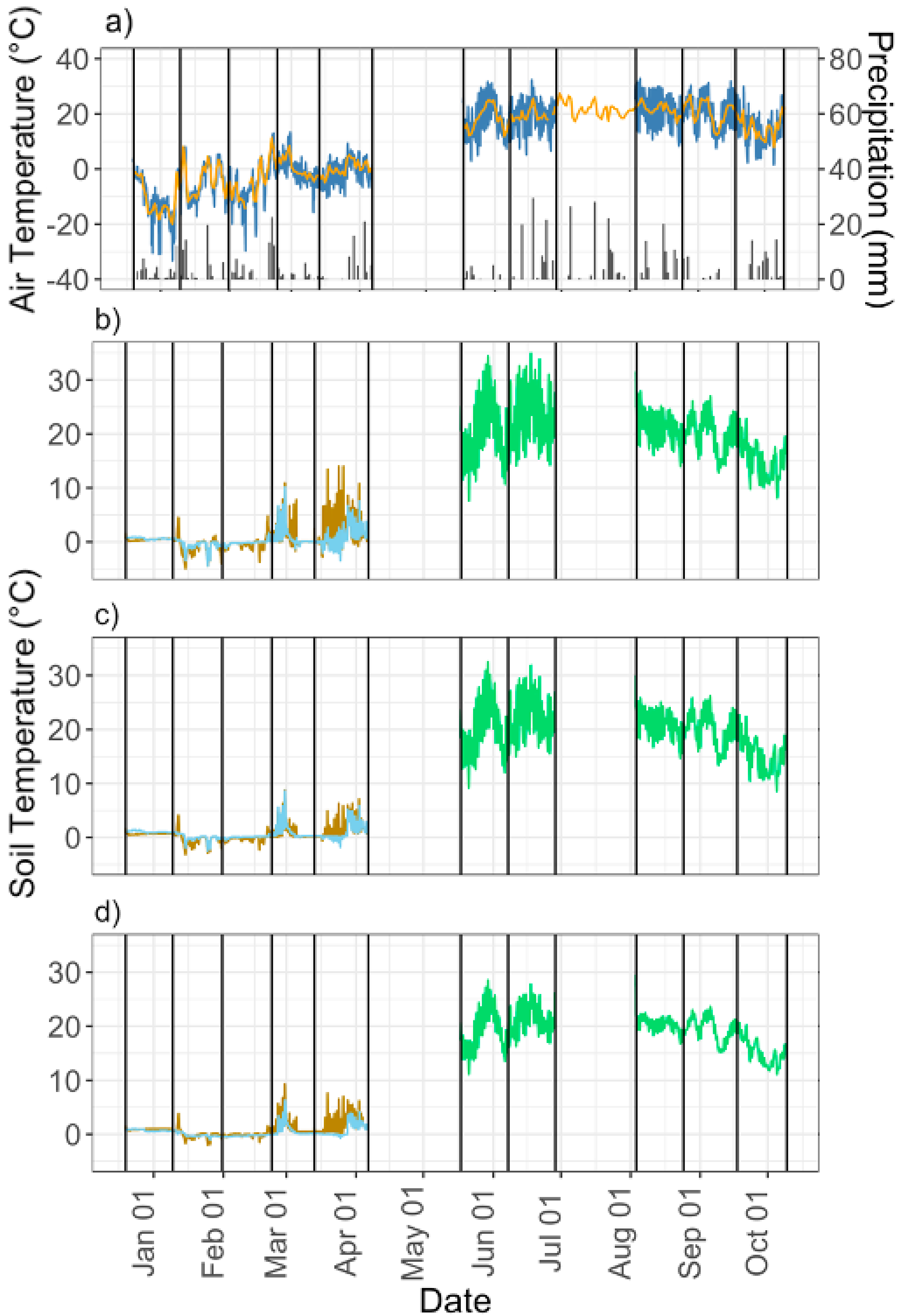
The relationships between the observed changes in WEP, and P_{trans} rates over the time period against climatic measurements (number of FTCs, average soil temperature, average soil moisture content, and moisture range) over the time period were considered. The variables were not normally distributed according to a Shapiro test when the data was tested by depth and condition or when grouped together. Therefore, a Spearman rank correlation plot was completed using the corrplot package (Wei & Simko, 2017) on the R Project for Statistical Computing (version 3.6.2) for the annual data. To compare observed changes in WEP and P_{trans} rates between the low snow (LS) and snow (S) plots in the winter by depth, a series of Mann Whitney Wilcoxon tests were completed. Statistical tests were completed using the R Project for Statistical Computing. A paired two sample t-test was used to determine if VWC significantly differed between the LS and S plot. The NGS and GS differences in the P_{trans} rate and observed changes in WEP were tested with a one-way t-test using R Project for Statistical Computing.

The fresh soil WEP was compared to sample GWC for each depth. Fresh WEP was not normally distributed according to a Shapiro test, therefore Spearman rank correlation plots (described above) were created to determine the relationship with GWC. Spearman rank correlation plots for WEP~GWC were created by depth with similar results found, so all data pooled together is presented.

3.4 Results

3.4.1 Climate and Soil Conditions Historically, During the Study Period, and the Impact of Snow Removal on Soil Conditions

Precipitation and air temperatures throughout the study period were largely consistent with long-term seasonal trends, with the coldest air temperatures from January to mid-February, and warm air temperatures throughout the summer (Figure 3.2). The annual precipitation totals (2017: 817.8 mm, 2018: 762.7 mm) and mean temperatures (2017: 7.8°C, 2018: 7.5°C) were typical of long-term normals (916.5 mm, 7.0°C), December and April were slightly cooler (~3-4°C) than normal whereas May, August and September were slightly warmer (~2-3°C) than normal. This data was for the station ‘Waterloo Wellington A’, which is the nearest site to the field site that had normals estimated from 1981-2010 (ECCC, 2019).



a)
Air Temperature (°C)
40
20
0
-20
-40
Precipitation (mm)
80
60
40
20
0
b)
c)
d)
Soil Temperature (°C)
30
20
10
0
Jan 01
Feb 01
Mar 01
Apr 01
May 01
Jun 01
Jul 01
Aug 01
Sep 01
Oct 01
Date

Figure 3.2. a) Daily mean air (orange line) and air temperature 1 m above the soil (dark blue line) temperature, and precipitation (grey bars). Soil temperatures for each plot at the 2 cm, 5cm and 10cm depths are shown in **b**), **c**) and **d**), respectively. The brown lines are the low-snow condition, the light blue line is the snow condition, and green is the GS. The vertical black lines indicate soil testing dates.

Very little precipitation in winter occurred as snow (6.7%), and there were approximately three major melt events (Figure 3.3). The summer months were typical for the region, with 16 precipitation events. Soil moisture content was greatest in the NGS and least during the GS (Table 3.3). However, following rainfall in autumn, large soil moisture increases were observed (Table 3.3). Soil temperatures were highest in the GS (July, August) and lowest in the winter months (January, February). Some brief periods of soil frost were observed during the NGS; however, this freezing was restricted to surface depths (above 10 cm).

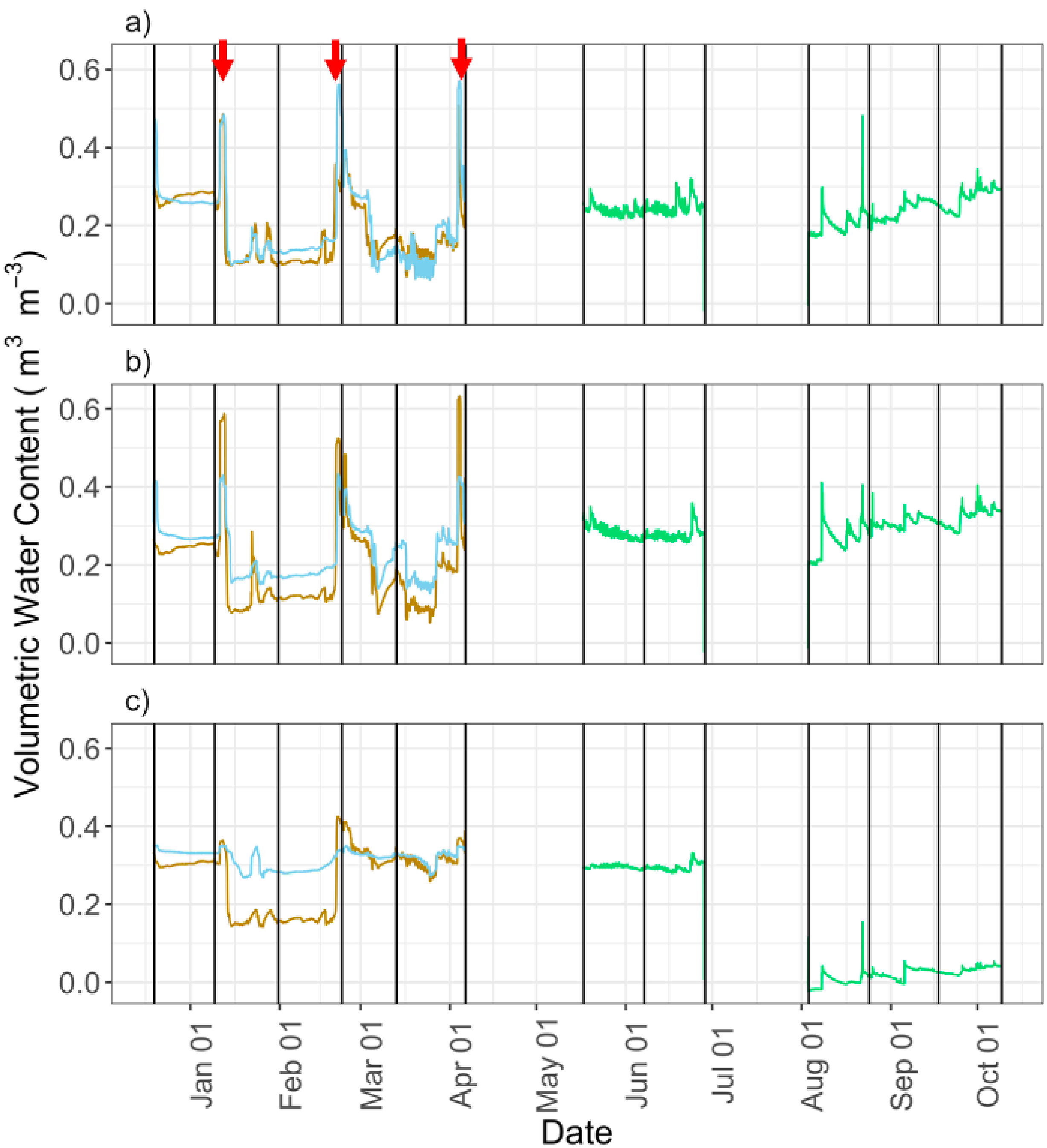


Figure 3.3. Volumetric water contents (m^3 water per m^3 of soil) of the soil at **a**) 2 cm, **b**) 5 cm, and **c**) 10 cm. The tan line shows data from the low-snow plot, the blue line from the snow condition, and the green from the GS. The three red arrows represent large melt events. The vertical black lines indicate sampling dates.

Table 3.3. The average temperature (°C), temperature minimum and maximum (°C), number of freeze-thaw cycles (FTCs), volumetric water content (VWC) (cm^3 water per cm^3 of soil), average and VWC minimum and maximum in the soil (S: surface, M: middle, B: Bottom) over the incubation period at the two plots (low snow and snow).

Time	**Depth**	**Mean Soil Temperature (°C)**		**Soil Temperature (°C) Minimum – Maximum**		**Mean VWC (cm^3 water per cm^3 of soil)**		**VWC (cm^3 water per cm^3 of soil) Minimum – Maximum**		**FTCs**	
		Low-Snow	**Snow**	**Low-Snow**	**Snow**	**Low-Snow**	**Snow**	**Low-Snow**	**Snow**	**Low-Snow**	**Snow**
1	S	0.4	0.6	0.1 – 1.6	0.3 – 0.9	0.28	0.27	0.25 – 0.30	0.26 – 0.47	0	0
1	M	0.7	1.1	0.4 – 1.6	0.8 – 1.4	0.25	0.28	0.23 – 0.27	0.27 – 0.42	0	0
1	B	0.9	0.7	0.7 – 1.6	0.5 – 1.0	0.30	0.33	0.29 – 0.33	0.33 – 0.35	0	0
2	S	-0.9	-0.6	-5.0 – 4.5	-4.5 – 0.6	0.16	0.17	0.10 – 0.49	0.10 – 0.49	4	4
2	M	-0.4	0.0	-3.2 – 4.1	-2.5 – 1.0	0.17	0.21	0.08 – 0.59	0.15 – 0.43	3	5
2	B	-0.1	-0.1	-2.0 – 3.8	-1.0 – 0.7	0.20	0.31	0.14 – 0.36	0.27 – 0.35	6	1
3	S	1.1	0.9	-1.7 – 10.9	-1.3 – 10.1	0.21	0.22	0.10 – 0.39	0.08 – 0.51	7	3
3	M	1.0	1.1	0.0 – 8.8	0.0 – 8.6	0.22	0.26	0.07 – 0.48	0.14 – 0.4	0	0
3	B	1.3	0.8	0.2 – 9.3	-0.1 – 6.3	0.34	0.33	0.29 – 0.42	0.32 – 0.35	0	4
4	S	1.7	0.9	-2.9 – 14	-3.5 – 7.6	0.16	0.16	0.07 – 0.51	0.06 – 0.57	16	11
4	M	1.5	0.9	-0.6 – 7.1	-1.8 – 5.9	0.17	0.23	0.05 – 0.63	0.13 – 0.43	2	9
4	B	1.8	0.8	0.1 – 7.6	-0.7 – 4.3	0.31	0.32	0.26 – 0.39	0.27 – 0.35	0	3
5	S	19.7		7.6 – 34.4		0.24		0.22 – 0.3		0	

5	M	19.7	9.2 – 32.4	0.28	0.26 – 0.35		0	
5	B	19.2	11.1 – 28.5	0.30	0.29 – 0.31		0	
6	S	22.3	14.1 – 35.1	0.25	0.00 – 0.32		0	
6	M	21.8	15.0 – 31.9	0.28	0.00 – 0.36		0	
6	B	21.2	16.2 – 27.8	0.29	0.01 – 0.33		0	
7	S	20.8	14.0 – 31.6	0.20	0.00 – 0.48		0	
7	M	20.8	14.7 – 29.9	0.27	0.00 – 0.41		0	
7	B	20.4	16.7 – 29.4	0.00	0.00 – 0.15		0	
8	S	15.0	8.1 – 23.4	0.27	0.22 – 0.34		0	
8	M	15.1	8.6 – 23.0	0.32	0.28 – 0.40		0	
8	B	15.3	11.1 – 21.0	0.03	0.02 – 0.05		0	

The lack of soil frost is consistent with historical soil temperatures measured at the field site over six years prior to this study (Figure 3.4). Indeed, cold soil temperatures (<2.0 °C on average) were observed between mid-December and mid-March in all years; however, soil frost was only observed in two of the six years, at a depth of 17 cm. When soil frost occurred, the soil did not remain frozen for significant periods of time. Indeed, freezing occurred 17 cm in the soil profile in only three of the six winters, with 20.6 days frozen in total over a six-year period. No freezing occurred at 35 cm depth for the same time period.

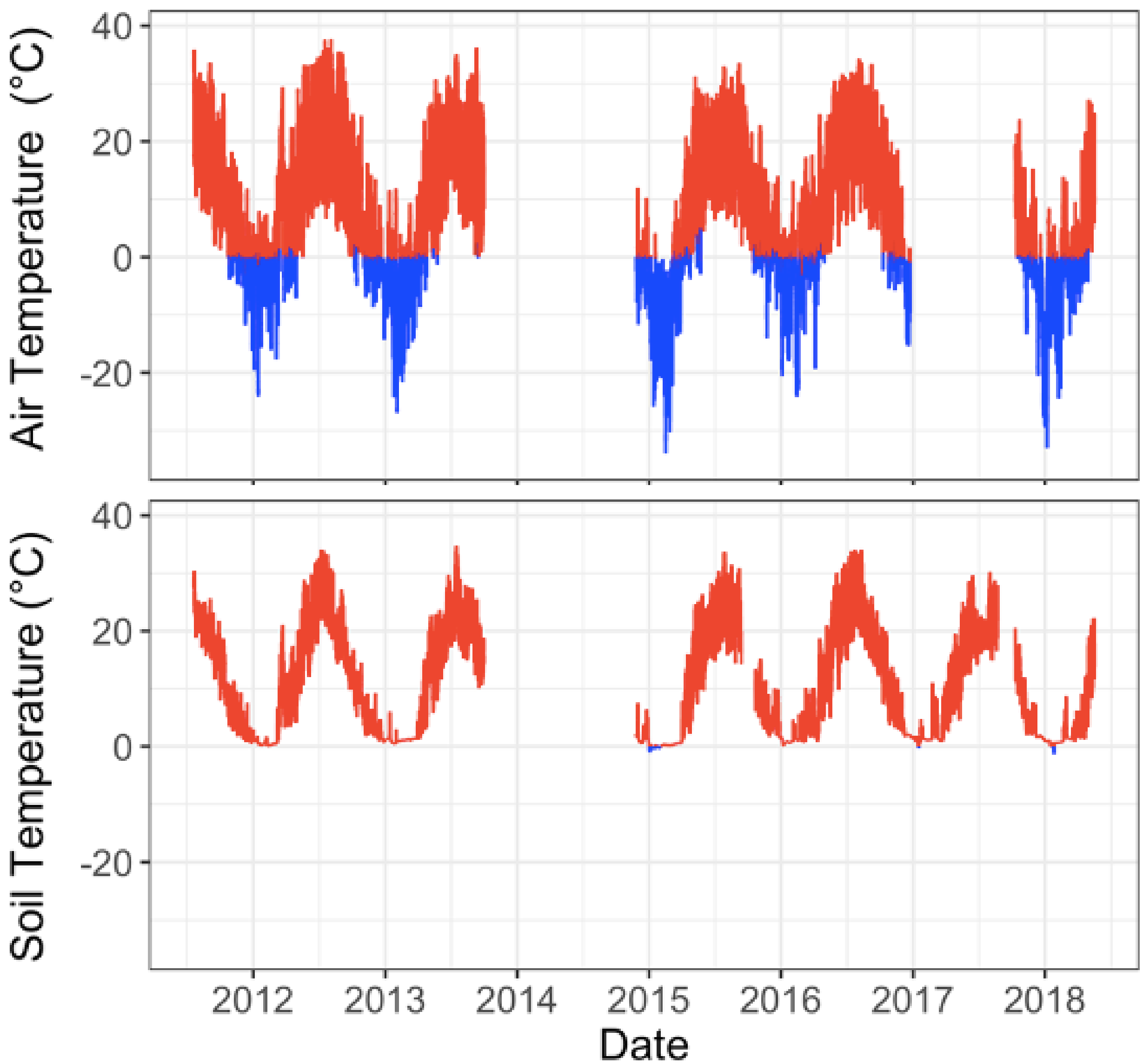


Figure 3.4. Historical hourly air temperature (grey), soil temperature at 17 cm depth (red when above zero, blue when equal to or below zero) and soil volumetric water content (green) from the same agricultural field as this study in St. Mary's, Ontario.

The removal of snow cover (i.e., low-snow (LS)) treatment led to differences in both soil temperature and soil moisture (volumetric water content) between the two plots. Although the two plots were similar, the LS plot experienced more extreme soil temperatures (colder and warmer) and more FTCs than the snow (S) plot (Table 3.3, Figure 3.2). As air temperatures exceeded zero during the day in the spring, FTCs in the soil occurred daily (warming in the day and freezing at night) for approximately 10 days in the LS plot (and had 16 FTC total for T_4), while the S plot cycled daily for 9 days, missing the first warm cycle likely as the snow melted (the S plot had 11 total FTC for T_4). By the end of T_4, the plots matched in temperature as snow had completely melted from the field. There were subtle differences in moisture between the plots. In general, volumetric soil moisture content in the S plot was greater than in the LS plot, especially at the surface (Figure 3.3; Table 3.3). Soil moisture declined with depth in both plots; however, soil moisture fluctuations deeper in the soil were greater for the LS plot than the S plot. There were statistically significant differences between the moisture of the LS and S plots according to a paired t-test ($p < 0.001$).

3.4.2 Annual Trends of Soil Available Phosphorus and Net Phosphorus Transformations and the Impact of Snow Removal on P Availability and Transformations

Qualitative differences in soil P dynamics were observed both with soil depth and season (Figure 3.5). Water extractable phosphorus concentrations were greater and more variable during the NGS than the GS. The top two soil depths (0-5 cm) were greater and had more variability (mean WEP for fresh 0-2 cm soils: 3.62 mg kg^{-1}, mean 2-5 cm WEP: 1.87 mg kg^{-1}) while the same variability was not apparent in the deeper soil samples (5-10 cm) and were less variable (mean bottom WEP: 0.86 mg kg^{-1}). Water extractable P concentration medians were greatest at the surface and declined with depth across seasons, net P_{trans} did not vary with depth. The variability in WEP and net P_{trans} was greatest at the surface and decreased with depth

(Figure 3.5 a). The observed P was greatest in the NGS especially for surface and middle depths and declined in the GS at these depths (Figure 3.5 a).

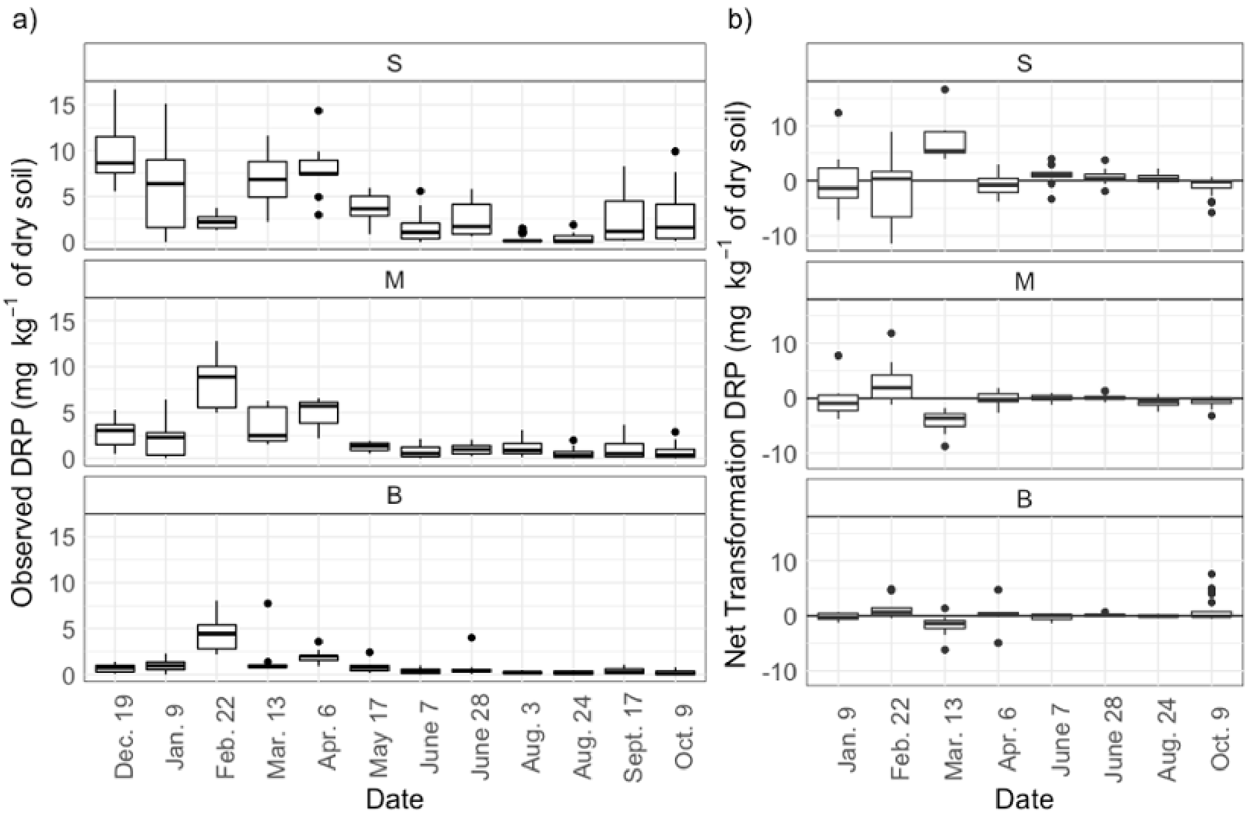


Figure 3.5 Plot **a**) shows SRP concentrations over time, and **b**) shows net P transformation rates, the difference between the soil at the beginning of the time period to the soil in bags at the end of the time period. The end of the time period is the date reported. A positive value indicates mineralization through the time period, while a negative value indicates immobilization for the time period in the incubation bags. The NGS and growing season data are presented for three depths, surface (S), middle (M) and bottom (B). The top and bottom of the boxplots show the interquartile range (IQR) of the data between the 75th percentile and 25th percentile respectively, with median in the middle of the box. The outliers are outside of the whisker's length, that are less than Q1-1.5*IQR, or more than Q3+1.5*IQR. The plots depict typical field conditions for the year, in the NGS is labelled snow (S), as the snow condition in the study was the typical weather condition.

Seasonal differences in WEP and P_{trans} were evident, though largely not significant. The median observed changes of WEP did not statistically differ between the GS and the NGS for all data pooled or when divided by depth ($p > 0.05$) according to a one-way t-test. Clearly, the

P_{trans} rates were more variable during the NGS for all three depths (Figure 3.5 b), however median P_{trans} rates did not differ significantly between the NGS and GS ($p > 0.05$), except for the bottom depth ($p < 0.05$).

Observed changes in WEP against net P_{trans} rates demonstrate comparable rates that follow a 1:1 line consistently (Figure 3.6) and are supported by a significant ($p < 0.001$), moderate positive relationship (0.56) in a Spearman's Rank correlation matrix (Figure 3.7). The samples along the 1:1 line represent the changes in WEP are consistent between the fresh soil samples and the hydrologically controlled soil samples in the bag. Samples above the 1:1 line show that observed changes in WEP was greater than transformation rates of WEP, while below the 1:1 line, the opposite is true.

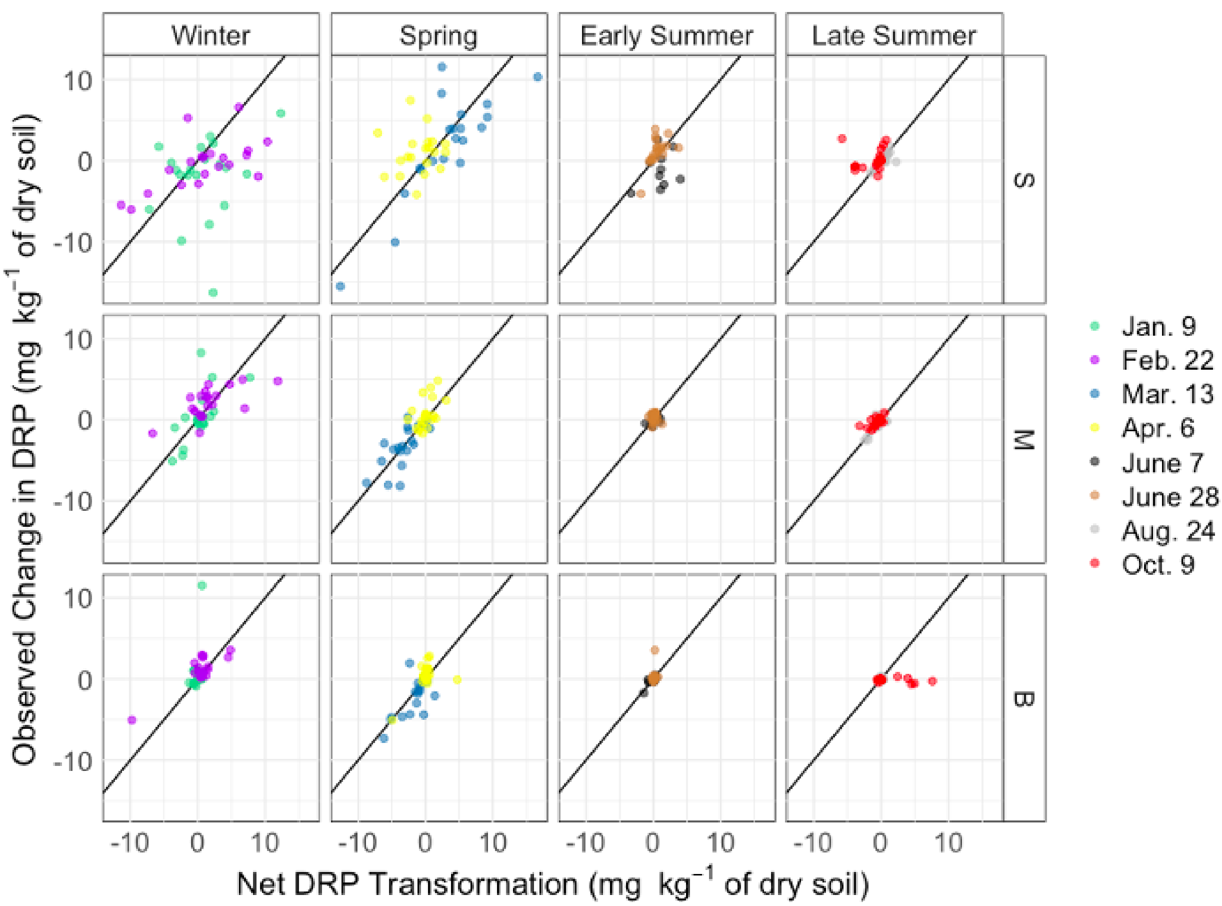


Figure 3.6. Observed change in WEP compared to net P_{trans} with the surface, middle and bottom depths separated, and four general time periods: winter (January, February), early spring (March, April), early summer (June), and late summer (August, October). The colours further delineate the time periods. The depth of the soil is faceted by surface (S; 0-2 cm), middle (M; 2-5 cm), and bottom (B; 5-10 cm). There is a one-to-one line for reference. Values above this line indicate observed change values were greater than P_{trans} values, and values below this line indicate P_{trans} values are greater than observed change values.

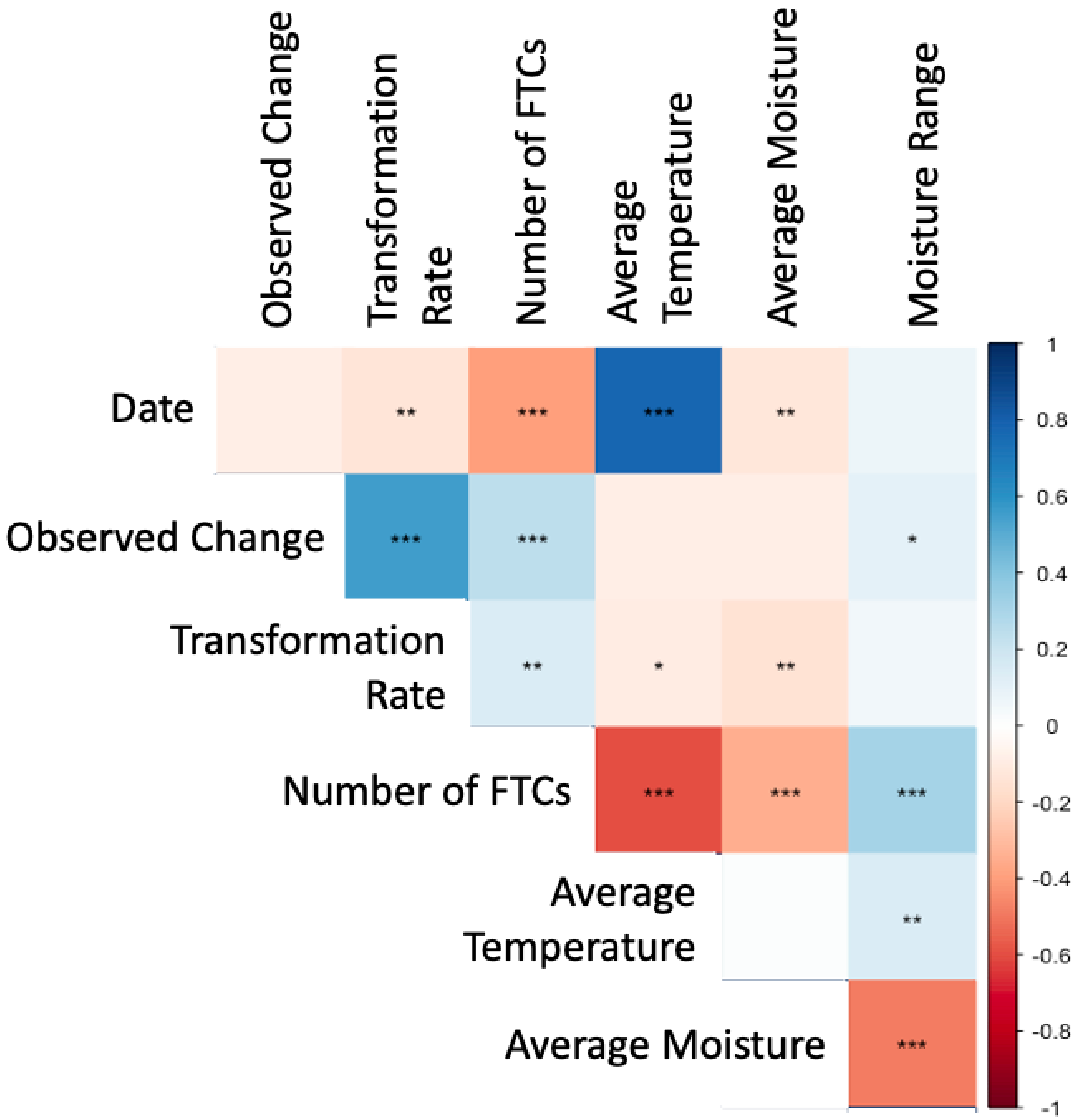


Figure 3.7. A Spearman rank correlation matrix with all data pooled (i.e., all seasons, all soil depths and experimental treatment (LS and S)). The date was reduced to time period number to have numerical input for the model. The P variables considered were the observed change in WEP (the WEP from after three weeks, subtracted by the WEP from the beginning of the time period) and P transformation rate (P_{trans}; the WEP after three weeks which had been held in an incubation bag subtracted by the initial soil WEP at the beginning of the time period). The climate variables considered were the number of freeze-thaw cycles (FTCs), average soil

temperature, average soil moisture, and the moisture range (maximum – the minimum volumetric water content). The colour depicts the direction of the relationship, and the Asterix's depict the p value with * < 0.05, ** < 0.01, and *** < 0.001.

Largely the P_{trans} rates are greater than observed changes in WEP at the surface in winter, while at lower depths the opposite is true, indicating WEP is translocated down the soil profile. On February 22nd, a major melt event occurred at which point WEP was greater at the middle and bottom depths than at the surface depth (Figure 3.5). While this shift was apparent in the ambient soil, it was not apparent in the buried bags that protected the soil from runoff losses as there were a number of samples below the 1:1 line (Figure 3.6), suggesting that this shift in WEP with depth was driven by the melt event. The return of soil WEP to pre-melt levels was apparent in both the ambient soil samples and buried bags in the time period that followed this thaw event (March 13th), as the majority of the samples were below the 1:1 line. In the early summer (June 7th), the observed SRP change were smaller than the transformation rates, especially at the surface (Figure 3.6) which follows a translocation pattern, however there was no significant rain events prior to that sample collection period. Likely, between May 17th and June 7th, P_{trans} rates were stable at the surface in the bag, while P declined due to corn root growth in the soil (Figure 3.5 a). The following period (June 28th), the opposite was true (coinciding with increased soil moisture occurring at the surface, Figure SoilMois). In late summer, the August 24th time period had a moisture event at the end of the time period, and there were no large differences in observed WEP and P_{trans}. The October 9th time period had more observed P than P_{trans} at the surface and the opposite true at depth and the moisture was increased during this time period.

Although qualitative differences in soil moisture and temperature were seen between the snow and low-snow plots, a comparison of WEP and P_{trans} between the snow-covered and low-snow plot did not reveal statistically significant differences. Although observed WEP (Figure 3.8 a) appeared to be higher in the snow-covered plot than in the low-snow plot, this was the case for all time periods including prior to when the treatments were implemented (December 19th) suggesting that the observed differences were spatial differences between the two plots, however examination of the spatial distribution of WEP and P_{trans} did not demonstrate any in-field spatial patterns (Appendix A1). There were subtle differences in P_{trans} between the plots (Figure 3.8 b) however, no consistent differences occurred between the two plots. A Mann Whitney Wilcoxon test found no significant differences between the snow and low-snow plots for observed change and P_{trans} rate ($p > 0.05$) for each depth, or with all data pooled. Notably, the two plots presented differently for the February 22nd melt event. Following the thaw, soil WEP was smaller under the snow plot than the low-snow plot. This reduced WEP in the snow plot was concomitant with increased WEP at depth, as well as increased soil moisture. Although the low-snow plot also had increased WEP at the middle and bottom depths, it did not show decreases at the surface, and VWC did not increase at the surface to the same extent as the middle and bottom depths did (likely due to lack of snow melt directly on the surface of the soil, but moisture translocating into the soil plot). Both of these observations for the plots were reflected in the net P transformation rates as the February 22nd time period P_{trans} was consistent with the time previous (not impacted due to the bag), and over the following time period (March 13th) the S surface soil increased, while the LS and S middle and bottom depths decreased in WEP.

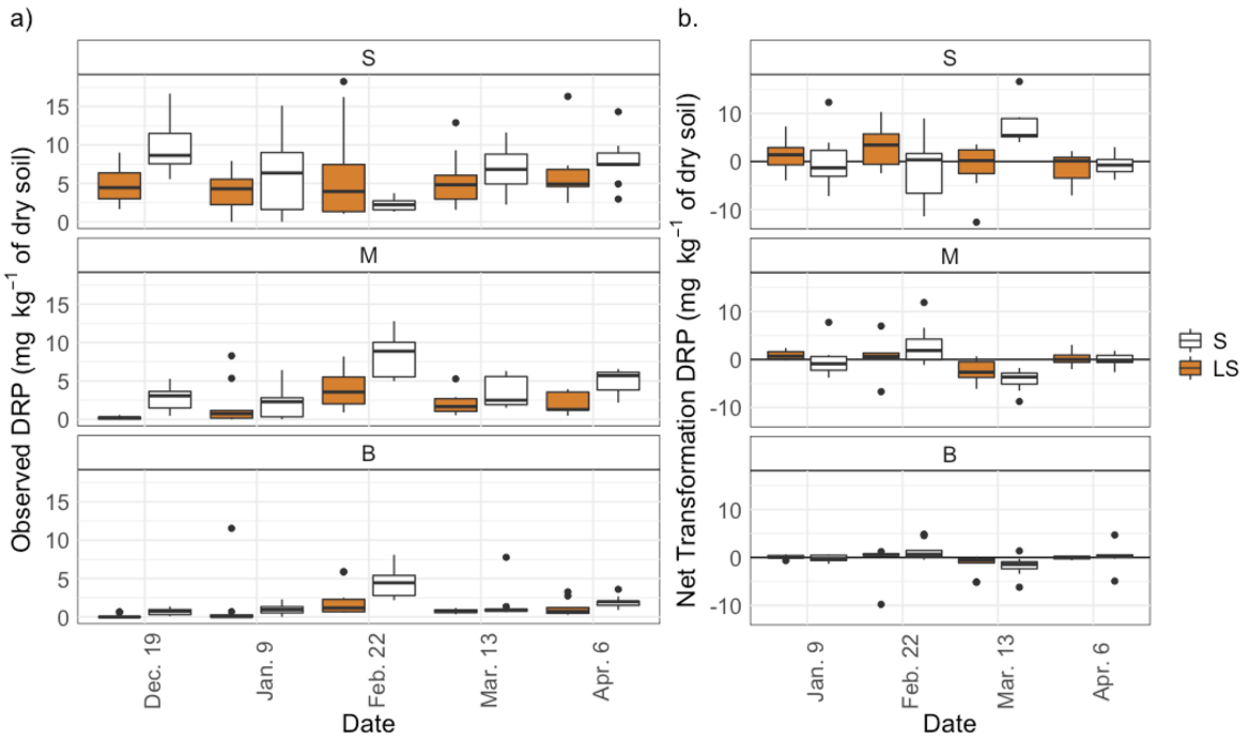


Figure 3.8. a) The boxplot shows the observed values of P in the NGS at each time period. Typical, snow (S) covered field condition is shown with the white filled boxplot, and the low-snow (LS) condition is represented with brown filled boxplots. The boxplots represent 10 samples at each time period for each depth. The top and bottom of the boxplots show the interquartile range (IQR) of the data between the 75th percentile and 25th percentile respectively, with median in the middle of the box. The three depths sampled are represented in order, with S indicating the surface soil depth (0-2 cm), M indicating the middle depth (2-5 cm), and B indicating the bottom soil depth (5-10 cm). The outliers are outside of the whisker's length, that are less than Q1-1.5*IQR, or more than Q3+1.5*IQR. While **b**) shows the net P transformation rates for each respective time period for typical field conditions, snow covered (S) represented with white boxplots and low snow (LS) conditions represented by brown boxplots. The three depths sampled are represented in order, with S indicating the surface soil depth (0-2 cm), M indicating the middle depth (2-5 cm), and B indicating the bottom soil depth (5-10 cm). The top and bottom of the boxplots show the interquartile range (IQR) of the data between the 75th percentile and 25th percentile respectively, with median in the middle of the box. The outliers are outside of the whisker's length, that are less than Q1-1.5*IQR, or more than Q3+1.5*IQR.

3.4.3 Relationship Between Environmental Conditions and Soil P Dynamics

Although significant differences in observed change in WEP and P_{trans} were not apparent between the snow-covered and low-snow plots, with observed change in WEP and P_{trans} rates annual differences with climate conditions were apparent (Figure 3.7). A Spearman Rank correlation found the observed change in WEP had a significant relationship ($p < 0.05$) with the moisture range over the time period, while the P_{trans} rates were significantly related to the average temperature ($p < 0.05$) and average moisture ($p < 0.01$) over the time periods (Figure 3.7). Both the observed change in P and P_{trans} had significant relationships to the number of FTCs (Figure 3.7; $p < 0.001$ and $p < 0.01$, respectively), as well, the number of FTCs were related significantly to average temperature, average moisture and range of moisture (Figure 3.7; $p < 0.001$). Furthermore, an examination of instantaneous soil moisture at the time of sampling (Figure 3.9) and soil temperature at the time of sampling (Appendix A2) suggests that soil moisture had an impact (Spearman Rank Correlation $p < 2.2e-16$) on soil P dynamics whereas soil temperature had little effect. An apparent threshold moisture existed in the soil, below which WEP was very low and did not exceed 2 mg kg^{-1}. This moisture threshold (25 g g^{-1}) was below the presumed field capacity of the soil (30 g g^{-1} for the 0-5 cm depth, 32 g g^{-1} from 5-15 cm depth) using textural data provided from this site by Plach et al. (2018a) and the approach of Elnesr (2013). This threshold was apparent during all seasons and at all depths (Figure 3.9). Although there were generally positive relationships between WEP and GWC, once the threshold of 25 g g^{-1} was exceeded, more scatter was present.

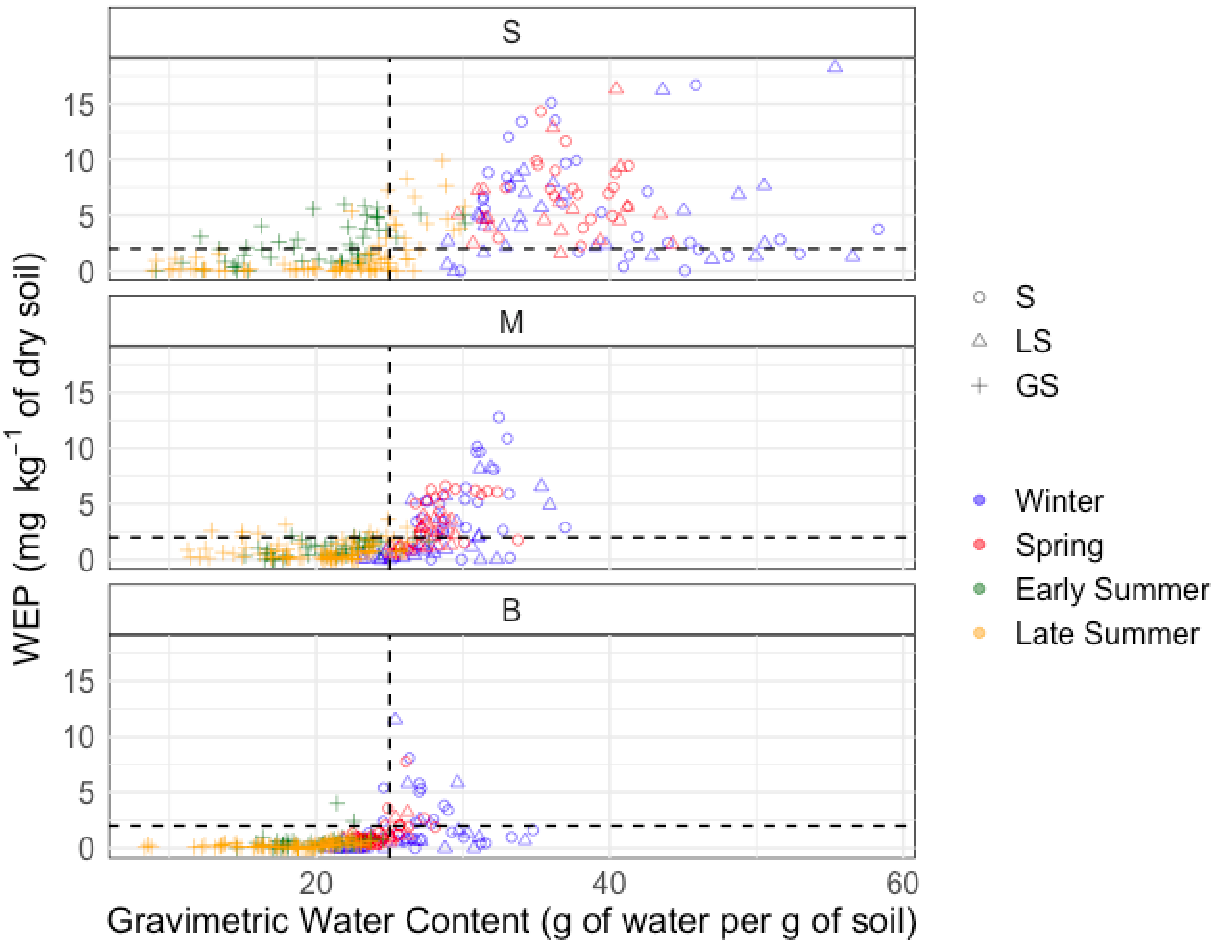


Figure 3.9. Comparison of WEP concentration (mg per kg of dry soil) with the gravimetric water content (in grams of water per gram of soil). Each colour represents the seasons, winter included samples from Dec. 19th, 2017, Jan. 9th, 2018, and Feb. 22nd, 2018; spring included samples from Mar. 13th, 2018, and Apr. 6th, 2018; early summer included samples from May 17th, 2018, June 7th, 2018, and June 28th, 2018; and late summer included samples from Aug. 3rd, , 2018 Aug 24th, 2018, Sept. 17th, 2018, and Oct. 9th, 2018. Shape represented plot distinctions, snow (S), low snow (LS) and growing season (GS). Depth in soil profile is faceted to show the surface to deepest depth, surface (represented by S; 0-2 cm), middle (represented by M; 2-5 cm), and bottom depth (represented by B; 5-10 cm). The horizontal line is at 2mg kg^{-1} of dry soil, and vertical line is at 25 g g^{-1}.

3.5 Discussion

3.5.1 Significance of Climate Variability in Nutrient Pools of Phosphorus

Soil WEP concentrations in this study varied by depth, as surface soil ranged from 20 mg kg^{-1} to below detection limits, 0 mg kg^{-1} and a median of 3 mg kg^{-1}, with middle and bottom depths reaching a maximum of 13 mg kg^{-1} and 12 mg kg^{-1}, respectively. The minimum for middle and bottom depth were below detection limit and the median was 1 mg kg^{-1} and 0.5 mg kg^{-1}, respectively. The stratification of soluble P in the agricultural setting is comparable to previous reports of surface soil WEP in Great Lakes Region agricultural settings (Smith et al., 2017). In a Canadian context, soil WEP concentrations reported here are below previous reports of surface soil WEP in Canadian agricultural settings. For example, soil WEP concentrations in two calcareous mineral soils in MB averaged 41 mg kg^{-1} and 4 mg kg^{-1} (Kashem et al., 2004), while in an acidic BC soil, an average of 3.7 (mg kg^{-1}) was found (Messiga et al., 2021). From 1981 to 2006 Ontario saw an increase in WEP from 1.18 to 1.84 (mg kg^{-1}), which is well below the environmental WEP threshold of 4 mg kg^{-1} (Van Bochove et al., 2012). Overall, this is greater than WEP values reported in this study, however methodology is different with this study as WEP was taken on fresh samples, whereas the Self-Davis WEP procedure was used in these studies to determine WEP, which dries soils prior to extraction. In this study field moist samples were tested for WEP as drying soil is known to increase P concentrations by as much as 6 times in a laboratory setting (Bartlett & James 1980); however kept the same ratio of soil:water for extraction as the Self-Davis procedure, so there was overall more moisture exctracting the soils in this study as soils were field moist. With these considerations, the fresh soil samples had an average below the environmental WEP threshold, even at the surface where the highest WEP concentrations were found.

Median soil WEP concentrations were larger and variable during the NGS relative to the GS. This change in available P is consistent with the findings of Sorn-Srivichai et al., (1988) (in New Zealand, testing WEP and Olsen-P), but contrasts the findings of Pfeifer-Meister et al. (2007) (in Oregon testing Olsen-P) and Omer et al. (2018) (in New Mexico testing WEP) as P decreased in the NGS and increased in the GS. Given that concentrations of WEP in soil are controlled by a variety of factors including sorption or precipitation (Zhu et al., 2018), pH (Penn & Camberato, 2019; Penn & Bryant, 2008), P solubilizing or immobilizing microorganisms (Alori et al., 2017; Pfeifer-Meister et al., 2007), crop uptake (Piotrowska-Długosz et al., 2020), and plant freezing (Liu et al., 2013; Liu et al., 2014; Cober et al., 2019), contrasting seasonal patterns in soil WEP concentrations are likely caused by a combination of these factors.

In the Great Lakes Region in North America, it is well documented that SRP concentrations in streams, headwaters and tile drains are greater during the NGS in agricultural watersheds (Van Esbroeck et al., 2016; Lam et al., 2016; Huisman et al., 2013). While the increased loads of SRP and TP to runoff during the NGS are largely driven by the large volumes of runoff (Macrae et al., 2007, 2010), the current study suggests that the supply of P from soils may also be larger during the NGS when soil moisture is generally higher. This is the only study, as far as the researcher knows, to quantify soil WEP seasonally on an agricultural field in the Great Lakes Region of North America. The significant relationships between all climate variables and time period number speaks to the seasonal relationships between soil temperature and soil moisture in this region, although P_{trans} rate was related to date, the observed change in P did not relate to time of year. Although P concentrations in both surface runoff and tile drainage have been related to soil agronomic P (e.g. Duncan et al., 2017; Pease et al., 2018; Plach et al., 2018b), Wang et al. (2010) and Pote (1996) suggest that WEP is a better predictor of runoff P concentrations than other soil agronomic P tests. Given the dynamic nature of WEP throughout the year, our ability to predict P concentrations and loads in runoff may be improved through a better representation of temporal variability in WEP concentrations in surface soils.

3.5.2 Significance of Reduced Snow Cover on Soil P Dynamics

Large differences in WEP concentrations were expected between the low-snow and snow-covered plots; however natural within-field variability exceeded any differences in WEP between the plots, suggesting that reduced snow cover may not substantially impact the potential supply of WEP in soils. A lack of extensive frost at depth was found historically at this site (Macrae, unpublished data), and supports the decision to study shallow depths for FTC impacts. Although differences in both soil temperature and VMC were observed between the low-snow and snow plots, as has been reported in other snow manipulation studies (Reinmann & Templer, 2018; Ruan & Robertson, 2017). Temperature during the time period was not strongly related to fresh soil WEP in the field (Appendix A2), suggesting that soil WEP is controlled by other factors. While it has been hypothesized that P concentrations will change with increased FTCs due to microbial death (Feng et al., 2007; Yevdokimov et al., 2016), plant senescence (Riddle & Bergström, 2013; Lozier et al., 2017), and changes in soil degradation or aggregation (Kværnø & Øygarden, 2006; Edwards, 2013) which may decrease the capacity for soil buffering of P and increase the release of adsorbed P (Fan et al., 2014), all of these findings have been from laboratory studies which may not reflect field conditions. Indeed, despite prolonged cold air temperatures (between 0 °C and -9 °C for weeks at a time) over six winters at the field site, the soil seldom froze at 17 cm depth. This is consistent with observations from field sites near Londesborough and London, Ontario which are within 100km of the study site. Soil seldom froze in an 8-year period at the 10 cm depth for both field sites, and the minimum soil temperatures reached were -2.5 °C and -2.3 °C for the Londesborough site and the London site, respectively (Macrae, unpublished data).

Although soil microbial activity and soil degradation or aggregation could have differed between the low-snow and snow-covered plots in this study as the number of FTCs between the plots differed, these did not translate to differences in observed changes of WEP or P_{trans} rates. The differences in soil temperatures between the low-snow and snow-covered plots were consistent with soil temperatures caused by climate change so far, including warmer soil temperatures in the spring, likely caused by the coinciding reduced snowpack (Qian et al., 2011). Thus, this *in situ* study suggests that the anticipated changes in temperature may not lead to increased WEP or P_{trans} in soils. Climate change may, however, lead to differences in moisture regime and runoff processes which may impact P losses from fields.

3.5.3 Environmental Drivers and P Dynamics

Environmental conditions (i.e., number of FTCs, average volumetric water content over the study period, average soil temperature for the study period, and volumetric water content range) were considered against observed change in P and P_{trans} rates with significant results found with both and the number of FTCs. The observe change in P significantly related to moisture range, and P_{trans} rate significantly related to average temperature and average moisture. The P_{trans} rate also related significantly to date, and the temperature was significantly related to the date, therefore this may be the seasonal relationship at play. Although the average moisture was significantly related to date, the instantaneous soil temperature did not show clear relationships with fresh WEP concentrations (Appendix A2). It is clear moisture has a significant role in observed change in P, P_{trans} rates, and this was further explored in the instantaneous (fresh) WEP concentration.

The GWC of the soil and fresh WEP concentration had a strong positive correlation despite season, soil depth, or plot condition (LS or S). This relationship is likely controlled by an abiotic geochemical process and is potentially specific to agricultural settings as there is less organic molecules of P and larger inorganic P pools than in forested catchments (De Schrijver et al., 2012). Previous inorganic P (P_i) fractionation data has been reported from this site (site STM Plach et al., 2018a), and reported the proportion of loosely adsorbed P_i as comprising approximately 15%, in the surface soils (0-5 cm) which could be influenced by moisture in the soil (Pote et al., 1999). Whalen et al., (2001) found the addition of moisture stimulated soil mineralization of P, while physico-chemical controls dominantly release inorganic P over microbial mineralization (Oehl et al., 2004). Furthermore, soils that were dried for 15 days found fluxes of P in soil pore water declined significantly while the soil had increased iron-bound P, but when the dried soils were inundated with water, P fluxes increased to pre-dried soil concentrations and soils had decreased iron-bound P (C. Liu et al., 2019). Lozier et al. (2017) also saw inundated soils mobilize WEP and become subsequently depleted, similar to how this study describes the surface depth for the February time period, in both studies the plots were topographically lower in relation to the rest of the field and inundation occurred after a snowmelt event. Moisture in the field would have been from precipitation, which for Southern Ontario rainwater has a pH of 5.15 (National Atmospheric Chemistry (NATChem) Database), and as this is an organic surficial soil, and calcareous soil at depth with a pH around 7 in soils 0-15 cm (Plach et al. 2018a), there is the potential for dissolution of Ca-bound P phases and for P to be released into solution. As soil moisture decreases, P could be leached away or precipitated into a more stable mineral form. Whatever the mechanism causing increased WEP, the loosely adsorbed (soluble P) fraction was larger with increased moisture, independent of temperature. This is contrary to hypothesized impacts of FTCs on biogeochemical processes and the dominant source of WEP in field soils. However, this study increases the awareness that moisture regime shifts with climate change will likely have an important role in WEP supply and landscape runoff of SRP and deserves further research. Furthermore, the relationship between gravimetric water content and P availability in soils could improve sensitivity in modelling P runoff as moisture is an easy variable to test for in-field with probes.

3.5.4 Significance of Fall Manure Application and Crop Residues on Soil Phosphorus

Liquid dairy manure was applied at a rate of 17 kg P ha^{-1} in late September and winter wheat detritus was left on the field after harvest in the fall, both of these organic sources could have mineralized with FTCs to become sources of inorganic P during the study period. This is unlikely according to laboratory studies that have demonstrated relationships between manure and FTCs and estimates of P release from crop residues.

In one lab study, bioavailable P increased by over 23% from pig manure after FTCs, due to increased numbers of FTCs and increased moisture content caused physical degradation of the manure (Chen et al., 2019). That lab study froze the manure up to 30 times at -20°C and 18°C on a daily schedule, which is unrealistic for the climate of this study site. In a study of liquid dairy manure that was added to soil and incubated for just under six months, the liquid dairy manure increased WEP in the soil significantly when first applied, but between weeks 14 and 23, WEP increased by less than 1 mg kg^{-1} (Dagna & Mallarino, 2014). As dairy manure was applied at the end of September and this study commenced approximately three months later, this suggests the potential for mineralization from manure to occur during the study period is low. Additionally, temperatures were colder in the field than in the incubation temperature (25°C), which may have caused slower mineralization rates in the field. Therefore, the manure may have mineralized more available WEP over the study period but as the study started a few months after the application of manure when temperatures were cool or cold, it is unlikely that the manure application had a large impact on results. The fact that soil WEP did not decline throughout the NGS in the current study from the early winter to spring suggests that the stark seasonal differences in WEP are not driven by a release of the manure to runoff during snowmelt alone.

Phosphorus can also be supplied to soil from senescing or dead crop residues on fields. Studies have shown that cover crops and residues can release a considerable quantity of P (J. Liu et al., 2019; Elliott, 2013). However, the P released from crop residues is smaller than what is released by cover crops (e.g., Elliot, 2013; Lozier et al., 2017) with much of the P lost from vegetation that underwent FTCs, retained by soils (J. Liu et al., 2019). The P in the wheat grain can be as much as 90% of the P compared to the shoots and grain in specific wheat genotypes (Batten and Khan, 1987; Batten, 1992). Elliott (2013) found significantly more TP and SRP in living wheat crop after FTCs than in wheat stubble alone. Additionally, Lozier et al. (2017) found significantly more TP and SRP in straw with grain samples than stubble alone after a season of FTC on a field. In another field study, Cober et al. (2019) found WEP of wheat stubble declined after several FTCs, however remained significantly low throughout the NGS and was <5% of the total P available. Lozier et al. (2017) found wheat WEP, and TP did not vary significantly through the NGS. Therefore, in this study it seems plausible that the proportion of available P in the soil is either consistently or not greatly impacted by wheat stubble left on the field. However, future studies would do well to control and test for vegetation impacts on P as other studies have found different species to significantly contribute to P release after FTCs (Cober et al., 2019; Lozier et al., 2017).

3.6 Conclusion

Results of this field-based study demonstrated the importance of the NGS to significantly increase soil P availability relative to the GS within an agricultural field of the southern Great Lakes region. Within the NGS, the snow removal experiment successfully changed the soil temperature extremes to what is expected with climate change in Southern Ontario. While these temperature differences alone did not produce differences in P concentrations, climate change scenarios also anticipate increased moisture in the NGS for this region. Evidence suggests a strong relationship with GWC and WEP, potentially influenced by buffering capacity of the soil, pH, soil texture, or anoxic soil conditions. Future studies could systematically determine this relationship in other soil textures, soil pH's, and with different moisture contents to help inform modelling and management decisions. Furthermore, soil moisture is a simple, cost-effective variable to determine or monitor, therefore this study has significant implications when considering the efficacy of fertilizers or legacy P availability in soils.

Chapter 4

Impacts of Moisture, Freeze-Thaw Cycle Number, Duration and Magnitude on Potential Phosphorus Mobilization From Agricultural Soil

4.1 Abstract

Excess loading of agricultural phosphorus (P) from non-point sources is contributing to the eutrophication of freshwater systems. Much of these losses occur during snowmelt in cold regions. Climate change may exacerbate this problem by increasing the release of P from soils following freeze-thaw cycles (FTCs) and runoff events. This study employed a laboratory experiment to investigate the impacts of frost magnitude (-18°C, -4°C, or 4°C), frost event duration (1, 6 d), number of freeze-thaw cycles (1, 2, 3) and simulated rainfall for several characteristics: soil water extractable P (WEP), Olsen P, microbial biomass P (Mic-P), and soil aggregate stability. Leachate after simulated rainfall on soil cores was analyzed for species concentration (SRP, TDP, and TP). Contrary to expectations, soil freezing magnitude had little effect on P dynamics. However, a longer, weekly duration of temperature treatment led to significant increases for WEP, Mic-P concentration, and a decline in soil aggregate stability. The increased moisture supply was significantly related to a decline in aggregate stability, while gravimetric water content was positively related to WEP and Mic-P. An increased moisture supply had greater impacts than temperature variability on soil P dynamics, suggesting that the increased moisture supply due to climate change will have a greater impact on P release from soils than temperature.

Keywords: Freeze-thaw cycles, soil phosphorus, climate change, runoff phosphorus, soil microbial biomass, soil aggregate stability

4.2 Introduction

Eutrophic conditions that lead to harmful and nuisance algal blooms are a global issue. In freshwater systems, these blooms are driven by elevated phosphorus (P) loads from anthropogenic point and nonpoint sources (Correll, 1998; Carpenter et al., 1998). Elevated P loads in agriculture-dominated temperate watersheds largely result from non-point source pollution (Smith et al., 2019). Phosphorus concentrations and loads in runoff have been found to increase with soil-test P (Pote et al., 1996; Maguire & Sims, 2002; Schroeder et al., 2004) and water extractable P (Wang et al., 2015; Maguire & Sims, 2002). Although soil P supply is largely driven by land management practices (i.e., application of P), the release of P from soils can also differ with hydrology and environmental conditions (Pote et al., 1996; Pease et al., 2018; Duncan et al., 2017), both of which may change with global warming.

Most P loading occurs during the non-growing season, particularly during snowmelt (Pulikowski et al., 2015; Rosenberg & Schroth, 2017; Van Esbroeck et al., 2016). The increased losses of P from agricultural watersheds are attributed to flashy water movement through the system in the spring, the desorption of P from soil to runoff, and the mobilization of redox sensitive suspended sediments from saturated soil conditions (Rosenberg & Schroth, 2017). In cold agricultural regions, large volumes of surface runoff in spring efficiently transport both dissolved and particulate P forms from fields (Van Esbroeck et al., 2016; Plach et al., 2019). While it has been found that there is more P available after FTCs (Kreyling et al., 2020), the underlying mechanisms were not determined. The greater P supply after FTCs can be from vegetation (Tiessen et al., 2014), from fine root death (Fitzhugh et al., 2001), and less microbial mediation of P (Lipson et al., 2000) due to cell lysis. These processes can all increase the supply of P available for runoff.

Climate change has begun to impact both temperature and moisture regimes, particularly during the winter period (Casson et al., 2019; Contosta et al., 2019). Warmer temperatures and reduced snowpacks are already occurring (Contosta et al., 2019). Reduced snowpack has historically been coupled with less soil frost because of the warmer temperatures associated with snowmelt (Henry, 2008; Contosta et al., 2019); however, a smaller snowpack also has the potential to lead to increased occurrences of soil frost (Reinmann & Templer, 2018). Indeed, increased air temperatures during winter may lead to an increase in the number of freeze-thaw cycles (FTCs) experienced by soil (Henry, 2008; Bush & Lemmen, 2019), and rain-on-snow events (Bush & Lemmen, 2019).

The changes in soil temperature and moisture under climate change have the potential to exacerbate phosphorus losses. For example, an increased frequency of FTC has been shown to increase the solubility of P in soils (Sun et al., 2019), possibly due to increased root death (Fitzhugh et al., 2001), increased microbial death (Gao et al., 2021), and decreased microbial P uptake (Lipson et al., 2000). Aggregate stability can be reduced with an increasing number of FTCs (Bullock et al., 2001), and also with increasing soil moisture (Kværnø & Øygarden 2006). Such changes in aggregate stability can modify the sorption or desorption of P as sorption exchange sites are exposed. Decreased aggregate stability also increases the potential for soil erosion (Oztas & Fayetorbay, 2003), which is accompanied by P loss (Huang et al., 2015).

The hydrological regime changes with climate change will exacerbate transport processes. Rain-on-snow events have higher flows (Casson et al., 2019) and have increased P losses from agricultural landscapes (Van Esbroeck et al., 2016). An increase in the magnitude of flows, coupled with increased P supply, have the potential to increase the occurrence of 'hot moments' (McClain et al., 2003; Macrae et al., 2007) in winter and spring, exacerbating water quality issues. Although hydrological changes with climate change have been explored, potential changes in the winter supply of P are poorly understood. An improved understanding of the impacts of high flows and freeze-thaw conditions on soil P release is needed to better predict the impacts of climate change on water quality.

In this study, intact soil cores were subjected to different magnitudes, durations and numbers of freezing cycles, with a subset exposed to repeated flushing events to address the following objectives: i) to quantify the effects of freezing magnitude and duration on soil P availability (i.e., water-extractable soluble reactive (WEP), total dissolved P (WEP_T) and nonreactive P (WEP_N) forms and Olsen P), ii) to relate differences in soil P availability and speciation under the variable climatic conditions to biotic and abiotic drivers, and iii) to quantify differences in the magnitude and speciation of P in leachate (soluble reactive P (SRP), dissolved nonreactive P (NRP), total dissolved P (TDP), particulate P (PP), and total P (TP)) under the variable climate conditions.

4.3 Methods

4.3.1 Field Sample Collection and Experimental Treatments

Intact soil cores were retrieved from an agricultural field in Ontario, Canada and returned to the laboratory for experimental treatment. Soil within the study field is classified as orthic gray brown luvisol predominantly loam till (Presant & Wicklund, 1971) with a mean bulk density of 1.42 g cm^{-3} for the top 10 cm of soil. The field is cropped (corn-soy rotation) and samples were collected in November 2018, approximately three weeks following corn harvest. The field was tilled and fertilized in spring prior to corn.

117 undisturbed soil cores (10cm depth x 5 cm inner diameter) were collected in pre-cut PVC pipe from within a 2m x 2m plot to minimize spatial variability. Samples were taken between crop rows, and surface plant residues were not included. Samples were kept in coolers with icepacks until the beginning of the experiment, approximately 36 hrs after sample collection. Coarse nylon mesh screening was placed over the bottom of half of the cores (the subset to receive simulated rainfall) to ensure that soil cores did not fall out of tubes during experiments. Prior to commencing the experiment, three soil cores were tested for initial concentrations of water-extractable phosphorus i.e., total dissolved form (WEP_T; median = 2.9 μg g^{-1}), water-extractable phosphorus, soluble reactive form (WEP; median = 2.6 μg g^{-1}), Olsen (bicarbonate extractable) phosphorus (Ols-P; median =14 μg g^{-1}), and microbial biomass phosphorus (Mic-P; median = 18 μg g^{-1}). Laboratory analysis of soil extractions are described in section 4.3.2.

The factorial design of this experiment compared four variables: air and soil temperature (-18°C, -4°C, 4°C), duration of freeze (24 hrs or 6 days), freeze-thaw cycle number (1^{st}, 2^{nd}, or 3^{rd}) and moisture condition (field moist with no rainfall, or rained on with simulated rainfall; Figure 4.1), done in triplicate (3 temperatures x 2 duration x 3 cycles x 2 moisture conditions x triplicate = 108). The 6-day incubation treatment was selected to mimic length of frost cycles observed in the field (i.e., Chapter 3; Figure 3.4).

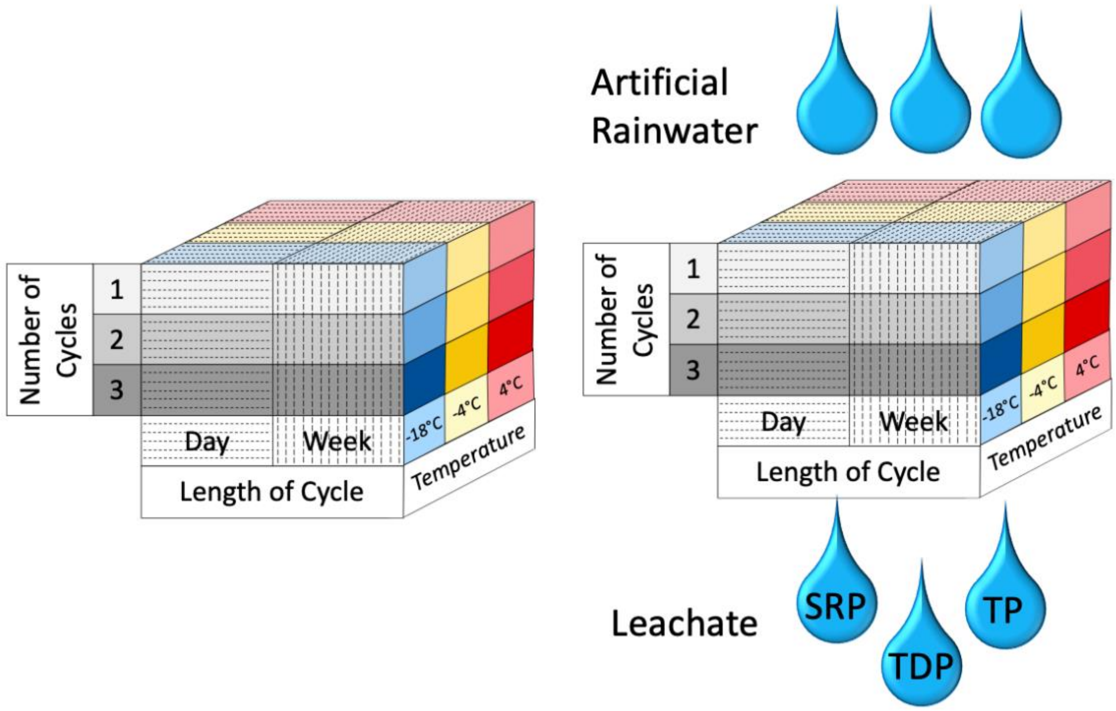


Figure 4.1 A representation of the factorial design of the experiment showing the different treatments the soils underwent. Soils were subjected to 1, 2, or 3 cycles, with cycles lasting 24 hours or 6 days (week), and the temperature magnitude was -18°C, -4°C, or 4°C, with some the exact same conditions duplicated and those cores rained on with artificial rainwater, for a total of 36 conditions. Each condition was done in triplicate for a total of 108 samples.

For the moisture condition treatment, directly after being taken out of the temperature condition, the rained-on cores received 40 mm (a medium sized rain event for this region) of artificial rainwater dripped on the surface of the soil using custom-drilled polyethylene reservoirs above each core. Artificial rainwater had ions added in similar proportions from rainwater collected in southern Ontario (National Atmospheric Chemistry (NATChem) Database) with a pH of 5.15±0.05. This includes: 2.17 mg L^{-1} SO_4^{2-}, 2.64 mg L^{-1} NO_3^-, 0.19 mg L^{-1} Cl^-, 0.81 mg L^{-1} NH_4^+, 0.10 mg L^{-1} Na^+, 0.48 mg L^{-1} Ca^{2+}, 0.08 mg L^{-1} Mg^{2+}, and 0.05 mg L^{-1} K^+. The simulated rainfall was added over a 1-hour period (40mm/h), ponded, and seeped into the soil. Any leachate from the cores was collected in clean polyethylene containers. A subsample was immediately filtered through 0.45 µm cellulose acetate filters (typically completed within 4 h) for subsequent analysis of soluble reactive P (SRP) and total dissolved P (TDP). An unfiltered subsampled was acidified to 0.2% H_2SO_4 for subsequent total P (TP) analysis.

For all soil cores, samples were thawed in coolers with icepacks (~ 10°C) for 24h and returned to the refrigerator or freezer. At each time step, a subset of cores for each condition were destructively sampled for analysis. Therefore, 108 of the 117 soil cores were used for the experimental treatments. An additional three were used to determine initial soil field conditions (prior to treatments), an additional three were used for bulk density measurements, and three more were used for logging temperatures throughout the experiments to ensure that soil temperatures reached the desired temperatures.

4.3.2 Laboratory Analysis

Soil samples were held in coolers for 24 hours after being taken out of the temperature treatment condition, as some samples underwent simulated rain and frozen soils needed time to thaw. Soils were sampled and extracted within 48 hours after being taken out of the temperature treatment condition. Soils were placed in clean polyethylene bags, homogenized, and had any large organic pieces removed. Subsamples were collected from each bag for the determination of Mic-P, Ols-P, WEP, and gravimetric water content. All extractions were done on moist (not dried) samples as drying can enhance WEP estimates (Pote et al., 1999). Bulk density was determined on three destructively sampled cores using standard techniques.

4.3.2.1 Microbial Biomass Phosphorus or Soil Extractions

Analysis for microbial biomass P followed the chloroform fumigation-extraction method of Brookes et al. (1982) and Voroney et al. (2006). Briefly, ~2 g of field moist sample was placed into a desiccator with 50 mL of $CHCl_3$ with boiling chips and moist paper towel. A vacuum pump vented the desiccator in a fumehood for several minutes, then was kept under pressure for 24 hours in the dark at room temperature. The samples were flushed of chloroform several times and then extracted with 40 mL of bicarbonate. Another ~2 g of field moist soil was bicarbonate extracted, and another ~2 g of field moist soil had a bicarbonate extraction with a 250 $\mu g\ mL^{-1}$ spike of P. All bicarbonate extracted samples were filtered with Whatman No. 42 filter papers for subsequent analysis of SRP. Microbial biomass was conducted in duplicate.

Calculations of microbial biomass P were determined by the equations outlined by Voroney et al. (2006):

$$\text{MB-P } (\mu g\ g^{-1}\ \text{soil}) = [(P_F - P_{UF})/k_{EP}] \times (100/R)$$

Where P_F is the weight of P_i in the fumigated soil samples, P_{UF} is the weight of P_i in the unfumigated soil samples, $k_{EP} = 0.40$ and represents the efficiency of extraction of microbial biomass P, and R = 100[(P_i spiked soil – soil P_{UF})/P_i spike], and is the percent recovery of the P_i spike, and P_i spike = 250 µg P_i. These weights were corrected to dry weight of the soil.

For the determination of WEP, approximately ~5 g of field moist soil was shaken with 50 mL of distilled water for one hour. The sample was gravity filtered through Whatman No. 42 filter papers and then syringe filtered through < 0.45 µm cellulose acetate filters (Sharpley et al., 2008). Although there is evidence that drying soils contributes to microbial biomass death (Turner & Haygarth, 2001; Turner & Haygarth, 2003) and as such, soils were extracted at field moist.

All soil extractions were expressed per unit of dry soil. To determine the mass of dry soil in a field-moist sample, the gravimetric water content was determined by weighing approximately ~5 g of moist soil then oven drying for 24 hours at 105°C (in duplicate).

All soil extracts and filtered leachate samples were frozen until colorimetric analysis could be done in the Biogeochemistry Lab at the University of Waterloo. All filtered samples were analyzed for SRP (Seal Analytical, Method no. G-103-93) and TDP (inline UV/ persulfate digestion Seal Analytical, Method no. G-092-93) using a Bran Luebbe AA3 (Seal Analytical, Seattle USA). Unfiltered leachate samples were digested with H_2SO_4 and $K_2S_2O_8$ in an autoclave (EPA/600R-93/100, Method 365.1) and subsequently analyzed for P colorimetrically (Seal Analytical Method no. G188-097).

To calculate NRP, the TDP concentration for a sample was subtracted by the SRP concentration. To calculate PP, the TP of a sample was subtracted by the TDP of the sample.

4.3.2.2 Aggregate Stability

Automated wet-sieving method was used according to Kemper and Rosenau (1986). Aggregate stability was performed on samples to represent the extreme of the conditions: rained-on or field moist, day or week duration, 4°C or -18°C, and 1 or 3 FTCs. Soil samples were air-dried then passed through < 1 mm and < 2 mm sieves to collect aggregates 1-2 mm in diameter. Using an automatic sieving apparatus (Eijkelkamp Agriserch Equipment 08.13. Giesbeek Netherlands), ~4 g of sample were moistened in a sieve, then submerged in cans of distilled water automatically at a rate of 34 times/min for three minutes. The slaked soil and distilled water cans were replaced by cans of dispersing solution (2 g of sodium hexametaphosphate L^{-1}). The sieve was continually submerged until the sand and root fragments remained. All pieces were oven-dried at 110°C until the water evaporated. Both cans and sieves were compared to their initial weight to find the weight of stones or roots, stable, and slaked soils, so that the percentage of water stable sediments could be calculated while correcting for sand or roots. The fraction of stable soil aggregates (WSA) was calculated from Moebius-Clune et al. (2016):

WSA = Wstable/Wtotal

Wstable = Wtotal – (Wslaked +Wstones)

Where W is the weight (g) of each respective portion of soil. The fraction of WSA was represented as a percentage (multiplied by 100) in the results.

4.3.2.3 Data Analysis

A Spearman rank correlation considered the temperature magnitude, cycle number, temperature duration, WEP species (SRP, NRP, TDP), leachate species (SRP, TDP, NRP, PP, TP), microbial biomass phosphorus (Mic-P) and water stable soil percentage (WSS). Individual relationships from the correlation plot were chosen and tested for significance including WEP with Mic-P, WEP_N with leachate NRP, leachate species with WSS, and WEP species with WSS.

Shapiro-Wilk's tests were used to determine whether data was normally distributed, and Bartlett tests were used to determine similar variability. Where data could not be transformed to a meet the assumptions needed for one-way ANOVAs, the non-parametric Kruskal-Wallis rank sum test was used. The effects of temperature magnitude, moisture condition, temperature duration and cycle number were tested using a series of one-way ANOVAs for Ols-P and WSS, and a series of Kruskal-Wallis rank sum tests for WEP, WEP_T, WEP_N, Mic-P and WSS.

To determine correlations for samples that met the normal distribution requirement, a simple linear regression was performed. Several variables including GWC, WEP, Ols-P, WSS were not normally distributed unless divided by the moisture condition first, additionally WEP was log transformed to meet the normal distribution condition. Two linear regressions were performed for the samples which needed to be divided by moisture condition, one for the field moist condition and one for the rained-on condition. Linear regressions tested GWC with WEP, Ols-P with WEP, and Ols-P with WSS.

4.4 Results

4.4.1 Available Phosphorus in Soil

Temperature magnitude (-18 °C, -4°C, +4°C) did not have a significant effect on soil P concentrations (WEP, WEP_N, WEP_T, and Ols-P, $p > 0.05$ for all relationships; Figure 4.2, Figure 4.3). However, concentrations of WEP, WEP_N, WEP_T, and Ols-P were significantly greater ($p < 0.05$) for the longer frost duration (weekly) than the short frost duration (daily) treatment. When data were split between the field-moist and rained-on treatments and retested, significant relationships between temperature magnitude and soil P species were not found (Appendix B1). Furthermore, the number of FTCs and the number of flushing events did not have a significant result for soil P concentrations WEP, WEP_T, and Ols-P ($p > 0.05$) except for WEP_N ($p < 0.05$; Figure 4.3), which was impacted by both FTC and flushing cycles.

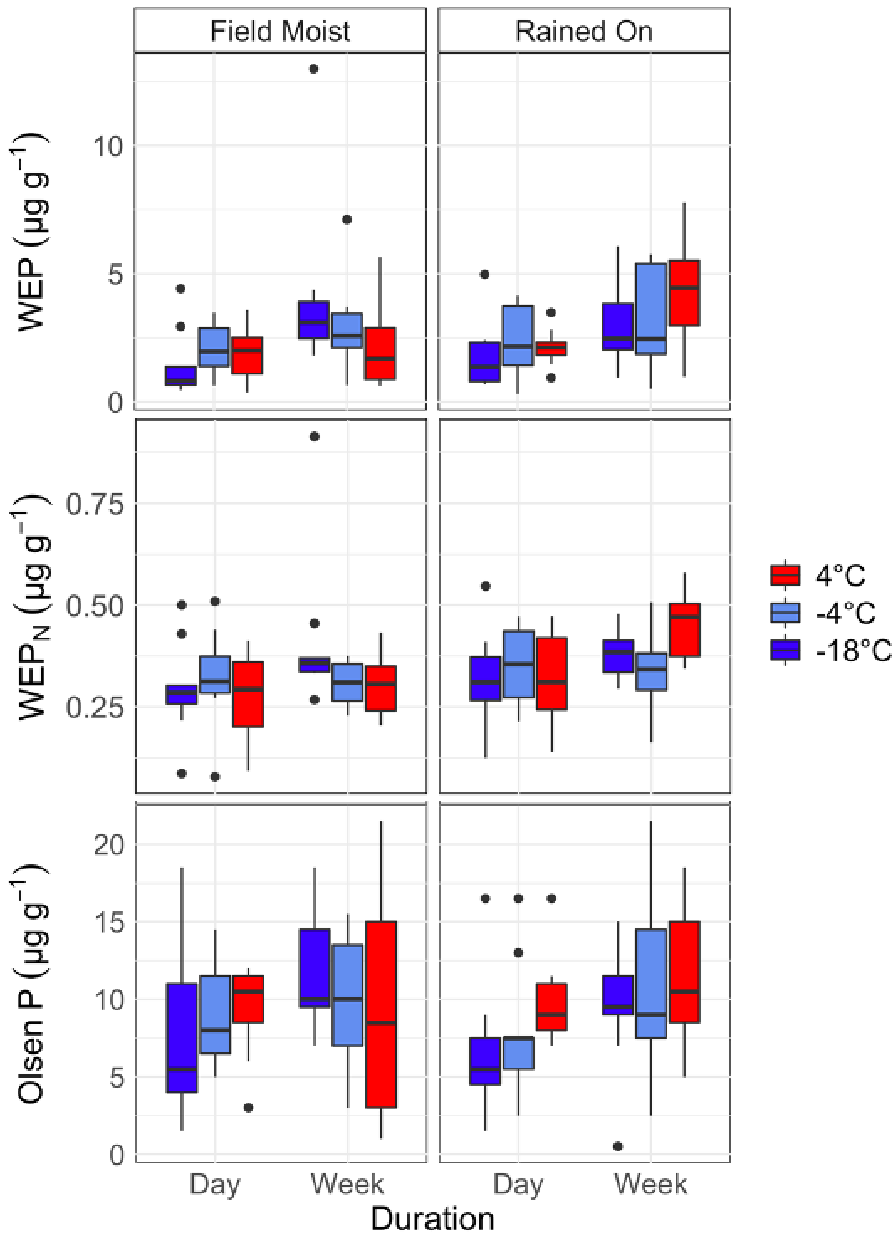


Figure 4.2 Phosphorus concentrations (µg per gram of dry soil) shown for water extractable soluble reactive phosphorus (WEP), nonreactive phosphorus (WEP_N) and Olsen P. Note that the concentrations are different Y-scales. Rained-on and field moist soil cores are separated. The data is further divided by duration of the freeze thaw-cycle, either day or week. Red represents 4°C, light blue -4°C, and blue -18°C. The top and bottom of the boxplots show the interquartile range (IQR) of the data. The 75th percentile and 25th percentile respectively, with the median line inside the box. The outliers are less than Q1-1.5*IQR or more than Q3+1.5*IQR.

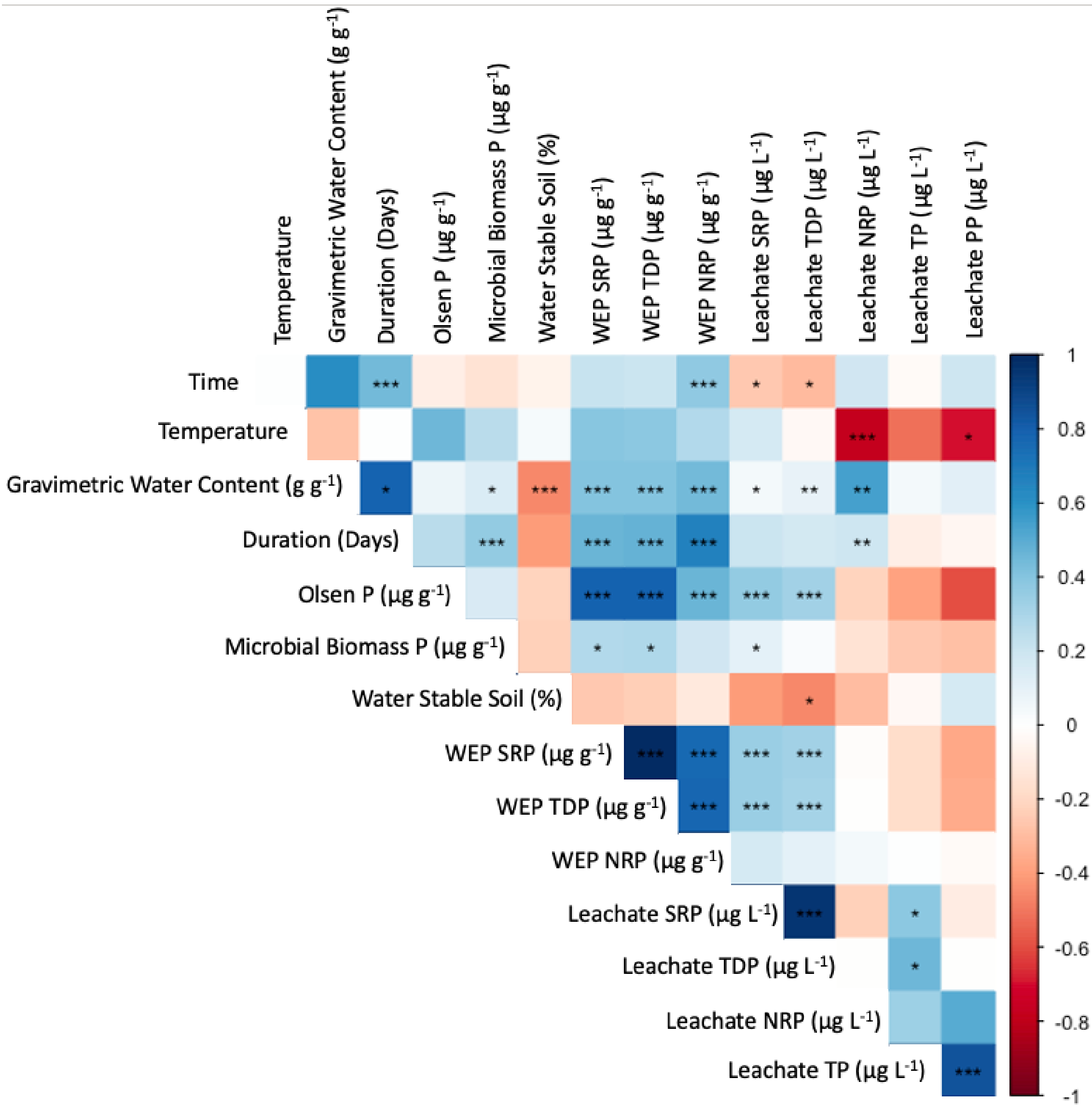


Figure 4.3 Spearman rank correlation between time period, temperature (-18°C, -4°C, 4°C), gravimetric water content (g g^{-1} of dry soil), duration in days, Olsen P (µg g^{-1}), microbial biomass P (µg g^{-1}), water stable soil (%), water extractable soluble reactive phosphorus (WEP) (µg g^{-1}), total dissolved phosphorus WEP (WEP_T) (µg g^{-1}), nonreactive phosphorus (WEP_N) (µg g^{-1}), leachate soluble reactive phosphorus (SRP) (µg L^{-1}), leachate total dissolved phosphorus (TDP) (µg L^{-1}), leachate nonreactive phosphorus (NRP) (µg L^{-1}), leachate total phosphorus (TP) (µg L^{-1}), and leachate particulate phosphorus (PP) (µg L^{-1}). Colour represents the direction and strength of the relationship, with -1 being red, 0 being white, and blue being

1. One Asterix represents a p-value of 0.05, two Asterix's represents a p-value of 0.01, and three Asterix's represents a p-value of 0.001 or less.

Although significant differences with temperature magnitude were not found, significant positive relationships were found between soil GWC and concentrations of all of the WEP species (Figure 4.4, Figure 4.3, $p < 0.001$). These significant relationships were present when all data were pooled, but also when data were split between the rained-on ($p < 0.001$) and field moist ($p = 0.002$) treatments (Figure 4.4**)**. Significant positive relationships were also found between log(WEP) and Ols-P ($p < 0.001$) (Figure 4.3).

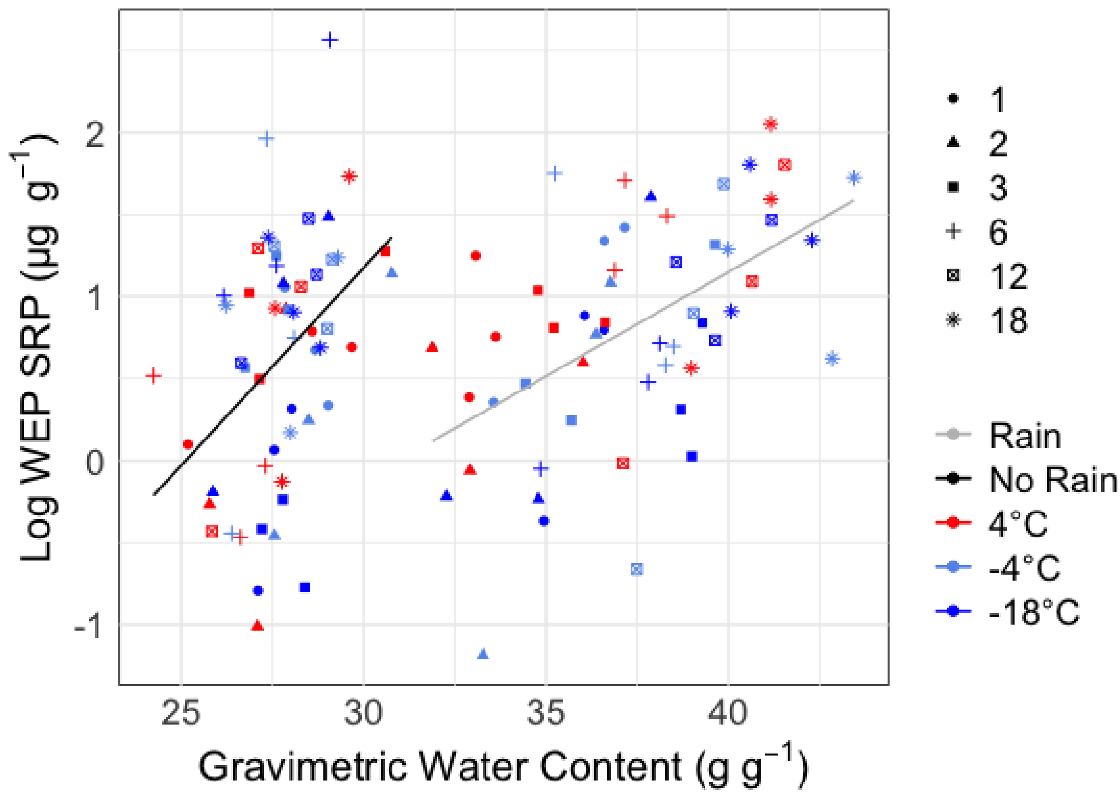


Figure 4.4 Relationships between the water extractable phosphorus soluble reactive fraction WEP SRP (µg g^{-1}) and soil gravimetric water content (GWC) (g g^{-1}). The black line is the linear regression between GWC and log (WEP) for the field moist (no rain) condition. The grey line is the linear regression between GWC and log (WEP) for the rain condition. The colours of the points are red, light blue, and blue for 4°C, -4°C, and -18°C, respectively. The shapes represent the duration in days the soil samples underwent the temperature treatment. Both relationships are significant ($p < 0.05$).

4.4.2 Microbial Biomass Phosphorus and Soil Stability

Similar to the WEP species, Mic-P was significantly greater with a longer frost duration (Figure 4.5, $p = 7.978e-08$), and Mic-P concentrations were significantly correlated with the duration of the experiment (Figure 4.3). Significant impacts of temperature magnitude were not found (Figure 4.3); despite qualitative differences observed for Mic-P at different temperatures, these were not statistically significant when divided by rained on condition ($p>0.05$) (Figure 4.5).

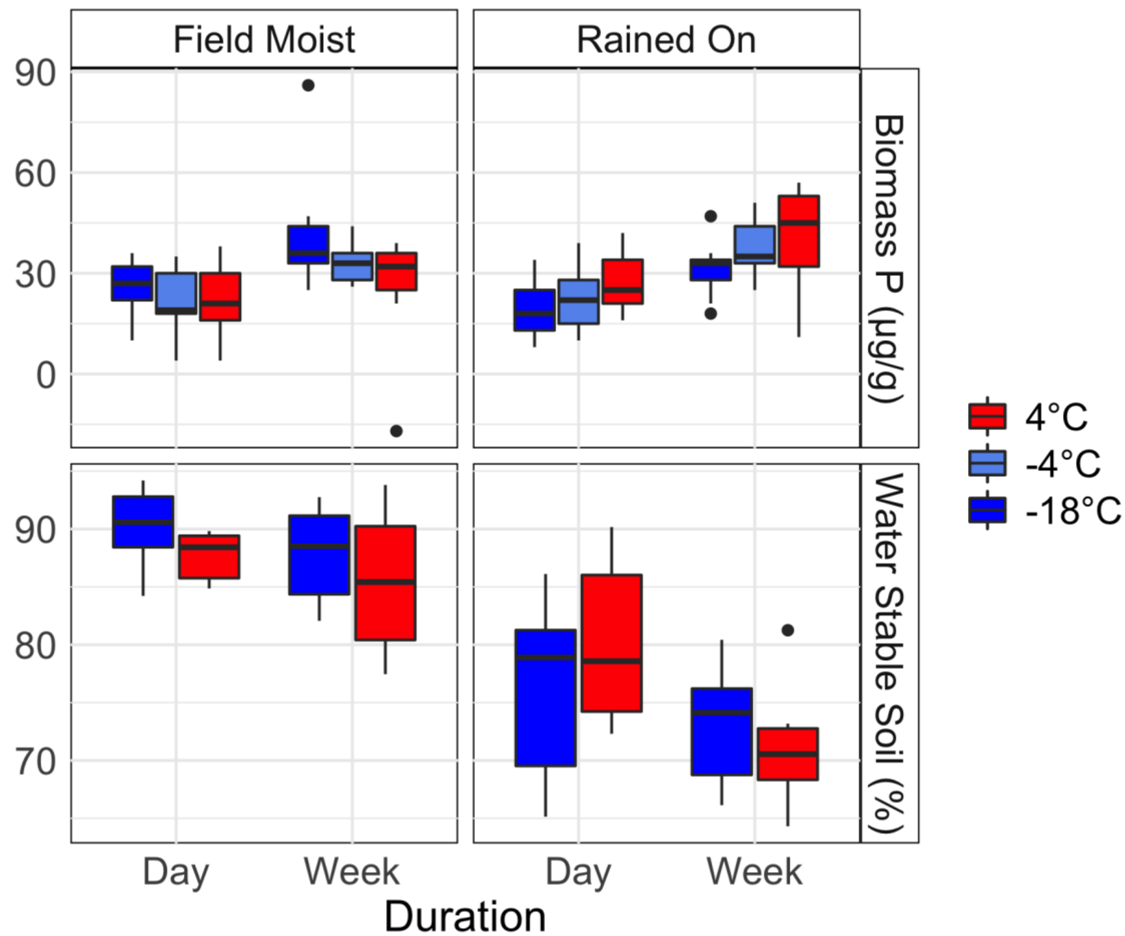


Figure 4.5 The microbial biomass phosphorus (Mic-P) concentration µg per gram of dry soil is shown compared to the percentage of water stable soil. The field moist cores and rained-on cores are divided, as is the duration of freeze thaw cycles. The temperatures the cores experienced are coloured by red for 4°C, light blue for -4°C, and blue is -18°C. The

interquartile range is represented by the extent of the boxes, and median is the line within the boxes, outliers are represented by dots. A negative Mic-P concentration is possible due to soil variability in P concentration. The unfumigated soil P concentration must have been higher than the fumigated soil P concentration, and thus shows Mic-P to be negative. See section 2.2 for calculation equation.

Soil GWC was significantly positively correlated with Mic-P (Figure 4.3). Microbial biomass P was also significant positively correlated with WEP, WEP_T and Ols-P (Figure 4.3). Microbial biomass P was significantly impacted by the number of FTCs when field moist ($p < 0.05$) but not by the number of flushing events ($p > 0.05$) (Appendix B2).

In contrast to soil P concentrations (WEP, Olsen-P) and Mic-P, temperature duration (daily versus weekly) did not have a significant effect ($p > 0.05$) on soil aggregate stability (Figure 4.5). The aggregate stability also did not have a significant effect with temperature cycle either ($p > 0.05$) (Appendix B2). Rather, soil aggregate stability declined with moisture. Aggregate stability was significantly ($p < 0.001$) lower in the rained-on soils (median WSS = 74%) compared to the field-moist soils (median WSS = 88%; Figure 4.5). Aggregate stability median values were consistently lower for 4°C than -18°C within field-moist (4°C median = 88%, -18°C = 90%) and rained-on (4°C median = 74%, -18°C = 76%); however, this was not significantly different ($p > 0.05$, Figure 4.3).

4.4.3 Leachate Phosphorus Concentrations and Species

Median concentrations of leachate TP, PP, NRP, and SRP were 541 μg L^{-1}, 398 μg L^{-1}, 28 μg L^{-1}, and 125 μg L^{-1}, respectively, whereby 76% of P was lost in the particulate form (Figure 4.6). Although, frost duration significantly ($p < 0.05$) increased leachate SRP, NRP and TDP concentrations, longer frost duration did not significantly affect the concentrations of PP or TP in leachate ($p > 0.05$). Colder temperatures significantly ($p = 0.05$) increased the concentrations of NRP in the leachate; however, temperature magnitude (4, -4 or -18°C) did not have a significant effect on any of the other P forms (PP, TP, SRP or TDP; Figure 4.6). The number of temperature and moisture cycles did significantly decrease TDP with more cycles ($p=0.07$; Appendix B3).

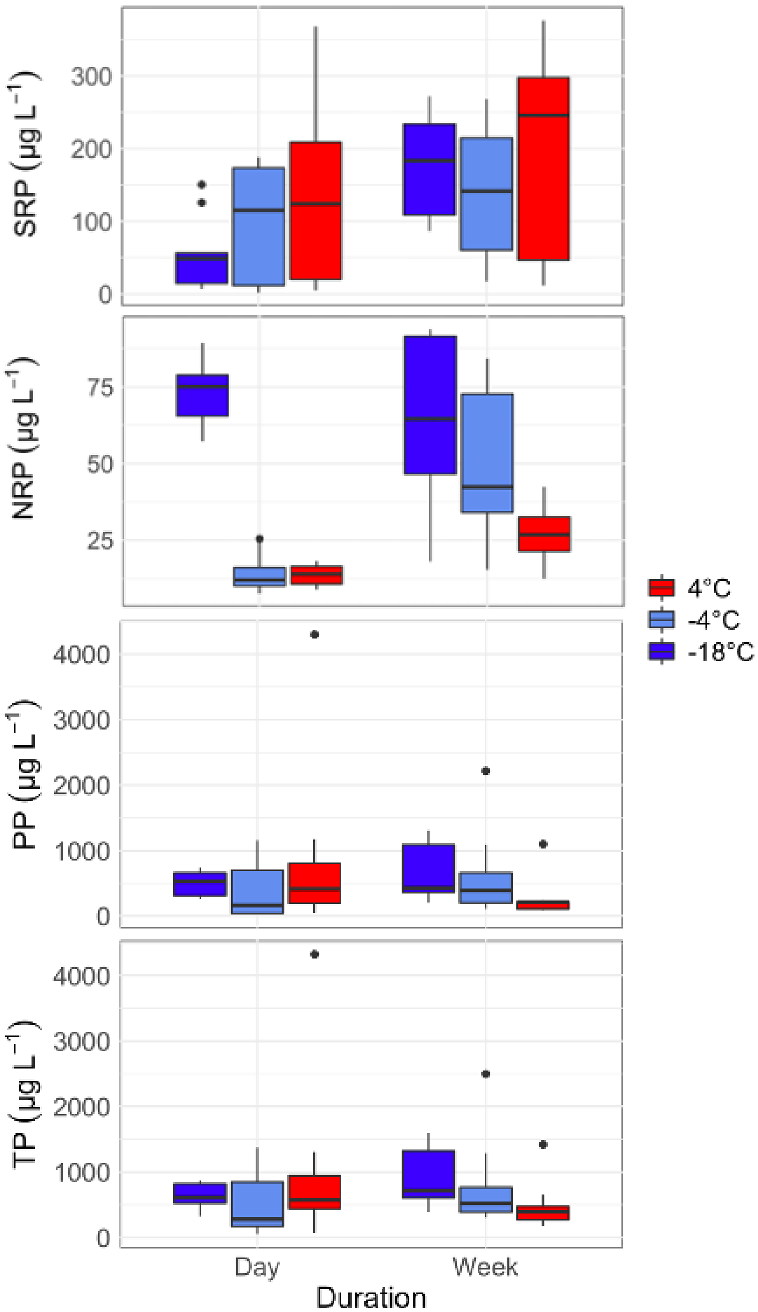


Figure 4.6 Soluble reactive phosphorus (SRP), dissolved nonreactive phosphorus (NRP), particulate phosphorus (PP), and total phosphorus (TP) concentrations (µg/L) from leachate collected after samples were rained-on. The concentrations are divided by colour for the temperature of the cycles they underwent, (red is 4°C, light blue is -4°C, and blue is -18°C). They are further divided by the duration of temperature cycle they underwent (day and week). The interquartile range is represented by the extent of the boxes, and median is the line within

the boxes, outliers are represented by dots. Note the different y-axis scales are adjusted for each P fraction.

The spearman rank correlation analysis on the leachate P fractions (Figure 4.3) showed that leachate SRP and leachate TDP species were positively correlated to soil available P concentrations (WEP, WEP_T, and Ols-P ($p < 0.001$); Figure 4.3 and 4.7 a), and negatively correlated with the number of times that the soils were flushed and frozen ($p < 0.05$). Both leachate SRP and leachate TDP concentrations were positively correlated with GWC ($p < 0.05$, and $p < 0.01$, respectively), while leachate SRP was also positively correlated with Mic-P concentrations ($p < 0.05$). In contrast, soil available P did not significantly affect ($p > 0.05$) concentrations of NRP (Figure 4.7 b), or TP and PP (Figure 4.3) in leachate. Rather, leachate NRP was negatively correlated with temperature magnitude ($p < 0.001$), as well as temperature duration ($p < 0.01$). Concentrations of PP (i.e., the largest pool of P loss) were negatively correlated with temperature magnitude ($p < 0.05$).

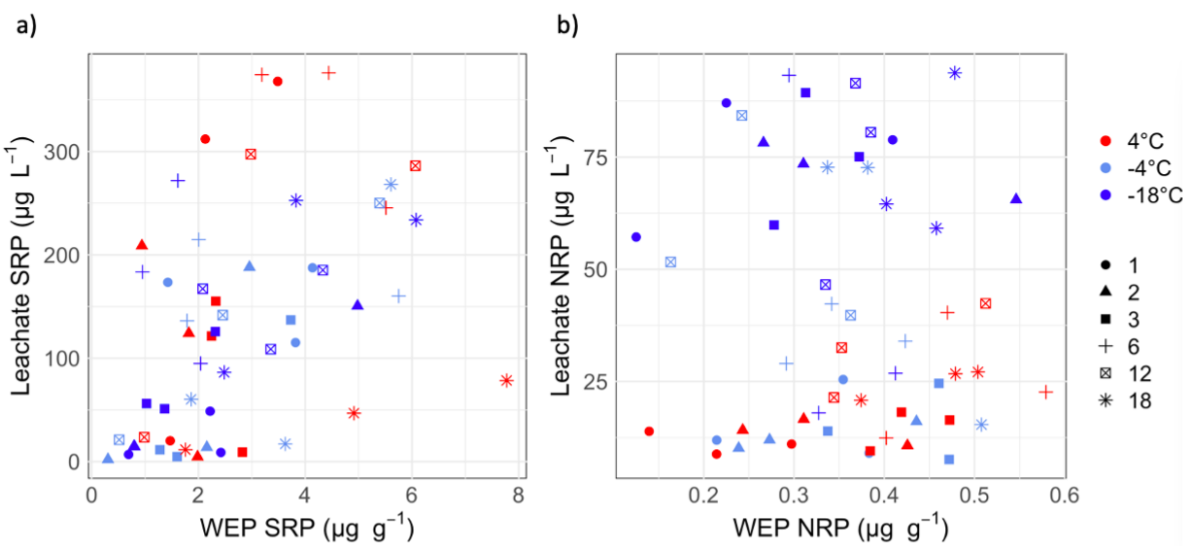


Figure 4.7 In panel a) the scatterplot shows the soluble reactive phosphorus (SRP) (µg L^{-1}) in leachate against the water-extractable phosphorus (WEP) (µg g^{-1}) concentration in soil. In panel b) the scatterplot shows the nonreactive phosphorus (NRP) (µg L^{-1}) in leachate against the WEP NRP (µg g^{-1}) concentration in soil. Between the panels the x- and y-scales differ. The points are coloured by temperature (red for 4°C, light blue for -4°C, and blue for -18°C). The shape of the points convey the number of days the soil had undergone a temperature condition

(1, 2, 3, being successive daily cycles, and 6, 12, 18 being successive weekly cycles for time periods 1, 2, and 3, respectively).

Although it was hypothesized that WSS would be related to erosive capacity of the soil, as well as soil sorption/desorption P dynamics, no significant correlations were found between WSS and soil available P (WEP_T, WEP_N, and Ols-P) (Figure 4.3). Although there was a significant negative correlation between leachate TDP concentrations and WSS (Figure 4.3, $p < 0.05$), the rest of the P species in leachate did not show a significant correlation with WSS (Figure 4.8 a). In addition, no relationships with temperature magnitude or duration of temperature with WSS were found (Figure 4.8 b).

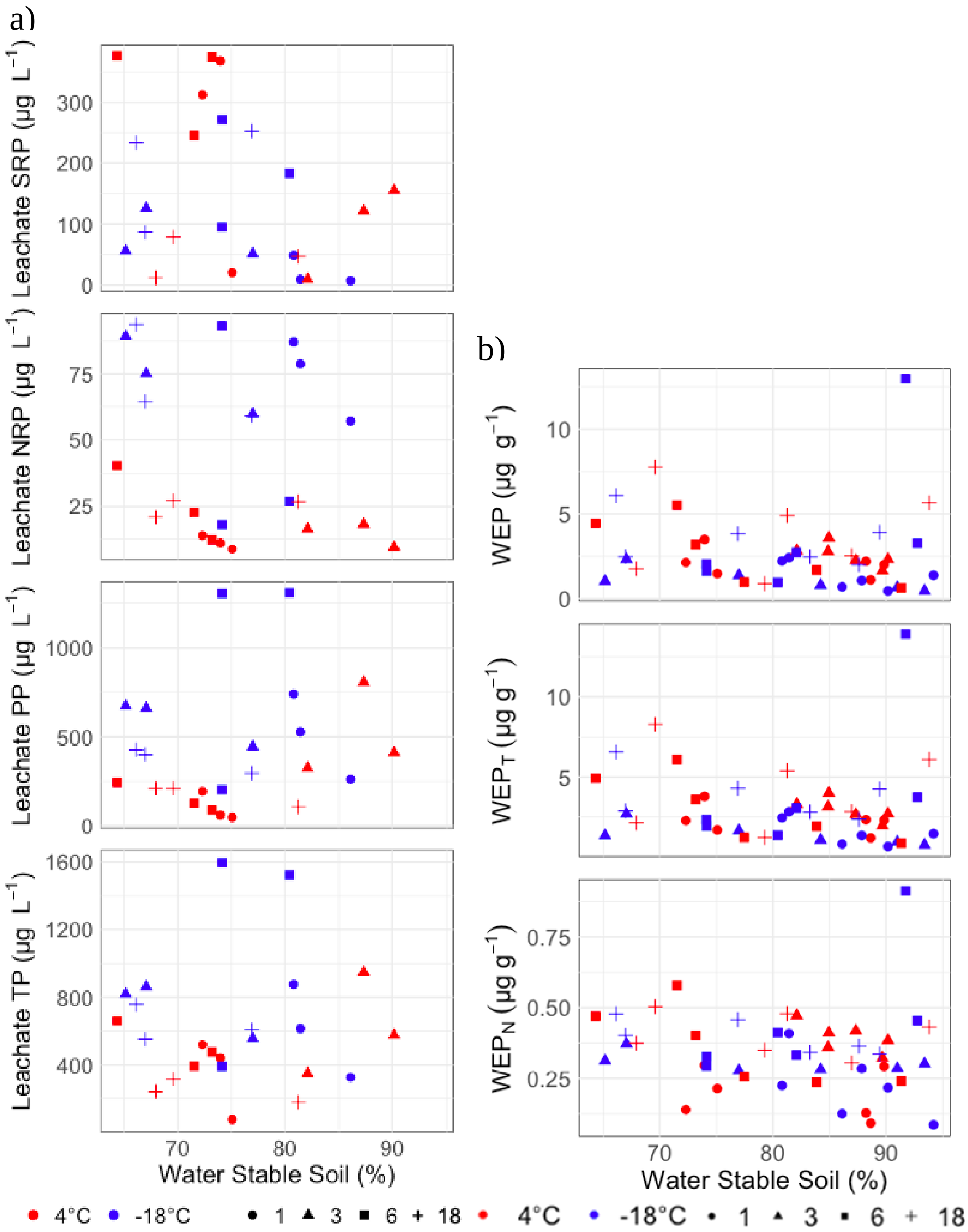


Figure 4.8 Leachate fractions soluble reactive phosphorus (SRP), nonreactive phosphorus (NRP), particulate phosphorus (PP), and total phosphorus (TP) plotted against water stable

soil percentage (WSS) respectively. The water-extractable phosphorus (WEP) fractions, soluble reactive phosphorus (WEP), total dissolved phosphorus (WEP_T), and nonreactive phosphorus (WEP_N) plotted against WSS. For both panels, red represents samples that underwent 4°C temperatures, blue represents -18°C temperatures, circles, triangles, squares and plus symbols represent samples that underwent one, three, six and eighteen days of those temperature conditions, respectively. Note the y-axes have different scales.

4.5 Discussion

4.5.1 Impacts of Freeze-Thaw Cycles (Magnitude and Duration) on Soil Phosphorus Dynamics and Leachate Phosphorus Concentrations

Previous experimental studies have shown that FTCs decrease soil Mic-P (Gao et al., 2021) and aggregate stability (Bullock et al., 2001). Thus, it was hypothesized that soil P supply would increase following FTCs. Studies on vegetation (cover crops) have shown that P release from vegetation increases with greater frost magnitude (i.e., colder temperatures; Cober et al., 2019). Thus, this study sought to determine if frost severity (magnitude, duration) or number of FTC impacted P loss from soils. Although soil P concentrations (WEP and Ols-P) and P concentrations in leachate were not related to temperature magnitude or number of FTC (1-3), they were significantly greater in soils that were exposed to a longer temperature duration (i.e., held weekly rather than daily), regardless of soil temperature or moisture. The lack of effect of frost magnitude or number of FTC on P dynamics contrasts Wang et al., 2017 who found increased desorption of P after FTCs and contrasts the findings of Gao et al., 2021, who observed an increase in salt extractable P, dissolved organic and inorganic P, and dissolved total P in leachate after FTCs.

Given that soil freezing has been related to microbial biomass P decline (Gao et al., 2021) and changes in aggregate stability (Bullock et al., 2001), these variables were explored with soil and leachate P in the current study. The average microbial biomass in this study (i.e., 28.5 $\mu g\ P_i\ g^{-1}$) was comparable to what has been observed in other agricultural systems (21.5 $\mu g\ P_i\ g^{-1}$, Brookes et al., 1982). It was hypothesized that increases in frost magnitude (temperature and/or duration) would lead to decreases in Mic-P, concomitant with the increased release of NRP in leachate in the rained-on cores. Contrary to expectations, frost temperature did not lead to decreased Mic-P in cores, although NRP losses were greater in leachate in cores exposed to colder temperatures. Although Mic-P was not impacted by frost temperature (4°C, -4°C and -18°C), it increased with frost duration (i.e., weekly soils versus daily). Moreover, NRP losses in leachate increased only under the coldest temperature treatment (-18°C) for the daily FTC, but under both -4°C and -18°C for the weekly FTC. The lack of effect of temperature on Mic-P may be explained by microbial adaptations against cell lysis under freezing conditions (Blackwell et al., 2010). While it appears that Mic-P is unaffected by short-term frosts, even severe ones, these populations may be affected by longer duration periods of frost according to this study. Although Yevdokimov et al., 2016, found microbial biomass P declined by 7.5 times after FTCs and no detectable microbial immobilization and Sorensen et al., 2018, found microbial biomass nitrogen decline by 85% after freeze-thaw cycles. The fact that NRP leachate increased with more severe frosts in this study, even under moderate frosts with longer duration, suggests that frost magnitude can indeed result in organic cell lysis of plant (Bechman et al., 2005) and microbial cells (Yanai et al., 2004) which enhanced P loss. However, it should be noted that such losses are small in comparison to other forms of P and may therefore not translate to significant changes in runoff P concentrations.

It was also hypothesized that aggregate stability would be impacted by freezing, which would lead to increased losses of PP in leachate through erosion. Indeed, Wang et al. (2012) found that the mean weight diameter of aggregates was smaller for aggregates following FTCs and that initial decreases in aggregate stability are followed by increases in stability after soils undergo numerous freeze-thaw cycles (Wang et al. 2012). Although such patterns were observed by others, there was surprisingly no impact of FTC on aggregate stability in this study. Potentially the soils did not undergo enough FTCs to make a significant difference in aggregate stability.

4.5.2 Impacts of Variable Soil Moisture on Phosphorus Dynamics in Soil and Leachate

Although temperature differences did not substantially impact soil P dynamics, differences in soil moisture did. Across all treatments, soil WEP increased with soil moisture conditions; however, the relationships between soil WEP and GWC differed between the field moist and rained on treatments. Fuhrman et al. (2005) considered surface soils (0-15cm) and found that by increasing water in the soil:water ratio, it increased the WEP concentrations. It is possible that in the current study, increased moisture within micropores in the soil cores led to increased desorption or dissolution of P caused by the change in pH from the acidic rainwater in a calcareous soil. Similar equilibration reactions have been found to take weeks (Penn & Camberato, 2019). Furthermore, others have found P runoff from soils increased with increased antecedent moisture (Hanrahan et al., 2021; Macrae et al., 2010). The inconsistent relationship for GWC and soil WEP between field moist and rained on samples needs to be explored in future studies, as factors such as equilibration time could be an important factor for soluble P and moisture after a flush event.

The longer duration in days had a positive relationship with soil WEP, WEP_N and WEP_T forms. This may be due to longer contact times of soil and soil moisture in the core. Sharpley et al. (1981) described the log of WEP release was linearly related to the log of contact time at any given water and soil ratio for the top ten centimeters of five southwestern soils of varying textures (sandy loam, clay, silt loam, silty clay loam, and loam). Modelling efforts of P have tried to estimate losses of P, with McGechan & Lewis (2002) concluding their massive review on modelling efforts that an equation which considers rate constants in a P model. Specifically, so that models take into consideration the processes of fast reversible sorption of P onto surface sites (adsorption), and slow reactions of absorption, below the surfaces of iron, aluminum oxide minerals or precipitate calcium phosphate. However, aside from Sharpley et al., 1981 this author could not find studies which consider soil P with moisture over different durations. This study supports duration of contact between soil moisture and soil contributed to increased soil WEP forms.

The reasons for the increased soil WEP with greater soil moisture may be partially explained by both biotic and abiotic mechanisms. Declines in microbial biomass have been observed under drier conditions in other studies (Blackwell et al., 2009; Brookes et al., 1982; He et al., 1997), supporting our finding that Mic-P and GWC were positively correlated. While positive correlations between P concentration in the soil and microbial biomass have been observed by others (Grierson et al., 1999; Butterly et al., 2009), Butterly et al. (2009) noted that the increase in soil P following a wetting and drying cycle is not caused by microbes. Although GWC was positively related to Mic-P in this study, the design of this study is not able to determine whether WEP increased directly because of Mic-P increases or due to P increases (caused by the increase in GWC) which allowed more Mic-P uptake of P.

The lack of relationships between aggregate stability and soil and leachate P dynamics is surprising. Water stable soil decreased with rained-on treatment, with a difference in medians of 14.3%, this is supported by Gu et al., 2018, who also found aggregate stability declined after dry and wet cycles. Although there were relationships between soil moisture and aggregate stability, and between soil moisture and soil WEP, there were no significant relationships between aggregate stability and soil WEP. Future studies could vary moisture contents to determine if varied moisture has impact on leachate P as this study has found no difference in leachate P forms when the same volume of water is rained on a soil core.

4.5.3 Risk of Phosphorus Loss in Water Under Future Climate Change

This study hypothesized that colder temperatures, and longer duration of frost would lead to an increase the supply of soil P through either biotic or abiotic mechanisms (or both) and that this would lead to increased P losses in leachate. Although differences in temperature did not impact soil P pools, colder temperatures increased losses of both NRP and PP during subsequent flushing events. Gao et al. (2021) described increases in P losses following FTC and attributed this to microbial death and changes in soil structure thus making organic matter more available. However, this study tested for both aggregate stability and microbial biomass directly and did not find Mic-P or soil structure to be related significantly with temperature, nor were they correlated with leachate P concentrations. The increased P loss observed in leachate under colder temperatures in the current study may be related to the erosion of colloidal material. Indeed, Gu et al. (2018) found that of the unreactive P in leachate, 81% was attached to colloids or nanoparticles. This is supported by negative correlations between aggregate stability and TDP concentrations in leachate ($p<0.5$; Figure 4.3). This evidence suggests the unreactive or organically bound portion on aggregates is more susceptible to being lost and decrease the stability of soils. This is supported by the fact that wet aggregate stability declined with moisture flushes.

Thus, this study suggests that although the increased FTC and associated flushing events anticipated under climate change may not lead to observable differences in soil P supply, they may lead to enhanced P losses in leachate, driven by both temperature and soil moisture. Although relationships between soil P runoff and leachate P are strong in many studies (Pease et al., 2018; Wang et al., 2010; Maguire & Sims 2002; Pote et al., 1996; Duncan et al., 2017), as well as in the current study (Figure 4.3), there is considerable variability in these relationships and the quantities of P loss in leachate are small relative to the total available soil P pool. Indeed, when comparing leachate P to P held in the soil, there is much less occurring in the leachate than what is available in the soil. For example, TP losses in leachate were on average 83.22 μg P, whereas the Olsen P pool in a single core averaged 2,783.93 μg P. Thus, due to soil variability and subtle only limited increases in P leachate, those losses may not be detectable in the soil P pool.

Subtle increases in soluble P from soils during the non-growing season, combined with changes in hydrological regime in the non-growing season anticipated under climate change (Bush & Lemmen, 2019) may lead to enhanced P losses from agricultural soils in cold agricultural regions (Eimers et al., 2020). Additional field studies on this topic, and investigations into the mechanisms behind soil increases in soluble P are needed.

4.6 Conclusion

Although more FTCs are expected in temperate climates with climate change, temperature does not have a significant impact on P availability in the soil but increases P losses in leachate. Although temperature did not increase soil available P, antecedent soil moisture did. This suggests that changes in soil moisture with climate change may lead to differences in the soil P pool, which could ultimately increase winter P losses during runoff and drainage events. Additional field studies investigating such relationships during successive thaw events are needed to better understand the potential impacts of changing winter conditions on P mobilization in agricultural landscapes.

Chapter 5
Major Conclusions of Thesis

Moisture is an integral indicator for P runoff, whether that is antecedent moisture (Kleinman et al., 2006; Macrae et al., 2010), discharge (Lam et al., 2016; Van Meter et al., 2020), and seasonality in areas with large snowmelt events (Macrae et al., 2010; Van Meter et al., 2020). Increases in NGS melt events and warm precipitation are expected to increase (Casson et al., 2019), and warmer temperatures are expected to increase FTCs in soils by decreasing snowpack (Reinmann & Templer, 2018). Therefore, this thesis set out to evaluate the supply of P in soil with moisture and temperature variability to better anticipate P supply changes with climate change.

Chapter 4 found significant correlation between soluble P and leachate SRP, as is supported in many studies (Pease et al., 2018; Wang et al., 2010; Maguire & Sims 2002; Pote et al., 1996; Duncan et al., 2017). Although there is considerable variability in these relationships, the quantities of P loss in leachate are small relative to the total available soil P pool but is still significant for eutrophication (Duncan et al., 2017). These studies typically report on soil fertility (soil test P, STP) which is typically monitored late in the growing season. Soil test P and water extractable P (WEP) are typically correlated, but WEP is more dynamic and may be a better predictor of P concentrations in runoff (Wang et al., 2010).

Given that P release from plants is increased with greater frost severity (Cober et al., 2018), it was hypothesized that significant temperature shifts might also impact P release from soils due to microbial death or decreased aggregate stability, which would be reflected in soil WEP concentrations. Although the primary goal of the experiments was to determine the impacts of temperature shifts on P mobilization, temperature had surprisingly little impact on soil P dynamics, and moisture shifts played a more significant role. For example, Chapters 3 and 4 found significant positive correlations between GWC and WEP. This relationship is likely controlled by an abiotic geochemical process and is potentially specific to agricultural settings as there is less organic P and larger inorganic P pools than in forested catchments (De Schrijver et al., 2012). Whalen et al., (2001) found the addition of moisture stimulated soil mineralization of P, while physico-chemical controls dominantly release inorganic P over microbial mineralization (Oehl et al., 2004). In chapter 3, the relationship between moisture and P was scattered at high GWC observed with snowmelt and might speak to depletion of readily soluble P with high moisture and contribute to the high variability in snowmelt runoff SRP observed by Macrae et al., 2010. In Chapter 3 and 4, WEP increased with increased moisture independent of treatment, therefore moisture is the dominant mechanism for loosely adsorbed fraction of P in agricultural soils.

Chapter 3 demonstrated greater concentrations of soil WEP during the NGS. This is similar Sorn-Srivichai et al., (1988) (in New Zealand, testing WEP and Olsen-P), but contrasts the findings of Pfeifer-Meister et al. (2007) (in Oregon testing Olsen-P) and Omer et al. (2018) (in New Mexico testing WEP). Although soil WEP was greater during the NGS, this thesis has shown that temperature did not significantly affect soil WEP. The snow manipulation field experiment led to an increased number of FTCs, similar to what has been shown by others (Reinmann & Templer, 2018; Ruan & Robertson, 2017), and soil cores also underwent varying numbers of soil FTCs in chapter 4. However, soil WEP did not increase with increased FTCs in either experiment. This is in contrast to Gao et al., 2021 who found increased P after FTCs, as well as others who found increased P availability after FTCs for a variety of reasons including microbial death (Feng et al., 2007; Yevdokimov et al., 2016), plant senescence (Riddle & Bergström, 2013; Lozier et al., 2017), and changes in soil degradation or aggregation (Kværnø & Øygarden, 2004; Edwards, 2013). Previous findings were from laboratory studies which may not reflect field conditions. This is also in contrast to Fitzhugh et al. (2001) who found that freezing soil temperatures increased inorganic P concentrations in soil solution.

Although frost severity did not impact soil P dynamics, Chapter 4 found that soil P concentrations (WEP and Ols-P) were significantly greater in soils that were exposed to a longer temperature duration (i.e., held weekly rather than daily). Although researching FTCs and P release has been studied significantly, (Henry, 2007; Zhao, 2021), the duration of FTC has not been flagged as a significant consideration for soluble P. This thesis suggests that frost duration could play an important role. Future studies should explore this phenomenon.

Although this thesis studied the impacts of temperature and moisture conditions on soil WEP and leaching losses (chapter 4), additional parameters were also examined to provide insight into mechanisms driving soil P dynamics, including microbial (Mic-) P and aggregate stability. Chapter 4 found Mic-P is positively impacted by moisture supported by others (Blackwell et al., 2009; Brookes et al., 1982; He et al., 1997), and found Mic-P is positively impacted by P concentration in the soil, also supported in the literature (Grierson et al., 1999; Butterly et al., 2009). However, temperature did not have a significant impact on Mic-P, this is supported by Blackwell et al., (2010) who describe microbial adaptations against cell lysis under freezing conditions.

Although aggregate stability was hypothesized to be reduced following FTC, Chapter 4 did not see changes in aggregate stability after FTCs. This is in contrast to other laboratory studies that have shown that initial decreases in aggregate stability are followed by increases in stability after soils undergo numerous FTCs (Wang et al., 2012). However, chapter 4 reported aggregate stability declined with flushes of moisture (Kværnø & Øygarden 2006). With increased aggregate degradation, erosion is more likely (Oztas & Fayetorbay 2003). Again, this speaks to the importance of moisture as a dominant control mechanism on P runoff.

This thesis set out to describe soluble P changes with climate change and has determined that soil moisture is a dominant variable for soluble P concentrations in soil. Previous work has described clear linkages between P concentrations in soils and P runoff in systems. This thesis quantifies the increase in soluble P with increased moisture. *In situ* underlying mechanisms for soluble P increase were not identified here but hypothetically, more soil moisture lowers the concentration of P in solution and forces labile P into solution P, then non-labile P is forced to labile P to compensate against sorption reactions for the difference in concentration. Additionally, the naturally acidic pH of precipitation in calcareous soils could dissolve Ca bound P, forcing more P into solution. Potential avenues for future research include to systematically determine the causes between soluble P with GWC, determine underlying factors controlling maximum soluble P to inform peak P release in snowmelt or high discharge periods, and ultimately improve the sensitivity of P export in modelling. With climate change anticipated to change hydrological regimes to new and more frequent extremes, the underpinning relationship of moisture and P could lead to significant insights on P export in a dynamic future.

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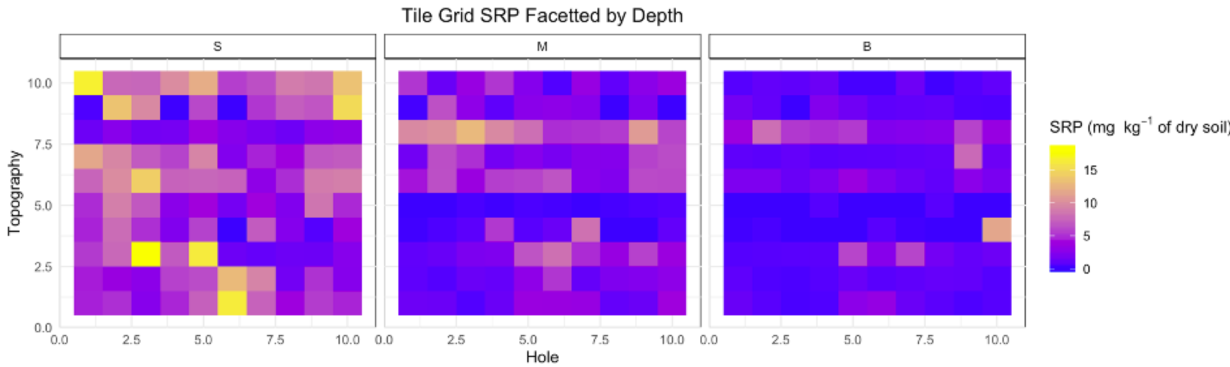
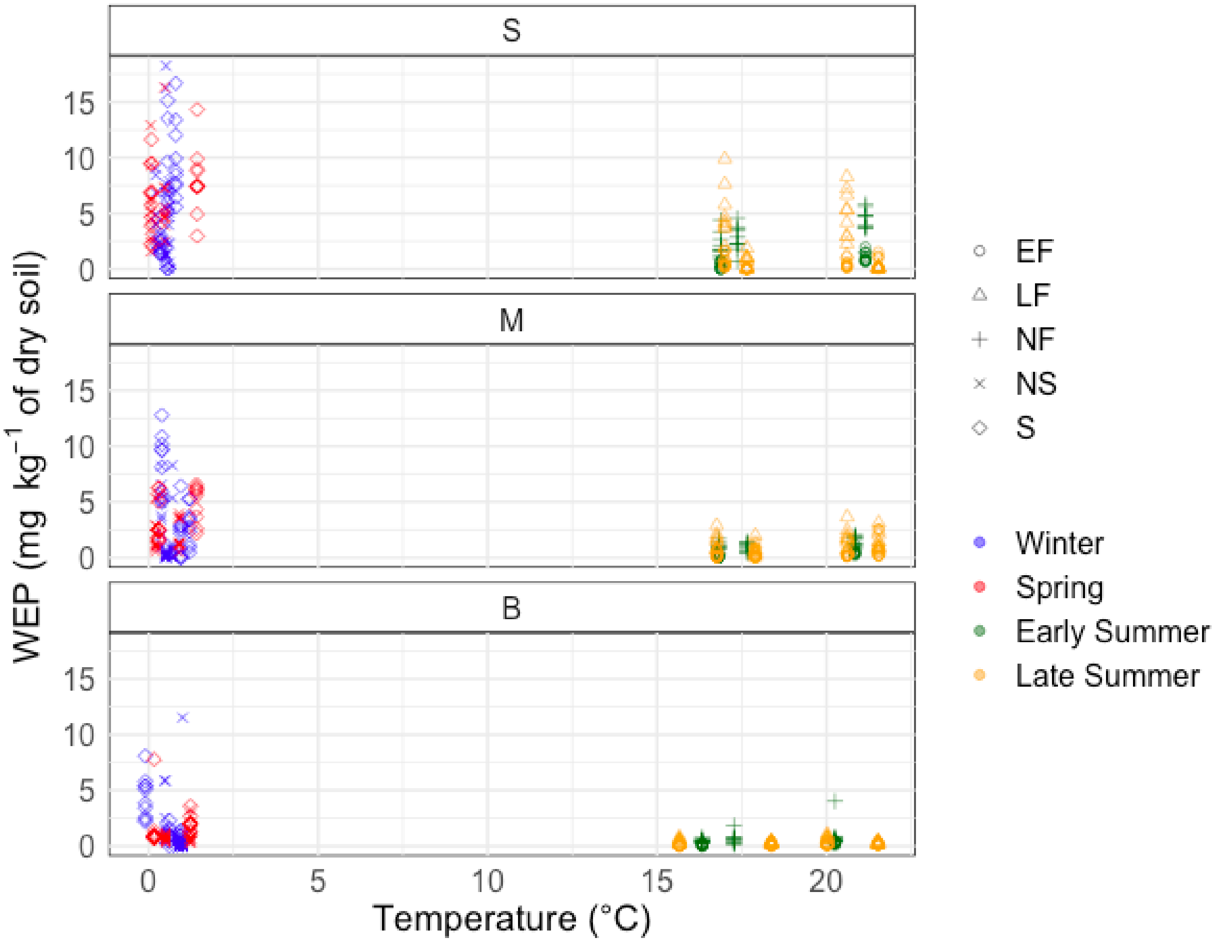
Appendix A

Supplementary Figures Chapter 3



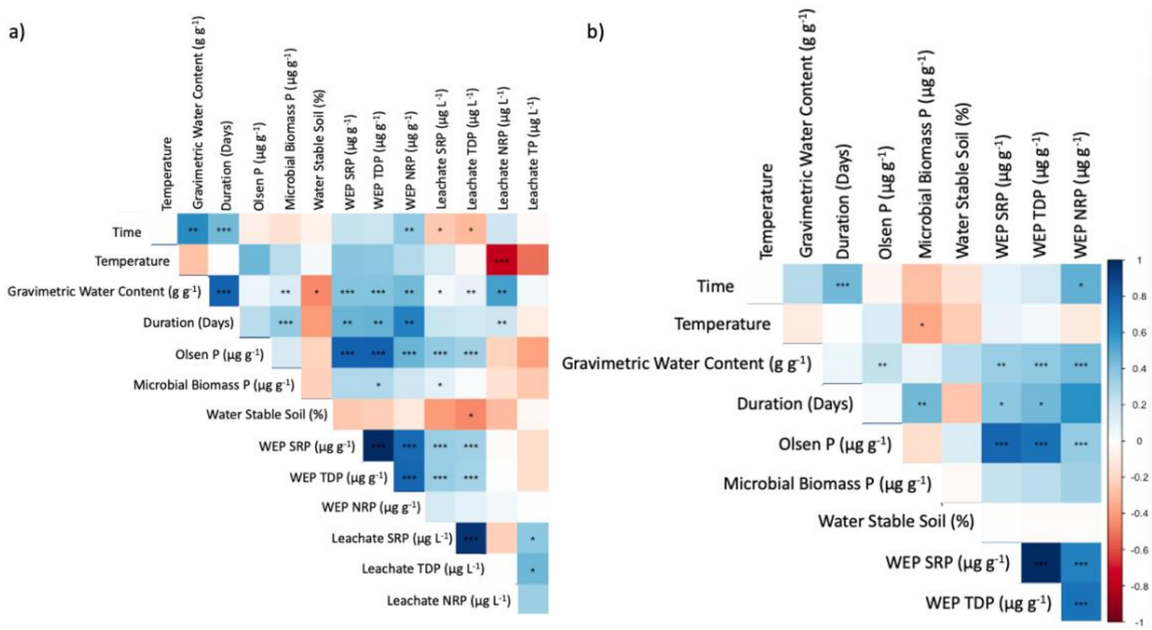
Supplementary Figure A1. Grid of fresh WEP concentrations by approximate geographic location on the field for the NGS. A higher topography number indicates a higher point on the field and the same topography number indicates the same sampling date. Hole number indicates the position perpendicular to the slope of the field that where the soil sample was taken. The graphs are divided by depth of surface, middle and bottom. This is a culmination of data from all time periods and different snow or no snow conditions to determine if there were spatial patterns in WEP concentration.



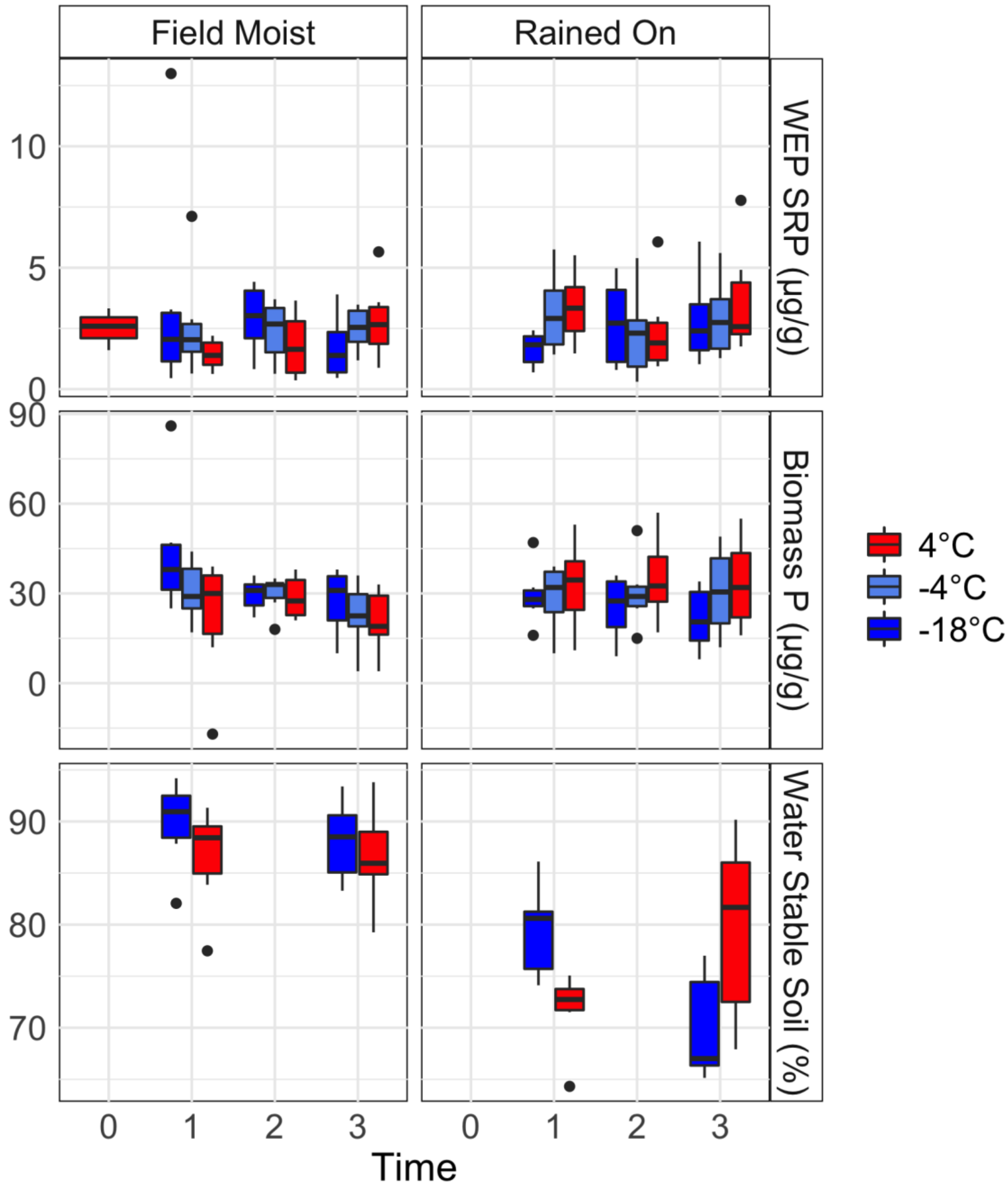
Supplementary Figure A2. Average temperature in degrees Celsius of the previous day before sampling, against the WEP concentration.

Appendix B

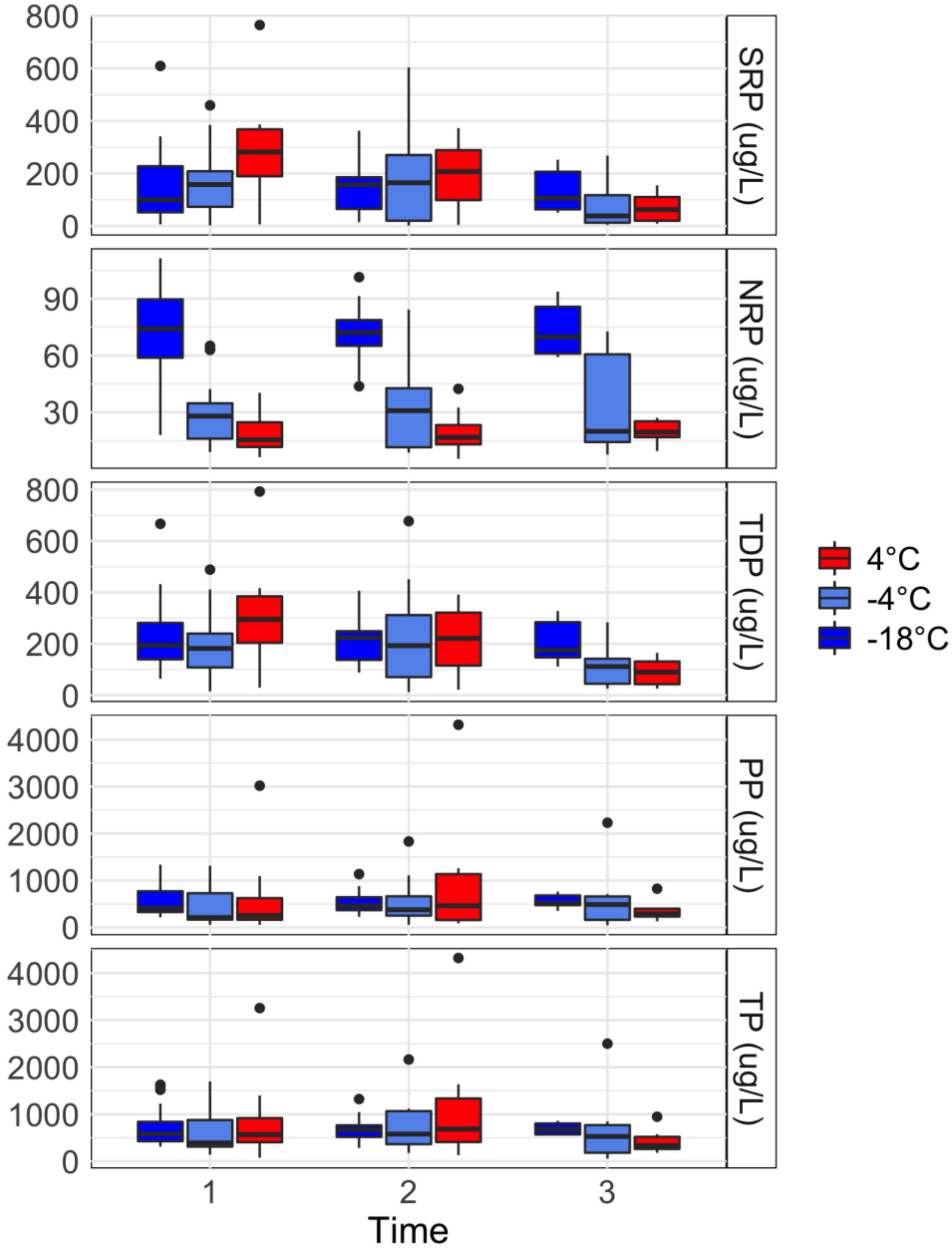
Supplementary Figures Chapter 4



Supplementary Figure B1. Spearman rank correlation between time period, temperature (-18°C, -4°C, 4°C), gravimetric water content (g g^{-1} of dry soil), duration in days, Olsen P (µg g^{-1}), microbial biomass P (µg g^{-1}), water stable soil (%), water extractable soluble reactive phosphorus (WEP) (µg g^{-1}), total dissolved phosphorus WEP (WEP_T) (µg g^{-1}), nonreactive phosphorus (WEP_N) (µg g^{-1}), leachate soluble reactive phosphorus (SRP) (µg L^{-1}), leachate total dissolved phosphorus (TDP) (µg L^{-1}), leachate nonreactive phosphorus (NRP) (µg L^{-1}) and leachate total phosphorus (TP) (µg L^{-1}). Colour represents the direction and strength of the relationship, with -1 being red, 0 being white, and blue being 1. One Asterix represents a p-value of 0.05, two Asterix's represents a p-value of 0.01, and three Asterix's represents a p-value of 0.001 or less. Data is divided by rained on (**a**), or field moist (**b**) samples.



Supplementary Figure B2. The WEP (µg g^{-1}), Mic-P (µg g^{-1}), and WSS (%) values after 0, 1, 2, and 3 cycles divided by rained-on or field-moist condition and temperature magnitude condition. The interquartile range is represented by the extent of the boxes, and median is the line within the boxes, outliers are represented by dots.



Supplementary Figure B3. The concentration of P forms from leachate over 1, 2, or 3 temperature cycles and flushes, by temperature magnitude. The interquartile range is represented by the extent of the boxes, and median is the line within the boxes, outliers are represented by dots.