Phosphorus speciation in submerged agricultural soils

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Abstract

Phosphorus (P) management in submerged agricultural soils is challenging as release of P in such soils occurs due to complex hydrological and biogeochemical processes that are influenced by inherent soil characteristics and external factors such as climate and agronomic practices. Thus, in depth understanding of P speciation in submerged agricultural soils is crucial to optimise P management and mitigate environmental risks, ensuring the sustainability of agricultural systems in diverse climatic regions. This thesis explores the dynamics of P speciation in submerged agricultural soils via three studies: one focusing on transformation of P in inorganic P fertiliser applied tropical paddy soils under long-term (>2 months) submergence to provide fundamental understanding of P dynamics in those soils to support inconsistent response of rice yields for applied P, and the others focusing on the potential risk of dissolved P release in critical source areas (CSAs) in temperate soils under short-term (hours to few days) submergence during rainfall events.

In tropical regions, long-term submergence of paddy soils leads to unique P dynamics due to the alternative oxic/anoxic conditions and high levels of iron (Fe) and aluminium (Al) oxy(hydr)oxides present in these soils. The challenge lies in understanding P dynamics in such soils to optimise fertiliser management strategies and enhance rice productivity sustainably. An incubation study was conducted in Sri Lanka to investigate P release and transformations in three contrasting paddy soils (Ultisols, Alfisols and Entisols) with applied two types of inorganic P fertilisers. This study revealed that the P fertilisers did not increase dissolved reactive P (DRP) into porewater in all soils, except immediately after fertiliser application because the P released by dissolution of calcium (Ca) phosphates and P associated ferrihydrite under reduced conditions were translocated to deeper soil layers and resorbed onto abundantly available Fe/Al oxy(hydr)oxides and reprecipitated as Ca minerals. Further, it was revealed that during submergence, moderately labile P pools (ie: sodium hydroxide extractable P) increased in P applied soils, which can be available for plant adsorption under unique micro-environment of the rice plant rhizosphere.

Contrastingly, in temperate regions, short-term submergence events, such as heavy rainfall, or flooding, pose risks of dissolved P release from soils, and subsequently diffuse P loss to overlying floodwater leading to freshwater quality concerns. The CSAs are nutrient hotspots in a farm which have active hydrological connectivity to surface waters. These areas often saturated/submerged during rainfall events. Hence, P release from CSAs can contribute to eutrophication in nearby freshwater bodies, posing environmental and agricultural sustainability challenges. Two studies were conducted to explore P release and transformations from three contrasting soils upon short-term submergence of CSAs during rainfall in New Zealand. A glasshouse study revealed that two soils (Recent and Pallic soils) released P to porewater while the other soil (Allophanic soil) sorbed P during short-term submergence suggesting the potential use of the Allophanic soil as a P sorbing material to mitigate P loss. A field study conducted in two CSAs (Recent and Pallic soils) connected to the Manawatū River revealed elevated DRP in porewater and floodwater during winter aligned with the findings of the glasshouse study. The findings of these studies can be applied to mitigate P losses from these CSAs during periods of high-risk for surface runoff such as in winter and to select suitable sites/soils for edge of farm mitigation practices such as wetlands and detainment bund constructions.

To the scientists who sacrificed lives
for the betterment of the world…
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from whom I inherited my mitochondrial DNA
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Due to New Zealand’s borders closure associated with Covid-19 pandemic, nearly the first and half years of this PhD study was conducted in Sri Lanka. The experiment conducted in Sri Lanka is outlined in Chapter 3. The rest of the study was conducted in New Zealand upon arrival after reopening the borders. The experiments conducted in New Zealand are outlined in Chapters 4 and 5.

List of Publications

Peer reviewed paper:

Palihakkara, J., Burkitt, L., Jeyakumar, P., Attanayake, C.P., 2024. Exploring phosphorus dynamics in submerged soils and its implications on the inconsistent rice yield response to added inorganic phosphorus fertilisers in paddy soils in Sri Lanka. J Soil Sci Plant Nutr 24(1), 1-20. https://doi.org/10.1007/s42729-023-01553-4

Conference abstracts and presentations:

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Palihakkara, J., Burkitt, L., Attanayake, C.P., Jeyakumar, P., 2024. Redox-induced phosphorus release in different soils under short-term submergence [Extended Abstract]. 36th Annual Farmed Landscapes and Research Centre Workshop, Massey University, February 2024. https://flrc.massey.ac.nz/workshops/24/Manuscripts/Palihakkara_Janani.pdf. (Oral presentation)

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Palihakkara, P.D.B.J., Attanayake, C.P., Burkitt, L., Jeyakumar, P., 2021. A preliminary study on phosphorus dynamics in submerged paddy soils [Abstract]. The Soil Science Australia and the New Zealand Society of Soil Science Joint Conference, July 2021. (Oral presentation)

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Abbreviations

The abbreviations are defined at the first use and then without definitions throughout the thesis. Abbreviations are redefined in each chapter.

Al	Aluminium
$Al_2(SO_4)_3 \cdot 18H_2O$	Alum
Am	Amorphous material
ASC	Anion storage capacity
Ca	Calcium
$CaCO_3$	Calcium carbonate
Ca-P	Calcium bound phosphorus
$CaSO_4 \cdot 2H_2O$	Gypsum
CEC	Cation exchange capacity
CH_4	Methane
CO_2	Carbon dioxide
CSA	Critical source area
Cu	Copper
DAS	Days after submergence
DCS	Department of Census and Statistics
DL	Low country dry zone
DOC	Dissolved organic carbon
DRP	Dissolved reactive phosphorus
e^-	Electrode
EC	Electrical conductivity
Eh	Redox potential
FAO	Food and Agriculture Organisation
Fe	Iron
Fe^{3+}	Ferric ion
Fe^{2+}	Ferrous ion
Fe_2O_3	Ferric oxide

Fe/Al-P	Phosphorus bound to iron and aluminium
H^+	Hydrogen ion
H_2	Hydrogen gas
HCO_3^-	Bicarbonate
HCl-P	Hydrochloric acid extractable phosphorus
H_2CO_3	Carbonic acid
H_2O	Dihydrogen monoxide
H_2O-P	Water extractable phosphorus
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IL	Low country intermediate zone
IM	Mid country intermediate zone
IU	Up country intermediate zone
K	Potassium
Mg	Magnesium
$MgSO_4$	Magnesium sulphate
Mn	Manganese
Mn^{2+}/ Mn^{3+}/ Mn^{4+}	Manganese cations
Mo	Molybdate
MnO_2	Manganese dioxide
MP-AES	Microwave plasma atomic emission spectroscopy
N	Nitrogen
N_2	Nitrogen gas
Na	Sodium
$NaHCO_3$-P	Sodium bicarbonate extractable phosphorus
NaOH-P	Sodium hydroxide extractable phosphorus
NH_3	Ammonia
NH_4-N	Ammonium nitrogen
NMR	Nuclear–magnetic resonance spectroscopy
NO_2^-	Nitrite
NO_3^-	Nitrate

NO_3-N	Nitrate nitrogen
O_2	Oxygen gas
OC	Organic carbon
P	Phosphorus
PSC	Phosphorus sorption capacity
PC	Principal component
Pi	Inorganic phosphorus
Po	Organic phosphorus
PTEF	Polytetrafluoroethylene
RRDI	Rice Research and Development Institute
S	Sulphur
S^{2-}	Sulphide
SHM	Stockholm humic model
SI	Saturation indices
SO_4^{2-}	Sulphate
SSP	Single superphosphate
TP	Total phosphorus
TOC	Total organic carbon
TSP	Triple superphosphate
WM	Mid country wet zone
WU	Up country wet zone
WL	Low country wet zone
Zn	Zinc
XANES	X-ray absorption near-edge structure spectroscopy
XRD	X-ray diffraction spectroscopy

Chapter 1

Introduction

1.1 Background and rationale of the study

With the world population projected to reach 9.8 billion by 2050 (UN, 2017), meeting food demand is a pressing concern, intensifying pressure on agricultural resources. Phosphorus (P) plays a crucial role in plant biology, influencing energy transfer, deoxyribonucleic acid, and ribonucleic acid synthesis, and building cell membrane structure (Malhotra et al., 2018). However, limited P rock resources in only a few countries (Brownlie et al., 2023) restrict widespread application of P fertilisers. Therefore, optimising P management in soil is imperative to ensure sustainable agricultural productivity and environmental stewardship. Additionally, loss of P in soil can lead to environmental issues such as eutrophication of water bodies, decreased agricultural productivity, and imbalances in nutrient cycling, aggravating challenges in sustainable land management (Panagos et al., 2018; Alewell et al., 2020; Walsh et al., 2023).

Phosphorus contamination of freshwater bodies in agricultural catchments is a global issue. It is predicted that 31% of the global catchment area may be affected by nuisance periphyton growth (McDowell et al., 2020). The nitrogen (N) to P ratio is the limiting factor in unnecessary growth of periphyton, algae, and microbes (Cleveland and Liptzin, 2007). While both N and P are crucial for eutrophication of freshwater bodies, P is more important in certain cases around the world. For example, around 75% of undesirable periphyton growth in agricultural catchments in America and Europe were caused by P enrichment (McDowell et al., 2020). Therefore, a profound understanding of P mobilisation from agricultural lands to freshwaters is needed in order to apply effective mitigation strategies.

Agricultural land area represents ~37% of the global land surface (FAOSTAT, 2021). About 67% of this consists of meadows and pastures while the rest is used as croplands (FAOSTAT, 2021). Submerged agricultural lands are used to predominantly grow rice, which accounts for ~12% of the global arable lands (FAOSTAT, 2021). Furthermore, there are agricultural lands that submerge temporarily due to flooding (Lucas et al., 2023). In intentionally submerged agricultural soils, the focus is on enhancing P availability for plant uptake and mitigating P loss from soil.

Increasing P availability for plant uptake is a major challenge for tropical soils that are known for their ability to sorb P, making the management of P in submerged tropical soils particularly difficult. For example, an inconsistent response of rice yield to inorganic P fertiliser applications in paddy soils has been observed in several tropical countries including in Sri Lanka (Sirisena and Suriyagoda, 2018; Nishigaki et al., 2021). This problem has been neglected for more than a decade in Sri Lanka (Palihakkara et al., 2024). There is a lack of studies that offer empirical evidence regarding P release and transformations in P fertiliser applied to rice paddy soils under submergence in Sri Lanka. A lack of in-depth research, lack of clear guidelines and poor awareness amongst farmers has led to the application of more P fertilisers than are recommended, with the hope of increasing yield responses. This practice leads to increased legacy P in soils, which exerts more pressure on already scarce P fertiliser resources and the economy of the country (Palihakkara et al., 2024). Therefore, unravelling the reasons behind inconsistent yield response to added P fertilisers is crucial to improve the efficiency of P management in rice paddy soils.

Submerged conditions can occur in temperate soils include snowmelt flooding (Kumaragamage et al., 2020), rainfall driven flooding in river-floodplains (Young and Ross, 2018) and temporary submergence of lowland hydrologically sensitive areas in agricultural landscapes such as critical source areas (CSAs) during rainfall events (Sharpley et al., 2008; Smith et al., 2021). Mitigating P loss from submerged agricultural lands in the temperate regions is crucial because these soils have lower P sorbing capacity compared to the highly weathered soils in the tropics (Brenner et al., 2019). On the other hand, artificial submerged conditions such as constructed wetlands, detainment bunds, and sediment ponds are used to mitigate P losses from agricultural lands (Levin et al., 2021; Li et al., 2021; Robotham et al., 2021). A substantial amount of research has been conducted on P losses caused by snowmelt flooding, rainfall driven flooding in river-floodplains, and related mitigation measures (Kumaragamage et al., 2020; Preiner et al., 2020; Vitharana et al., 2021). These research publications highlighted the unique P dynamics under submergence such as redox-induced P release (Schönbrunner et al., 2012; Concepcion et al., 2021). Similarly, sufficient research has been conducted on dissolved P loss in diffuse runoff following rainfall in agricultural lands including CSAs (Hahn et al., 2013; Hanrahan et al., 2021). However, there is very limited research on the potential and/or magnitude of dissolved P release from surface soils within the flow pathway of CSAs. Further, limited data has been previously reported on dissolved P release from CSAs in New Zealand. The diffuse P loss from soils within CSAs in the form of dissolved P poses a risk to eutrophication of freshwater bodies, as CSAs by definition are hydrologically connected to freshwater bodies (Djodjic and Markensten, 2019) and dissolved P is readily available for nuisance algal and plant uptake.

1.2 Research hypotheses and objectives

1.2.1 Research hypotheses

Since paddy soils in tropical areas are submerged for long periods (eg: months) and soils in CSAs are saturated during temporal rainfall events, especially in winter, the redox potential of soils in both circumstances can be reduced. Therefore, the overall hypothesis of the research was that the reductive dissolution of Fe/Mn oxy(hydr)oxides during submergence would release sorbed P, consequently elevating the P concentration in the soil solution and increasing the risk of P loss to ponded water. In addition, for the case study on paddy soils, it was hypothesised that urea application would delay the reductive dissolution of Fe/Mn oxy(hydr)oxides by increasing the NO_3^- concentration in soils, thereby impairing P release through reductive dissolution.

1.2.2 Research objectives

The primary objective of this thesis was to explore transformations of P release in tropical and temperate soils under long-term and short-term submergence, respectively related to three studies in Sri Lanka and New Zealand. The specific objectives proposed to achieve the main objective were:

1. To investigate the P release and transformations in contrasting rice paddy soils fertilised with inorganic P fertilisers, and to assess how the application of urea influences P release and transformations in the P fertilised soils under long-term (>3 months) submerged conditions.
2. To explore the potential of different soils to release P to porewater upon short-term (3 days) and frequent (every 10 days) submergence and subsequently, release of P to overlying pondwater during simulated rainfall events.
3. To investigate the potential of pastoral soil CSAs to release P to porewater and to overlying floodwater over intermittent rainfall events and to elucidate the mechanisms of P release in these soils under submergence.

1.3 Thesis outline

This thesis is organised into six chapters. Chapter 1 introduces the selection of three studies from Sri Lanka and New Zealand and focusses on understanding P dynamics in submerged soils. Chapter 2 reviews the existing knowledge of inconsistencies of rice yield to added inorganic P fertilisers in Sri Lanka, dissolved P release from agricultural soils during rainfall events in New Zealand, and mechanisms and factors involved in P speciation in submerged soils. Chapter 3 investigates the release and transformations of P in rice paddy soils fertilised with two forms of mineral P fertiliser, and how the application of nitrogen fertiliser influences P release and transformations in the P fertilised soils under long-term (>3 months) submergence. Chapter 4 explores the potential of three contrasting soils to release P to porewater upon short-term (3 days) and frequent (every 10 days) submergence and subsequent release of P to overlying pondwater. Chapter 5 investigates the potential of two different pastoral soils within CSAs to release P to overlying floodwater over intermittent rainfall events under field conditions. Chapter 6 summarises the key findings of the research chapters and suggests strategies to increase P availability for plant uptake in tropical soils and mitigate dissolved P loss from temperate soils during submergence in order to improve the management of P in soils subject to submergence.

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Chapter 2

Literature review

Part of this chapter has been published in:

Palihakkara, J., Burkitt, L., Jeyakumar, P., Attanayake, C.P., 2024. Exploring phosphorus dynamics in submerged soils and its implications on the inconsistent rice yield response to added inorganic phosphorus fertilisers in paddy soils in Sri Lanka. J Soil Sci Plant Nutr 24(1), 1-20. https://doi.org/10.1007/s42729-023-01553-4

2.1 Introduction

Phosphorus (P) is essential for plants in all-development stages from germination to maturity, and is therefore essential for food production. To address the deficiency of plant available P concentration in many agricultural soils, as a result of continuous removal of P at harvest, P fertiliser is applied to soils in either inorganic or organic forms (Dougherty et al., 2004). It is estimated that mineral P fertiliser use needs to be doubled by 2050 to ensure global sustainable crop and grassland production (Sattari et al., 2016). However, since they are non-renewable, the global natural P reserves (rock phosphate deposits) used for producing inorganic P fertilisers are limited in both quantity and distribution (Cordell and White, 2013; Roberts and Johnston, 2015). Approximately 85% of the global rock phosphate reserves are concentrated in only five countries: Morocco (70%), China (5%), Egypt (4%) Algeria (3%), and Syria (3%) (Brownlie et al., 2023). Moreover, it is predicted that the economically minable rock phosphates reserves would be exhausted within the next 100 years (Chen and Graedel, 2016).

In general, the efficiency of inorganic P fertilisers is low, with estimations suggesting that around 70% of the P fertiliser applied to soils annually are not used by crops (Brownlie et al., 2021). Further, it is estimated that P fertilisers are overapplied by 30-40% to agricultural lands globally (McDowell et al., 2024). Repeated P fertiliser applications including overapplication, result in a build-up of largely inaccessible ‘legacy P’ in agricultural soils or risk lost from soil (Doydora et al., 2020; Walsh et al., 2023). The global P losses from land to freshwater have doubled during the last century (Beusen et al., 2016). Globally, it is estimated that 9.0-13.2 million tonnes of P is lost from agricultural soils to freshwater bodies annually (Chen and Graedel, 2016).

Efficient P management in agriculture poses a common challenge across all agricultural systems, including submerged agricultural soils. In tropical submerged paddy soils, increasing P use efficiency poses a major challenge to rice production, while in temperate submerged soils, effectively managing P release from pasture soils during temporary submerged periods is important to reduce P loss to freshwater. This literature review aims to summarise the current understanding around two such challenges of P management in submerged agricultural soils in Sri Lanka and New Zealand, representing tropical and temperate agricultural soils.

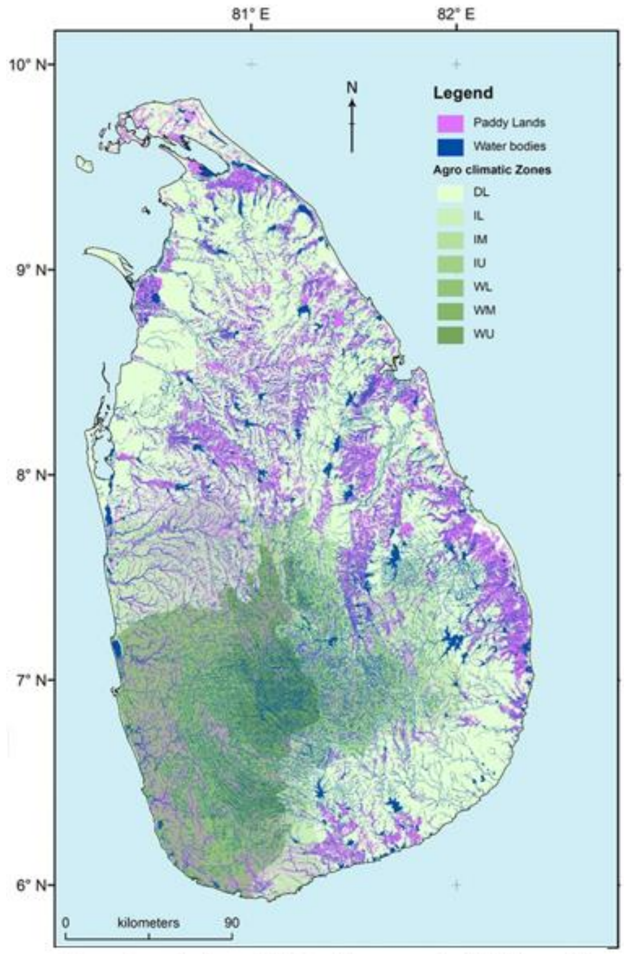
2.2 Sri Lanka

2.2.1 Rice-growing paddy soils in Sri Lanka

Rice (*Oryza sativa* L.) is a semi aquatic crop which serves as the staple food of the majority of Sri Lankans. Sri Lanka has been almost self-sufficient in rice since 2010 and it provides 45 and 40% of total calorie and protein requirements of an average Sri Lankan (Plan of the Department of Agriculture 2022-2023, 2022). On average, 107 kg of rice is consumed by a Sri Lankan in a year (RRDI, 2024). The average annual rice production of Sri Lanka between 2013 to 2022 was 4.18 million MT (DCS, 2024). Rice contributes to 1.8% of national gross domestic product of Sri Lanka and 1.8 million farming families are engaged in its production (FAO, 2022). Sri Lanka has highly weathered tropical soils in most parts of the country (Indraratne, 2020). Rice covers 14% of the total land area (65,610 km^2) of Sri Lanka, occupying the largest extent devoted to a single crop (Mapa, 2020). Of this area, 50% is grown in the dry zone (<1750 mm mean annual rainfall) and 30% and 20% are grown in the wet (>2500 mm mean annual rainfall) and the intermediate zones (1750-2500 mm mean annual rainfall), respectively. The distribution of paddy lands across the agro-climatic zones of Sri Lanka is shown in Fig. 2.1. Reddish Brown Earth, Non-calcic Brown, Low Humic Gley and Alluvial soils are major rice-growing soils in the low country dry zone (DL). Red Yellow Podzolic, Low Humic Gley, Non-calcic Brown, Reddish Brown Latosol, Immature Brown Loam and Alluvial are rice-growing Great Soil Groups in the low country intermediate zone (IL). Red Yellow Podzolic and Reddish Brown Loam are the main rice-growing soils in the mid country wet zone (WM).

2.2.2 Phosphorus fertiliser usage in rice cultivation in Sri Lanka

In Sri Lanka, there is a tendency among farmers to excessively apply inorganic fertilisers, despite the recommendations of the Department of Agriculture (Wimalawansa and Wimalawansa, 2015). Since 1962, Sri Lanka has implemented fertiliser subsidy programmes, which have undergone various changes to subsidy policies (Kanthilanka and Weerahewa, 2018). These fertiliser subsidy programmes were believed to play a significant role in the overuse of fertilisers among farmers, as they received fertilisers at a low cost (de Silva et al., 2020). Considering the consequences of P accumulation in surface water bodies, and the lack of a good yield response, it is vital to promote efficient use of P fertilisers in rice cultivation.



Reproduced from Kadupitiya et al. (2022) with permission from Springer Nature.

Agro-climatic zones	Mean annual rainfall (mm)	Elevation (m)
DL	<1750	<300
IL	1750-2500	<300
WL	>2500	<300
IM	1750-2500	300–900
WM	>2500	300–900
IU	1750-2500	>900

Fig. 2.1 Distribution of paddy lands (Purple colour) in Sri Lanka across the seven agro-climatic zones. Mean annual rainfall (mm) and the elevation (m) of each zone are also provided.

DL: low country dry zone, IL: low country intermediate zone, WL: low country wet zone, IM: mid country intermediate zone, WM: mid country wet zone, IU: up country intermediate zone, WU: up country wet zone

In 2020, approximately 76,856 MT of triple superphosphate (TSP; ~19.7% P) was applied to the crop sector in Sri Lanka (AgStat, 2021). Of this amount, around 59% was used for rice cultivation, resulting in an average application rate of 25.8 kg P/ha for paddy soils (an area of 983,550 ha) (AgStat, 2021). Rice crops with an average grain yield of 6 MT/ha, remove about 20 kg P/season (Rathnayake et al., 2015). However, the P fertiliser requirements of paddy soils under sustainable production shows a significant variation among different paddy soils in Sri Lanka. For example, P fertiliser requirements vary from 10.9 to 32.8 kg P/ha/season across different paddy soils, even when the soil P levels are sufficient for optimal rice yield (Wickramasinghe et al., 2009).

2.2.3 Water management practices in rice

Generally, agronomic practices associated with rice cultivation encompass several steps. These include soaking the soil, ploughing the waterlogged topsoil (up to 15-20 cm) to establish homogenous conditions, puddling, maintaining a standing water column throughout the vegetative growth period, and draining the water prior to harvesting (Bouman and Tuong, 2001; Winkler et al., 2016). Sri Lanka experiences two distinct monsoonal seasons; the Southwest monsoon, locally known as the *Yala* season occurs from May to September, while the Northwest monsoon, referred to as the *Maha* season takes place from October to January. Rice is typically cultivated as rainfed when there is sufficient rainfall to meet its water needs throughout the season. However, in the absence of rainfall, farmers resort to replenishing water from nearby channels to maintain a consistent water level during the vegetative growth period.

Continuous ploughing of paddy soils leads to excessive water losses due to percolation and seepage. Further, the formation of hardpan (plough pan) is a prevalent structural characteristic in rice growing fields (Fig. 2.2). The primary causes of hardpan formation include heavy machinery usage and mechanical manipulation such as ploughing at consistent depths. Additionally, the migration of dispersed clay from the surface to deeper soil layers contributes to this phenomenon (Kumarathilaka et al., 2018). The hardpan is characterised by higher dry bulk density and lower hydraulic conductivity relative to the plough layer. Repeated tilling over years in the plough layer causes a reduction of macropores and an increase in the number of micropores. Despite hardpan formation typically being considered an undesirable practice, it serves a beneficial role in paddy soils by enhancing water retention (Kögel-Knabner et al., 2010). Furthermore, ploughing affects P distribution in soil layers in rice cultivated fields. For example, a field experiment conducted in China using two rice varieties (japonica and glutinous) and two tillage practices (conventional tillage and no-till) with annual P fertiliser application at a rate of 43.7 kg P/ha, reported that soil P storage of the 0-20 cm soil depth significantly ($p<0.05$) reduced with conventional tillage compared to no-till practice within a year (Yang et al., 2020).

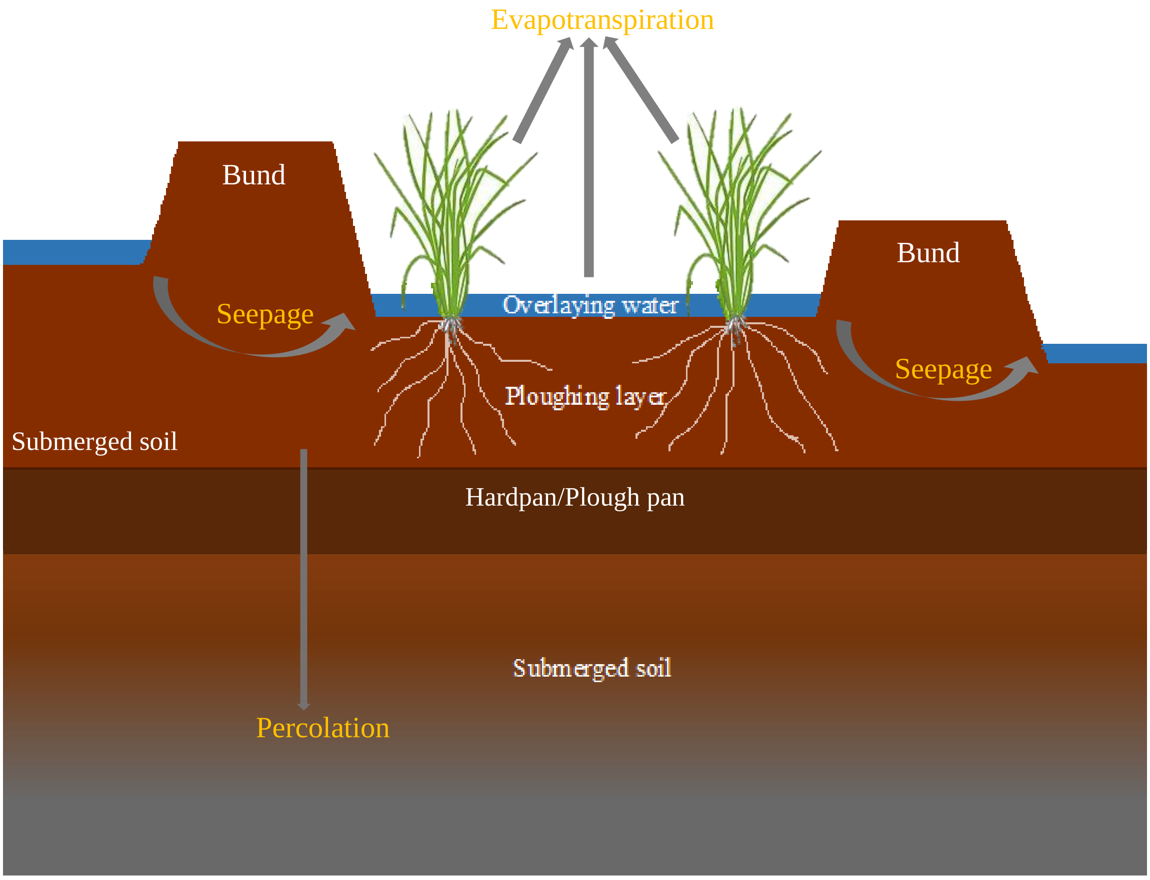


Fig. 2.2 Water management and hardpan formation in rice paddy plots; A longitudinal section of rice-growing paddy plots along the slope.

Fig. 2.2 shows a typical longitudinal section of paddy plots along the slope in Sri Lanka. Seepage occurs from the upper-level paddy plot to the lower-level paddy plots through the earthen bunds. This seepage serves as a pathway for water loss from the paddy fields, despite the reduced percolation caused by underlying hardpan. Water is also lost via evapotranspiration.

2.2.4 Rice yield response studies for added P fertilisers in Sri Lanka

The Olsen P method (Olsen and Sommers, 1982) is widely used in Sri Lanka to determine available P concentration in soil. The optimal threshold of Olsen P in rice-growing paddy soils varies across the agro-climatic regions in Sri Lanka. For example, in the DL and IL, the threshold ranges from 3 to 5 mg/kg, while in the low country wet zone (WL) and WM, it ranges from 10 to 35 mg/kg (Wickramasinghe et al., 2009). Approximately 44% of rice-growing soils in Sri Lanka have Olsen P concentrations of <10 mg/kg (Sirisena and Suriyagoda, 2018). However, these thresholds of Olsen P are not practicable in the field scale and need to be refined as they do not comply with yield response of rice in paddy soils as explained below.

The rice yield response to applied inorganic P fertilisers in paddy soils in Sri Lanka cannot be explained by Olsen P concentrations (Suriyagoda et al., 2014; Sirisena and Suriyagoda, 2018). For example, Sirisena et al. (2013) conducted a field experiment in four farm fields representing Low Humic Gley and Alluvial soils in the DL over four consecutive seasons using P fertiliser application rates of 19.7 kg P/ha in every season and in alternative seasons, separately (Table 2.1). Regardless of the initial Olsen P concentration of these four fields before commencing the experiment which ranged from 1.5 to 18 mg/kg, the researchers did not observe a significant (p>0.05) yield increase in four seasons, whether P application was done in every season or in alternative seasons. Another study conducted at 71 experimental sites in three rice-growing districts with a range of initial Olsen P concentrations before commencing the experiment (2.7-34.2 mg/kg), showed no significant (p>0.05) increase in rice yield to applied P fertilisers (Kulasinghe et al., 2020). Although the same P fertiliser rate (25.8 kg P/ha) had been applied to every plot in this study, the authors reported that as their general practice, most of the farmers who cultivated in these experimental sites previously, had applied lower or higher rates of P fertilisers than recommended by the Department of Agriculture, Sri Lanka. This indicates a heterogeneity of soil P management practices in the experimental sites which might have influenced the variability of initial Olsen P concentrations. An increasing trend of soil Olsen P in two paddy soils (Reddish Brown Earth and Low Humic Gley) were observed in relation to P fertiliser application in a short-term study conducted by Kendaragama et al. (2003). However, those researchers also did not observe a significant (p>0.05) yield increase of rice with different P fertiliser rates (0, 10.9, 21.9, 32.8, and 43.7 kg P/ha) in two consecutive seasons, despite having high variance in soil Olsen P concentrations in the experimental sites before commencing the experiment (4-49 mg/kg).

The existing literature on long-term research investigating the rice yield response to added P fertilisers in Sri Lanka is limited (Table 2.1). In the same manuscript, Kendaragama et al. (2003) reported results of long-term (>2 ½ years) research where the researchers observed seasonal variation in soil Olsen P, with greater availability of P, and rice yield responses at high P fertiliser rates (>32.8 kg P/ha) during the *Yala* season. This research was conducted for five consecutive seasons in Low Humic Gley soil in the dry zone and recorded a significant (p<0.05) rice yield increase only in *Yala* seasons with P fertiliser application. Since two different rice varieties were used in *Yala* (BG 276-5) and *Maha* (BG 450) seasons in this experiment, the significant yield increase in *Yala* season could be related to the performance of the variety. However, a study conducted for ten consecutive seasons in the same soil in the dry zone where the same rice variety (BG 300) was cultivated in both *Yala* and *Maha* seasons failed to report a significant (p>0.05) yield increase despite different fertiliser rates added (10.9-32.8 kg P/ha) to the experimental site where initial Olsen P concentration was 16 mg/kg (Senevirathna Banda et al., 2002). This study also reported higher yield in *Yala* than *Maha* within the ten consecutive seasons. Another study conducted in a farmer field in the dry zone having the same soil type where P fertiliser had not been applied for 10 years prior to the experiment, demonstrated no significant (p>0.05) yield response to the applied P fertilisers in the subsequent three consecutive seasons including two *Yala* seasons and one *Maha* season (Kodagoda et al., 2022). These studies pinpoint the necessity for future research on residual or legacy P in paddy soils, the modelling of long-term changes in soil P in paddy soils, and the potential for developing separate P fertiliser recommendations for *Yala* and *Maha* seasons.

Table 2.1 Rice yield response studies for applied inorganic phosphorus and other major non-phosphatic fertilisers across diverse soil orders in Sri Lanka

Soil order/ Great Soil Group	Initial Olsen P (mg/kg)	Number of seasons	Rice variety	Fertiliser rates	Average rice yield (Mt/ha)	Reference
<u>Short-term studies</u>						
Alfisol Entisol	2.7-34.2	3	BG 352 BG 300 BG 367	0 kg P/ha (P omitted) or 25.8 kg P/ha with 57.3 kg K/ha and 152 kg N/ha	5.7 5.8	Kulasinghe et al. (2020)
Low Humic Gley Alluvial	1.5-17.0	4	BG 352	0 kg P/ha (P omitted) or 19.7 kg P/ha in alternative season or in every season with 33.2 kg K/ha and 120 kg N/ha	6.0 6.2 6.3	Sirisena et al. (2013)
Reddish Brown Earth Low Humic Gley	4-49	2	*Maha*: BG 380 *Yala:* BG 276-5	0 kg P/ha (P omitted) or 10.9 kg P/ha or 21.9 kg P/ha or 32.8 kg P/ha or 43.7 kg P/ha with 49.8 kg K/ha and 150 kg N/ha	5.9 6.0 6.1 6.1 6.2	Kendaragama et al. (2003)

Table 2.1 cont.

Soil order/ Great Soil Group	Initial Olsen P (mg/kg)	Number of seasons	Rice variety	Fertiliser rates	Average rice yield (Mt/ha)	Reference
Long-term studies						
Low Humic Gley		No fertilisers for 10 years + 3 seasons with fertilisers	CIC Tikiri Kekulu	*Maha*: 0 kg P/ha (P omitted) or 10.1 kg P/ha with 28.2 kg K/ha and 111 kg N/ha *Yala*: 0 kg P/ha or 14.9 kg P/ha with 38.2 kg K/ha and 146 kg N/ha	5.2 (P omitted) 5.6 (P ample)	Kodagoda et al. (2022)
Low Humic Gley	12.5	5	*Maha:* BG 450 *Yala:* BG 276-5	0 kg P/ha (P omitted) or 10.9 kg P/ha or 21.9 kg P/ha or 32.8 kg P/ha or 43.7 kg P/ha with 49.8 kg K/ha and 150 kg N/ha	5.9 (*Maha*); 5.7 (*Yala*) 6.1 (*Maha*); 6.0 (*Yala*) 6.3 (*Maha*); 6.2 (*Yala*) 6.0 (*Maha*); 6.5 (*Yala*) 6.1 (*Maha*); 6.2 (*Yala*)	Kendaragama et al. (2003)
Low Humic Gley	4-16	10	BG 300	0 kg P/ha (P omitted) or 10.9 kg P/ha or 21.9 kg P/ha or 32.8 kg P/ha with 37.4 kg K/ha and 150 kg N/ha	6.2 6.4 6.2 6.2	Senevirathna Banda et al. (2002)

P: phosphorus, K: potassium, N: nitrogen

There are limited studies conducted on factors affecting rice yield response to added P fertilisers in Sri Lanka, other than soil test P (Olsen P). For example, there are no detailed studies published on P sorption capacity of paddy soils in Sri Lanka. However, it has been reported that the P sorption capacity varies among major rice-growing soils of Sri Lanka under both dry and submerged conditions (Damayanthi, 2001). This factor, alongside stress conditions such as iron (Fe) toxicity, nutrient deficiencies (eg: Zinc), and low pH, presents challenges in accurately assessing the yield response to applied P fertilisers in most studies (Wickramasinghe et al., 2009). Kulasinghe et al. (2020) revealed that factors such as irrigation schemes, soil texture, pH, electrical conductivity, total carbon content, and available Fe and magnesium (Mg) concentrations did not affect yield response to applied P fertilisers in paddy soils tested in the three rice-growing districts. They further highlighted the importance of assessing the other factors such as P reserves in rice-growing soils and P management practices by farmers related to rice yield response to added P fertilisers. However, no comprehensive study on the effects of these factors on inconsistent rice yield response to applied P fertilisers has been undertaken to date. Further, soil P species and their transformations during submergence could play a significant role in the yield response of rice plants to applied P fertilisers (Palihakkara et al., 2024).

2.3 New Zealand

2.3.1 Soils, pasture lands and P fertiliser usage in New Zealand

New Zealand has 15 soil orders according to *New Zealand Soil Classification* (Hewitt et al., 2021). According to age, these soil orders are categorised into three categories as young (Raw, Recent and Anthropic soils), mature (Semiarid, Pallic, Brown, Podzol, Gley, Organic, Melanic, Pumice and Allophanic soils), and old soils (Ultic, Granular and Oxidic soils). The Brown soil order is the most widely occurring soil order covering 40% of New Zealand. The second largest group is Podzol, Pallic, Pumice, and Allophanic soils covering 5-13% of New Zealand. The rest of the soil orders collectively cover 20% of the country.

Nearly half of the total land of New Zealand is used for agriculture and forestry (40%-grassland, 8%-exotic forest, 2%-cropping and horticulture) (Hewitt et al., 2021). New Zealand economy is hevaily dependent on the productivity of pastoral industries (Caradus et al., 2023) and pastoral industries contribute to around 50% of the countries export value (MPI, 2021).

Phosphorus fertiliser applied to New Zealand farms between 2021-2022 was 765,100 MT (Stats NZ, 2023). The most prevelant P fertiliser source is single superphosphate (SSP; ~8.3% P). Of the total P used by farm sectors in New Zealand in 2021/2022, pastoral farms applied 93% with 49% for dairy cattle, 43% for sheep and beef and 1% for deer farming (Stats NZ, 2023). Excessive use of P fertilisers under intensive agriculture over long periods has resulted in elevated soil test P levels (Hansen et al., 2002; Withers et al., 2019). In New Zealand, soil sampling conducted between 2014-2018 revealed that Olsen P concentrations exceeded the target range in 94 out of 154 sites on dairy farms (61%) and 67 out of 223 sites (30%) on drystock farms (Stats NZ, 2021).

2.3.2 Freshwater resources and quality in New Zealand

Freshwater has cultural and spiritual significance for Māori people (the indigenous people) of New Zealand. They consider freshwater resources as taonga (treasures) (Miller et al., 2015). New Zealand also relies on freshwater resources for economic, social, and cultural well-being (Larned et al., 2016). Moreover, a general social survey conducted in 2018 revealed that 80% of New Zealanders are concerned about the state of freshwater resources in New Zealand (Stats NZ, 2019).

Eutrophication is excessive growth of phytoplanktons (cyanobacteria and micro-algae) in water bodies due to nutrient enrichment including P and N (Yang et al., 2008; Akinnawo, 2023). The environmental and socio-economic costs of eutrophication of surface water bodies are high (Pretty et al., 2003; Dodds et al., 2009). Phosphorus loss from agricultural soils is one of the key non-point source pollutants responsible for eutrophication of freshwater bodies in New Zealand (McDowell, 2012; Smith et al., 2016). Although large lakes and rivers in New Zealand tend to naturally have low levels of P (McDowell et al., 2020), there is a risk of algal bloom in most rivers with catchments containing urban or pastoral land covers (Ministry for the Environment and Stats NZ, 2021). Freshwater quality monitoring of rivers in New Zealand during 2016-2020 revealed that 30% of rivers recorded substantially elevated dissolved reactive P (DRP) concentrations exceeding the Australian and New Zealand guidelines for the fresh and marine water quality (2018) default guideline value (0.011 mg/L), potentially leading to eutrophication (Stats NZ, 2022). Further, according to 20-year trend (2001-2020) of DRP concentrations in rivers, it was recorded that 67% of the monitoring sites were improving while 25% were worsening (Stats NZ, 2022). The attribute band A limit for median instream DRP concentration under the National Objectives Framework is 0.006 mg/L (Ministry for the Environment, 2024).

2.3.3 Loss of phosphorus from agricultural lands

The major transport pathways through which P enters waterways from agricultural lands in New Zealand include soil erosion from P-rich soils (McDowell et al., 2019) and the mobilisation of dissolved P when water moves over soils abundant in readily available P, or soils that have been recently fertilised with P (McDowell et al., 2005). Agricultural soils with high soil test P concentrations exceeding the P requirement for optimal plant growth have the potential to lose P from soil (McDowell and Sharpley, 2001; Djodjic et al., 2004; Tóth et al., 2014) via surface runoff, subsurface flow and leaching (Zhang et al., 2003; Owens and Shipitalo, 2006). Phosphorus loss by surface runoff depends on soil type, topography (Wu et al., 2018), land use, rainfall intensity (Pietrzak et al., 2020; Yao et al., 2021), Olsen P content of the topsoil layer (Dougherty et al., 2008; Burkitt et al., 2010), P sorption capacity of soil (McDowell and Condron, 2004) and management practices such as fertiliser application (Daverede et al., 2004; Hart et al., 2004). Soil characteristics (eg: P sorption capacity, preferential pathways) and drainage design (tile drainage) affect subsurface flow of soil P (King et al., 2015). Subsoil properties such as P sorption capacity (Djodjic et al., 2004; Andersson et al., 2013; Ulén and Etana, 2014; Andersson et al., 2015), the presence of macropores and water transport mechanisms (Makowski et al., 2020) are important in P leaching.

Dissolved P and particulate bound P, two forms of soil P, have the potential to be lost via surface runoff and subsurface flow (Smith et al., 2016; Thomas et al., 2016; Dupas et al., 2017; Smith et al., 2021a). The P loss in the form of dissolved P is critical in terms of eutrophication as this form is readily bioavailable for nuisance microorganism and aquatic plant growth in freshwater bodies (Trentman et al., 2021). Therefore, there is a significant concern about the transportation of dissolved P from agricultural soils to waterways.

2.3.4 Recent studies on P loss from agricultural catchments in New Zealand

A substantial amount of research has been undertaken on P loss from agricultural catchments in New Zealand over the last decade (Table 2.2). These include P losses via surface runoff, subsurface loss, and leaching from contrasting soils via laboratory experiments (Smith et al., 2021a; Smith et al., 2023), simulated rainfall studies (Simmonds et al., 2017), and field studies (Gray et al., 2022; McDowell and Smith, 2023b) (Table 2.2). A field lysimeter study conducted on Brown and Pumice soils revealed that N application decreased the load of DRP leached by 53–76% (Dodd et al., 2014). In support of this, Smith et al. (2021a) reported that nitrate (NO_3^-) inhibits the dissolution of Fe-oxides and associated P in Gley soils. Another laboratory incubation study conducted on a Pallic Firm Brown soil revealed that a 24 hour anoxic period was not long enough to exhaust nitrate in the soil system and to release DRP by reductive dissolution of metal oxides (Smith et al., 2023). Field-scale studies have been conducted in New Zealand to quantify subsurface P losses and/or associated mechanisms of P release in several soil types including a Melanic Orthic Gley soil (Smith et al., 2021a), and Recent and Brown soils (Smith et al., 2016).

Table 2.2 Selected recent studies (10-year period) on P loss from agricultural soils in New Zealand

New Zealand Soil Classification	Location	Soil depth	P loss processes interested	Experimental condition	Key findings	References
Typic Firm Brown soil Acidic Allophanic Brown soil	Korokoro and Ramiha sub catchments, Palmerston North		Surface runoff	Field study	Total P and DRP losses via surface runoff were lower in well-drained soil (Acidic Allophanic Brown soil) compared to imperfectly drained soil (Typic Firm Brown soil). Strategic positioning of supplement feed in farms could potentially reduce sediment and nutrient loss via surface runoff.	Fransen et al. (2022)
Immature Orthic Pumice Soils Typic Perch-gley	Reporoa catchment, Waikato	0-220 cm	Leaching	Field study	Soil Olsen P concentration >200 mg/L and anion sorption capacity (ASC) <50% were thresholds for causing accelerated P losses via leaching.	Lizarralde et al. (2023)
Pallic Firm Brown soil	Canterbury	0-10 cm	Surface P loss	Laboratory incubation study	Twenty-four-hour anoxic period was not long enough to exhaust NO_3^- in soil system and to release DRP by reductive dissolution of metal oxides.	Smith et al. (2023)
Pallic soil	Otago		Surface runoff	Field study	The increase in animal grazing/treading duration contributed to greater volumes of surface runoff. Grazing/treading had no significant effect on DRP concentration in surface runoff.	Gray et al. (2022)

Table 2.2 cont.

New Zealand Soil Classification	Location	Soil depth	P loss processes interested	Experimental condition	Key findings	References
Semi-arid soil Recent soil Pallic soil Gley soils	Manuherikia River catchment, Otago	30 cm 50 cm	Leaching	Field lysimeters established under irrigation – 700 mm in every 4-5 days	Where low P sorption soils overlay, dissolved organic P leached at a faster rate than orthophosphate.	McDowell et al. (2021)
Gley soil	Mossburn	0-30, 30-60, 60-80 cm	Subsurface P loss	Field and laboratory studies	Saturated/anoxic conditions increased Fe oxide and P dissolution. Nitrate inhibited the dissolution of Fe-oxides and associated P.	Smith et al. (2021a)
Typic Orthic Podzol soil	Awahou Stream catchment, Rotorua		Surface runoff	Field study	Detainment bund decreased loads of DRP (19–69%) and total P (18–67%) discharged downstream.	Levin et al. (2021)
Typic Firm Brown soil Acidic Allophanic Brown soil	Korokoro and Ramiha sub catchments, Palmerston North		Surface runoff	Field study	Annual DRP loss via surface runoff under winter cropping from imperfectly drained soil (Typic Firm Brown soil) was 5.5times higher than well-drained soil (Acidic Allophanic Brown soil).	Burkitt et al. (2017)

Table 2.2 cont.

New Zealand Soil Classification	Location	Soil depth	P loss processes interested	Experimental condition	Key findings	References
Organic soil Brown soil	Waituna catchment, Invercargill	30-60 cm	Surface runoff and leaching	Laboratory study with simulated rainfall	Soil moisture influenced the concentrations of P fractions in both surface runoff and leachate. Mitigation to be focused on particulate P losses in surface runoff (Brown soil) and dissolved P losses in leachate (Organic soil).	Simmonds et al. (2017)
Organic soil Podzol soil Gley soil	Waituna catchment, Invercargill		Surface runoff	Field study	Identification of P sources (eg: effluent) and timings (season) of bioavailable and sediment loss to surface water from soils is needed before recommending mitigation practices.	McDowell et al. (2016)
Perched-gley Podzol soil		0-100 cm	Leaching and subsurface P loss	Laboratory and field study	Application of alum decreased total filtered P loss in subsurface.	McDowell (2015)
Allophanic, Brown and Pumice	Waikato, and Bay of Plenty	0-22 cm	Leaching	Lysimeters established in fields	In Brown and Pumice soils, N application decreased the load of DRP leached by 53–76%. Applying a half rate of P maintenance decreased DRP load leached by 62–68%.	Dodd et al. (2014)

2.3.5 Phosphorus loss from critical source areas

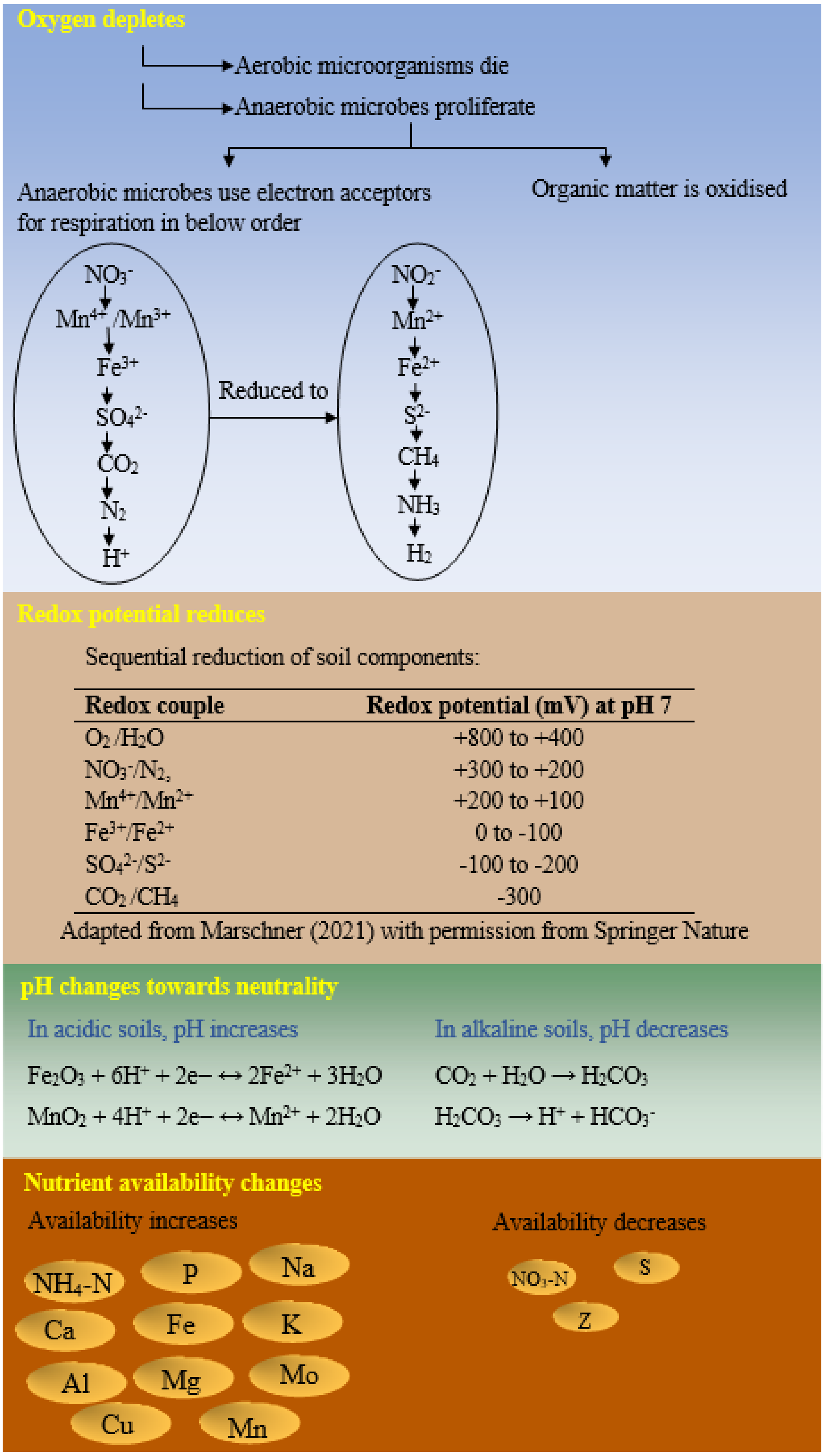
Critical source areas (CSAs) are nutrient hotspots in agricultural landscapes with active hydrological connectivity to surface waters (Sharpley et al., 2011; Thomas et al., 2016; Smith et al., 2021a). The concept of CSA was first introduced to describe areas where pesticides were being lost from land to water (Maas et al., 1985) and later it was used to describe other losses such as sediments, N and mainly P (McDowell and Srinivasan, 2009; Wei et al., 2017; McDowell et al., 2024). Critical source areas are proportionately small in extent, often representing only around 20% of farmed area but contribute significant amounts of P loss, often accounting for around 80% of total P loss (Pionke et al., 2000; Sharpley et al., 2011). These areas frequently get saturated, or form surface ephemeral flow pathways depending on their topography, within the agricultural landscape. This creates a unique environment within CSAs where soil properties including the redox status and pH can change due to alternative anerobic and aerobic conditions specially during rainfall events in winter. These changed conditions are likely to influence the P dynamics in soil which could enhance P release to soil porewater. Further, the released P could be diffused into the floodwater overlying the soil and can then be transported to surface waters via flow pathways (Amarawansha et al., 2015; McDowell et al., 2016) posing a threat of eutrophication of nearby waterways. However, since previous P loss studies have not measured P concentrations in overlying water, our understanding of the role of changed soil redox conditions in surface runoff of P from CSAs in New Zealand is limited. The effect of soil type on the release of P upon frequent and short-term submergence during rainfall events in CSAs, as well as the potential of CSAs to release dissolved P to surface runoff upon intermittent short-term submergence caused by different scales of rainfall events, has not been studied at a field-scale in New Zealand previously. Furthermore, the extent and mechanisms of P release by different New Zealand grassland soils to porewater and overlying water has not been explored.

2.4 Biochemical changes in soil under submergence

Submerged soils have been defined as “soil having free water at the surface at least during the growing season of arable crops or at least during the 2 months of the growing season of perennial crops, grassland, forest or other vegetation” (Sahrawat, 2004b). However, dryland crops which undergo temporary waterlogging were also classified as submerged soils (Ponnamperuma, 1972) but little research has been conducted on such soils compared to long-term submerged soils. Submergence induces changes in soil properties

(Fig. 2.3) through physical reactions and chemical and biological processes resulting from the interaction between soil, water, and microbes (Siam et al., 2019). These changes vary in different soil types based on various factors such as soil fertility levels, microbial biomass, quality and quantity of organic matter and the type of cultivar planted in soil (Fageria et al., 2011).

Generally, when a soil is submerged, there is a significant reduction in gas exchange between soil and the air (Ponnamperuma, 1972). During this time, aerobic microbes present in the soil will utilise the limited oxygen available for their respiratory processes. As a result, the oxygen level in the soil declines rapidly. The rate of oxygen diffusion through water filled pores of a submerged soil is around 1/10000th of that of a well-drained soil with air filled pores (Howeler and Bouldin, 1971). The rate of oxygen movement to soil through the overlying water layer is slower compared to the rate of oxygen reduction inside the soil profile (Fageria et al., 2011). This creates two distinct layers in the profile; an oxidised top layer (usually 1-20 mm in thickness) and a reduced soil layer underneath (Fageria et al., 2011). The oxygen content in a submerged soil becomes depleted within a day after submergence (Ponnamperuma, 1972; Kögel-knabner et al., 2010). The aerobic microbes in soil become quiescent due to a lack of oxygen under submergence and anaerobic microbes proliferate (Fageria et al., 2011). Anaerobic microbes proliferate because they use electron acceptors other than oxygen for their respiration in the following sequential order; NO_3^-, manganese(IV) (Mn^{4+}), iron(Ш) (Fe^{3+}) and sulphate (SO_4^{2-}) (Sahrawat, 2012). In addition, anaerobic microbes both facultative and obligate, use dissimilation products of carbohydrates, carbon dioxide (CO_2), nitrogen gas (N_2) and hydrogen ions (H^+) as electron acceptors (Fig. 2.3) in their respiration process (Ponnamperuma, 1972; Sahrawat, 2005; Fageria et al., 2011). Further, several electrochemical changes occur in a submerged soil, such as reduction of soil, alteration of soil pH, increasing ionic strength and specific conductance of soil solution, and large shifts in mineral equilibria and availability of nutrients due to sorption/desorption reactions (Ponnamperuma, 1972; Sahrawat, 2005).



Redox couple	Redox potential (mV) at pH 7
O_2/H_2O	+800 to +400
NO_3^-/N_2,	+300 to +200
Mn^{4+}/Mn^{2+}	+200 to +100
Fe^{3+}/Fe^{2+}	0 to -100
SO_4^{2-}/S^{2-}	-100 to -200
CO_2/CH_4	-300

Adapted from Marschner (2021) with permission from Springer Nature

$Fe_2O_3 + 6H^+ + 2e- \leftrightarrow 2Fe^{2+} + 3H_2O$

$MnO_2 + 4H^+ + 2e- \leftrightarrow Mn^{2+} + 2H_2O$

$CO_2 + H_2O \rightarrow H_2CO_3$

$H_2CO_3 \rightarrow H^+ + HCO_3^-$

Fig. 2.3 Major biochemical changes in soils under submergence with special reference to redox potential, soil pH and changes in nutrient availability. Source: Palihakkara et al. (2024)

P: phosphorus, K: potassium, Na: sodium, Ca: calcium, Al: Aluminium, Mg: magnesium, Mn: manganese, Fe: iron, Cu: copper, Mo: molybdate, S: sulphur, Zn: zinc, NH_4-N: ammonium nitrogen, NO_3-N: nitrate nitrogen, NO_3^-: nitrate, NO_2^-: nitrite, Mn^{2+}, Mn^{3+}, Mn^{4+}: manganese cations, Fe^{3+}: ferric ion, Fe^{2+}: ferrous ion, SO_4^{2-}: sulphate, S^{2-}: sulphide, CO_2: carbon dioxide, CH_4: methane, N_2: nitrogen gas, NH_3: ammonia, H^+: hydrogen ion, H_2: hydrogen gas, O_2: oxygen gas, H_2O: dihydrogen monoxide, Fe_2O_3: ferric oxide, e^-: electrode, H_2CO_3: carbonic acid, MnO_2: manganese dioxide, HCO_3^-: bicarbonate

Respiration of anaerobic microbes results in reduced soil conditions (Ponnamperuma, 1972). During this process of respiration, organic matter is oxidised while soil compounds are reduced. Therefore, the main requirements for soil reduction are the presence of decomposable organic matter, availability of other electron acceptors, absence of oxygen and anaerobic microbial activity (Ponnamperuma, 1972). Redox potential (Eh) of soils varies across a broad range in approximately the following manner: aerated soils (+700 to +500 mV), moderately reduced soils (+400 to +200 mV), reduced soils (+100 to -100 mV) and highly reduced soils (-100 to -300 mV) (Sahrawat, 2004a; Sahrawat, 2005). The Eh of submerged soils generally ranges from +200 mV to –300 mV, depending on organic matter content and reducible species (Sahrawat, 2005). An incubation study conducted using paddy soils in the IL of Sri Lanka reported an Eh range of +312 mV to -368 mV during first week of submergence (Akter, 2018).

Soil Eh controls the stability of several chemical compounds under submergence (Fig. 2.3). Under submergence, reduction of oxygen (O_2) to dihydrogen oxide (H_2O), NO_3^- to nitrogen gas (N_2) and nitrous oxide gas (N_2O), Mn^{4+} and Mn^{3+} to Mn^{2+}, Fe^{3+} to Fe^{2+}, SO_4^{2-} to sulfide (S^{2-}), CO_2 to methane (CH_4), N_2 to ammonia (NH_3) and H^+ to hydrogen gas (H_2) occur (Ponnamperuma, 1972; Gao et al., 2002). Even though some overlap may occur, the sequential reduction of the above soil components generally occurs only when the level of the previous oxidant in soil is negligible. For example, NO_3^- reduction begins only when the oxygen concentration of soil is very low and nitrate stabilises the redox potential at 0.2–0.4 V, preventing the reduction of the oxidants that comes later (Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2) in the sequential reduction process (Ponnamperuma, 1972). Parallel to these redox reactions, gasses such as CO_2, CH_4, N_2 and H_2 will accumulate in submerged soil (Fageria et al., 2011).

Generally, the pH of submerged soils changes towards neutrality (an equilibrium in between 6.5-7.5) (Fageria et al., 2011). The pH of acidic soils increases, and the pH of alkaline soils decreases under submergence. Most of the redox reactions in submerged soils involve the consumption of H^+ ions (Ponnamperuma, 1972). The main determinant of an increase of pH in acidic soils is the reduction of Fe and Mn oxides, which consumes H^+ ions (Equations 1 and 2) (Fageria et al., 2011).

$$Fe_2O_{3(s)} + 6H^+_{(aq)} + 2e^- \leftrightarrow 2Fe^{2+}_{(aq)} + 3H_2O_{(l)} \quad (1)$$

$$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \leftrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)} \quad (2)$$

The decomposition of organic matter causes the pH to decrease in both acidic and alkaline soils under submergence. The CO_2 produced in organic matter decomposition remain in soil due to restricted diffusion through the standing water layer on the soil surface. Carbon dioxides react with H_2O and form carbonic acid which dissociates into H^+ and bicarbonate ions as illustrated in Equations 3 and 4. Thus, accumulation of CO_2 will lower the pH of submerged alkaline soils (Ponnamperuma, 1972; Najafi, 2013). Although both consumption of H^+ ions by reduction of Fe and Mn oxides and releasing of H^+ ions by carbonic acid formed in organic matter decomposition occur simultaneously in acidic soils, as the net effect, the soil pH will be increased.

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} \quad (3)$$

$$H_2CO_{3(aq)} \rightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \quad (4)$$

The redox reactions and pH changes under submergence, therefore, change the concentrations and forms of soluble nutrients in the soil (Fageria et al., 2011; Sahrawat, 2012). Submergence improves the availability of several macro and micronutrients for plants and reduces the availability of some nutrients depending on other soil properties (Table 2.3).

Table 2.3 A summary of changes in nutrient availability following submergence in soils

Nutrient	Changes following the submergence	References
Ammonium-N	Production and accumulation favoured	Sahrawat (2012)
Nitrate-N	Reduced availability due to reduction into nitrite	Ponnamperuma (1972)
P	Improved availability via reductive dissolution of Fe(Ш) and Mn(IV)/Mn(Ш) oxy(hydr)oxides and hydrolysis of Fe and Al-P (in acidic soils), dissolution of Ca and Mg-P (in alkaline soils)	Fageria et al. (2011)
K	Improved availability as K ions being replaced from the exchange complex to the soil solution by substantially available Fe, Mn and NH_4^+ ions	Fageria et al. (2011)
Ca, Mg and Na	Release of cations to soil solution	Sahrawat (2005)
S	Reduced availability due to the formation of sulfides	Fageria et al. (2011)
Fe	Improved availability via reductive dissolution of Fe(Ш) oxy(hydr)oxides and phosphates but Fe toxicity may occur in acidic soils due to high content of reducible Fe	Sahrawat (2005)
Mn	Improved availability via reductive dissolution of Mn(IV)/Mn(Ш) oxy(hydr)oxides	Ponnamperuma (1972)
Cu and Mo	Improved availability because of the reduction of Fe(Ш) and Mn(IV)/Mn(Ш) oxy(hydr)oxides and the production of organic complexing agents	Ponnamperuma (1972)
Zn	Reduced availability due to increase in soil pH in acidic soils and formation of HCO_3^- ions	Ponnamperuma (1972)
Al	Except perhaps in acid sulphate soils, Al toxicity is generally absent because the solubility of Al minerals reduces due to the increase in soil pH with submergence	Sahrawat (2005)

P: phosphorus, K: potassium, Ca: calcium, Mg: magnesium, Na: sodium, S: sulphur, Fe: iron, Mn: manganese, Cu: copper, Mo: molybdate, Zn: zinc, Al: aluminium, Fe and Al-P: iron and aluminium bound P, Ca and Mg-P: calcium and magnesium bound P, HCO_3^-: bicarbonate, NH_4^+: ammonium, Ammonium-N: ammonium nitrogen, Nitrate-N: nitrate nitrogen

2.5 Phosphorus dynamics under submergence

The P solubility of soil increases under submerged conditions (Ponnamperuma ,1972; Weil and Holah, 1989; Fageria et al., 2011) and this is directly associated with the redox and pH changes which occur in submerged soils. Phosphorus is sorbed to different kinds of minerals or compounds and/or exists in the form of precipitates depending on soil properties such as pH, and availability of associated ions and minerals (Fig. 2.4). The water-soluble P concentration increases in acidic soils as a result of (1) hydrolysis of Fe(III) and Al phosphates, (2) release of P held by anion exchange sites on clay and hydrous oxides of Fe(III) and Al and (3) reduction of Fe(III) to Fe(II) releasing sorbed and chemically bound P (Ponnamperuma, 1972). Phosphorus release by the first two reactions is due to a pH increase in acidic soils. In neutral and alkaline soils, different forms of calcium phosphates (eg: dicalcium or octacalcium phosphates, hydroxyl apatite and apatites) govern P concentration in the soil solution (Sanyal and de Datta, 1991; Abolfazli et al., 2012). Phosphorus solubility increases in alkaline soils mainly due to release of P from Ca-P compounds when pH decreases following submergence (Fageria et al., 2011).

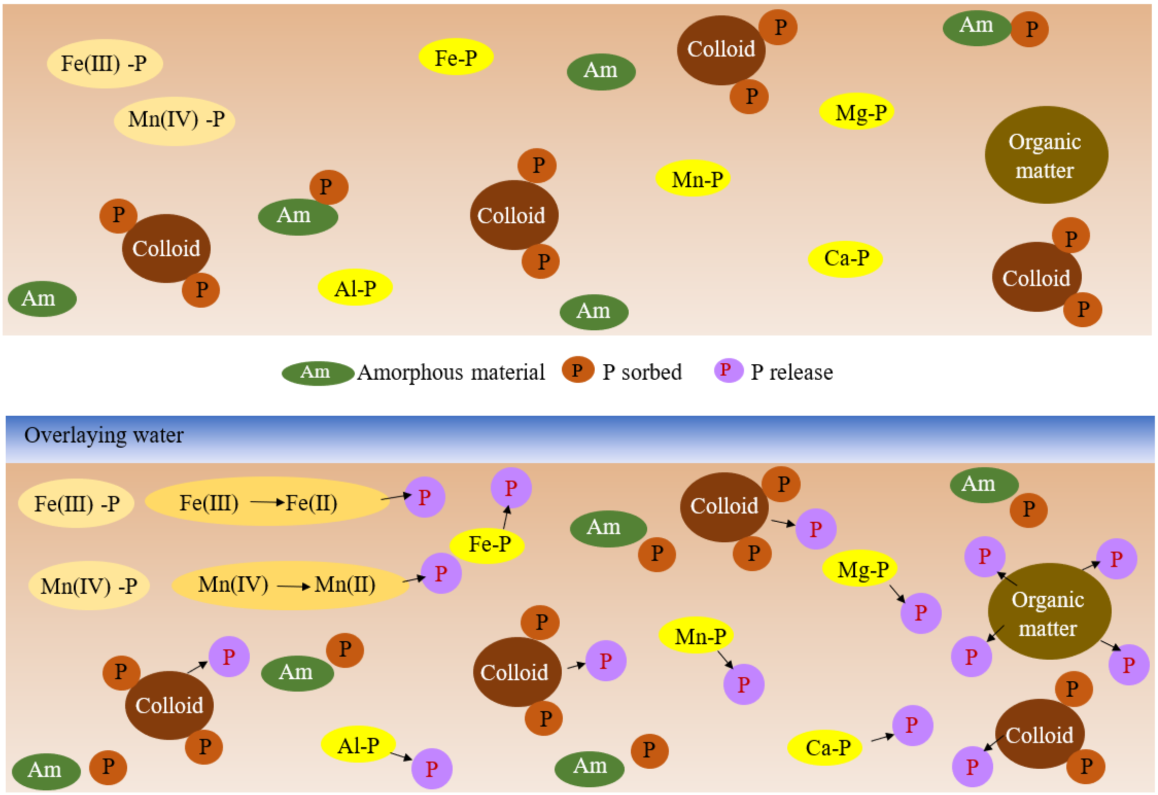


Fig. 2.4 Comparing the behaviour of P before and after submergence of soil; Top: Phosphorus sorbed to different surfaces such as colloids, amorphous materials, organic matter and other elements before submergence; Bottom: Phosphorus release into the soil solution upon submergence of soil. Source: Palihakkara et al. (2024)

P: phosphorus, Fe: iron, Mn: manganese, Al: aluminium, Ca: calcium, Mg: magnesium, Am: amorphous materials

The released phosphate ions by the above reactions and those released from organic matter decomposition, can then become available to be uptaken by plants, re-adsorbed by hydrous oxides of Fe and Al and clay in the anaerobic zone or may be diffused into the oxidised zones and reprecipitated (Ponnamperuma, 1972). Release of P under submergence depends on a collection of complex hydrological and biogeochemical processes (Jayarathne et al., 2016; Dharmakeerthi et al., 2019a). The amount and time of P release and its cumulative effect on porewater P concentration will depend on soil properties and other related factors as illustrated in Fig. 2.5.

2.6 Factors affecting P release in submerged soils

Phosphorus release under submergence mainly depends on inherent soil characteristics, external factors such as soil amendments, water management, and the cultivar grown in the soil (Fig. 2.5). Both organic and inorganic P pools release P under submergence. Therefore, clay mineralogy, soil microorganisms, and organic matter content/quality of soil can be considered as the main factors influencing P release under submergence. In addition, P sorption capacity, soil temperature, ions such as Fe, Al, Ca and Mg and cation exchange capacity affect P release under submergence.

2.6.1 Clay mineralogy

The main mineral groups involved in P release under submergence are clay minerals, such as Fe and Mn hydroxides and oxyhydroxides, Fe phosphates (Hutchison, 2003; O'Loughlin et al., 2013), Al hydroxides and Ca minerals (Schmieder et al., 2018) and 1:1 (Kaolinite) and 2:1 (Montmorillonite) type clay minerals (Amadou et al., 2022). Previous studies have measured P adsorption to clay minerals such as goethite, illite, gibbsite, montmorillonite, kaolinite, and hematite (Ioannou and Dimirkou, 1997; Gimsing and Borggaard, 2002; Violante and Pigna, 2002). Mineralogical evidence reported the presence of Al oxy(hydr)oxides such as gibbsite and boehmite, and 1:1 type clay minerals such as kaolinite in acidic wet zone soils of Sri Lanka (Indraratne, 2020), thereby providing possible sources of P sorption in such soils. Comparatively, in New Zealand, Allophanic soils contain Al-rich aluminosilicates; allophane, and imogolite, which have a strong affinity to adsorb P (Hewitt, 2021). Further, amorphous minerals present in the clay fraction (eg: amorphous Fe(OOH)) are also capable of P sorption by complexation (Watts, 2000). Several examples of the minerals involved in P sorption and release in soil are shown in Table 2.4.

Table 2.4 Several mineral names and their corresponding chemical formulae involved in phosphorus sorption and release in submerged soils

Mineral	Chemical formula
Strengite	$FePO_4·2H_2O$
Vivianite	$Fe_3(PO_4)_2·8H_2O$
Lepidocrocite	γ-FeOOH
Maghemite	γ-Fe_2O_3
Goethite	α-FeOOH
Variscite	$AlPO_4·2H_2O$
Ferrihydrite	$Fe_2O_3·0.5H_2O$
Hematite	Fe_2O_3
Gibbsite	$AlOH_3$
Alumina	γ-Al_2O_3
Berlinite	$AlPO_4$
Octacalcium phosphate	$Ca_4H(PO_4)_3·2.5H_2O$
Monetite	$CaHPO_4$
Brushite	$CaHPO_4·2H_2O$

Sources: Beauchemin et al., (2003); Hutchison, (2003); O'Loughlin et al., (2013); Schmieder et al., (2018)

2.6.2 Iron and aluminium ions

Tropical soils usually contain high amounts of Fe and Al oxy(hydr)oxides that sorb dissolved inorganic P (Agbenin, 2003; Rakotoson et al., 2016). A study conducted using 97 paddy soil samples covering the dry and wet zones of Sri Lanka reported high total Fe content with a high variability (Rubasinghe et al., 2021). According to this study, total Fe content in the dry zone paddy soils varied from 4255 to 31028 mg/kg and it varied from 2923 to 78400 mg/kg in the wet zone (Rubasinghe et al., 2021). Furthermore, Fe toxicity is largely reported in paddy soils in the up country wet zone (WU), WM, and WL of Sri Lanka (Siriwardana et al., 2019). Comparatively, in New Zealand, some soils are rich with Fe (Oxidic soil, Mafic Brown soil, Podzol soil), and Al (Allophanic soil, Oxidic soil, Podzol soil) (Hewitt, 2021). A meta-analysis of exchangeable Al using the National soil database in New Zealand soils, recorded exchangeable Al concentrations varying from 360 (Recent soil), 540 (Pallic soil), 1439 (Brown soil) to 1978 mg/L (Podzol soil)

(Whitely et al., 2019). Further, Al toxicity in high and hill country areas is considered a critical issue in New Zealand including in pasture soils (Bishop and Quin, 2013; Morton and Moir, 2018; Whitely et al., 2019).

Sorption and precipitation are the main mechanisms involved in P sorption to Fe and Al oxy(hydr)oxides. Adsorption occurs at low inorganic P concentrations and precipitation of Fe and Al phosphates occurs at high inorganic P concentrations (Darke and Walbridge, 2000). Generally, Fe is considered the most abundant redox sensitive species in soil (Kirk, 2004). However, soils with high Fe content will hinder the increases of soluble P content in submerged soils by reprecipitating with or resorbing P onto Fe(II) minerals (Amery and Smolders, 2012). Reductive dissolution of Fe(III) oxy(hydr)oxides increases Fe(II) concentration in soil solution even above 1 mM under submergence (Scalenghe et al., 2002). High concentrations of Fe(II) in soil solution induce precipitation of Fe(II)/Fe(III) carbonates and hydroxides that limit P release due to sorption or co-precipitation (Chacon et al., 2006; Amery and Smolders, 2012). There is also evidence suggesting that crystallinity of Fe oxy(hydr)oxides decreases with flooding, thereby increasing P sorption capacity (Darke and Walbridge, 2000; Zhang et al., 2003). Unlike Fe, Al is not redox sensitive; thus, the solubility of Al phosphates does not change due to redox reactions under submergence. In contrast, organic matter can complex with Al and prevent precipitation of amorphous Al oxides (Darke and Walbridge, 2000). A detailed dataset across five soil types in New Zealand recorded varying amorphous Fe concentrations in grazed pasture soils (Table 2.5) from 1100 to 17000 mg/kg and Al concentrations from 1100 to 66800 mg/kg (Shen et al., 2018) indicating the variability of potential P sorption by pasture soils.

Table 2.5 Amorphous Fe and Al concentrations in grazed pasture soils in New Zealand

Soil type	$Fe_{oxalate}$ (mg/kg)	$Al_{oxalate}$ (mg/kg)
Allophanic soil	5000-17000	13300-66800
Brown soil	3600	3500
Gley soil	3600-7300	3000-9200
Pallic soil	1100-4800	1100-3500
Recent soil	3900-8900	2100-10100

$Fe_{oxalate:}$ ion extracted by 0.1 M acid ammonium oxalate (pH =3); $Al_{oxalate:}$ aluminium extracted by 0.1 M acid ammonium oxalate (pH =3). Source: Shen et al. (2018).

2.6.3 Calcium and magnesium ions in alkaline soils

Calcium and Mg are present as the dominant cations in alkaline soils. Phosphorus will precipitate as different forms of calcium phosphate (eg: dicalcium or octacalcium phosphates, hydroxyl apatite, and less soluble apatites) in such soils (Hinsinger, 2001). The pH of alkaline soils decreases with submergence. This will increase the solubility of Ca-P minerals such as octacalcium phosphate, hydroxyapatite, ß3-tricalcium phosphate and fluorapatite in calcareous soils. Furthermore, acid anions of decomposing organic matter can form complexes with Ca^{2+} ions increasing the solubility of Ca bound P in submerged soils (Bhattacharyya et al., 2005).

The soils of the dry zone of Sri Lanka contain high amounts of Ca and Mg probably due to the presence of carbonate-bearing minerals. Further, there are evidence of high variability of Ca and Mg contents in paddy soils within the dry zone of Sri Lanka. A study conducted using 70 paddy soil samples of the dry zone revealed that Ca and Mg varied from 31 to 5600 mg/kg and 47 to 3660 mg/kg, respectively (Rubasinghe et al., 2021). This heterogeneity could be a contributing factor to inconsistent yield response of rice yield to added P fertilisers in Sri Lanka. Similarly, in New Zealand some soils such as Melanic soils (rich with Ca and Mg), and Oxidic soils (Mg-rich) show near neutral to slightly alkaline soil pH (Hewitt, 2021). A study conducted using 50 pasture soil samples covering 11 soil groups in New Zealand revealed that total Ca concentrations of the soils varied from 1265 to 9570 mg/kg (Walekin et al., 2013). The same study reported that exchangeable Mg concentrations of the pasture soils varied from 32 to 3186 mg/kg (Walekin et al., 2013).

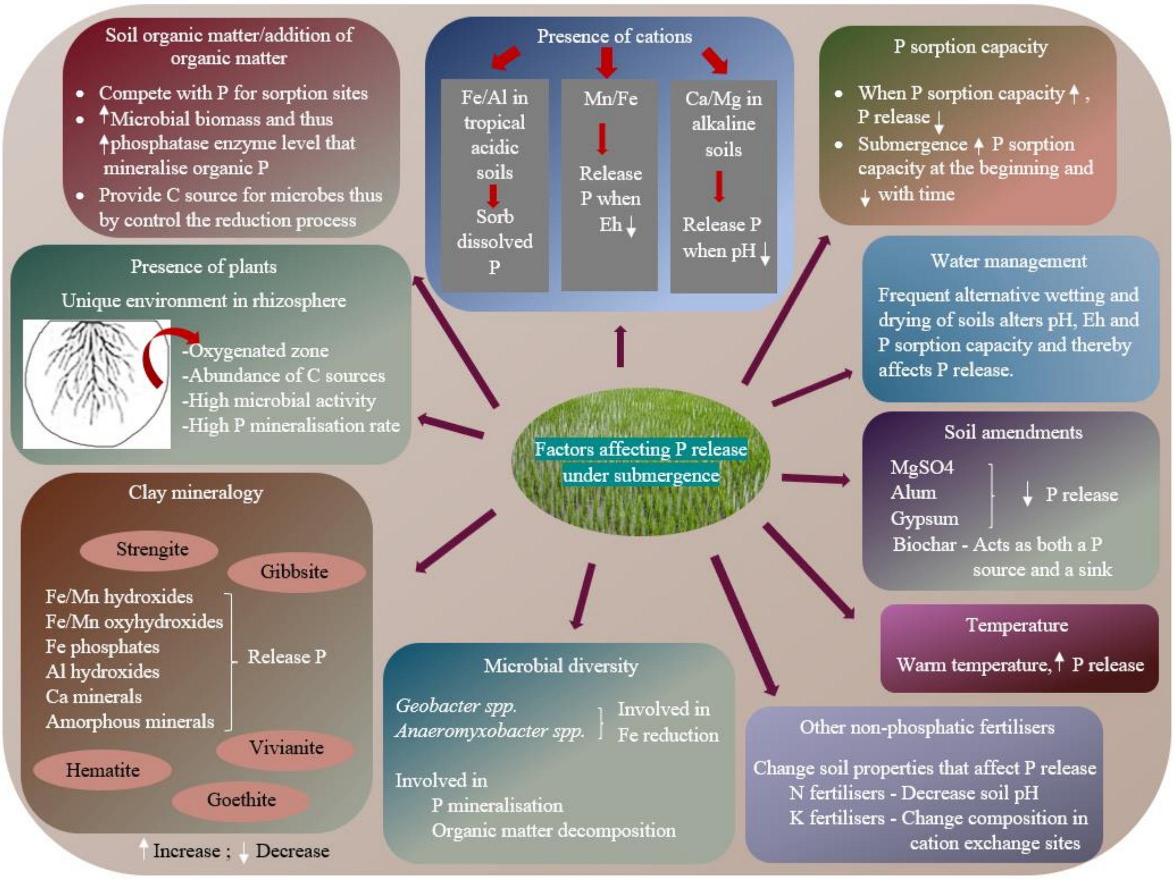


Fig. 2.5 Factors influencing P release during soil submergence, including soil and plant characteristics, as well as fertiliser and water management practices. This figure is based on the literature documents reviewed in section 2.6. Source: Palihakkara et al. (2024)

Eh: redox potential, $MgSO_4$: magnesium sulphate, C: carbon, P: phosphorus, N: nitrogen, K: potassium Fe: iron, Mn: manganese, Al: aluminium, Ca: calcium, Mg: magnesium

2.6.4 Manganese content

Manganese plays a key role in P release in soils that retain P via Mn(IV) oxides (Amarawansha et al., 2015). Phosphorus is released to soil solution by the reductive dissolution of Mn(IV) oxides upon submergence (Amery and Smolders, 2012; Zhang et al., 2021). A saturation experiment conducted in New Zealand using Melanic Orthic Gley soils revealed a significant positive correlation (r=0.559, p<0.001) between total dissolved P and soil solution Mn concentration (Smith et al., 2021a). Another laboratory experiment conducted in the UK on contrasting soils; a typical non-calcareous soil (sand 35%, clay 19%) and a typical brown earth soil (sand 77%, clay 11%) revealed a significant positive correlation (r=0.622, p<0.001) between total dissolved P and floodwater Mn concentration during 31 days of flooding (Khan et al., 2022). Manganese is present as Mn(II), $MnHCO_3^+$ and organic complexes in submerged conditions (Ponnamperuma, 1972). Manganese(II) ions can be removed from soil solution due to precipitation, adsorption and formation of organic complexes.

2.6.5 Soil organic matter content/quality or addition of organic matter

Organic matter increases soil solution P concentration by competitive sorption (Bhattacharyya et al., 2005). Organic compounds such as humic and fulvic acids, and low molecular weight aliphatic acids compete with P for sorption sites (Ajmone-Marsan et al., 2006). A laboratory incubation study revealed that the addition of cow manure and municipal solid waste to an Alluvial soil (Typic Fluvaquent) significantly ($p<0.05$) increased microbial biomass carbon and phosphatase enzyme concentrations in soil (Bhattacharyya et al., 2003), indicating the positive effect of organic matter addition on phosphate solubilisation. Organic matter slowly releases soluble P with time, via mineralisation (Ajmone-Marsan et al., 2006; Maranguit et al., 2017). A study using flooded tropical soils reported a significant positive correlation ($R^2=0.58$, $p<0.001$) with dissolved P and dissolved organic carbon indicating that organic P mineralisation from organic matter is driven by the need for carbon as the energy source for microorganisms (Maranguit et al., 2017). Organic matter, particularly dissolved organic carbon acts as an essential carbon source for the microbes which contribute to the reductive dissolution of Fe(III) and Mn(IV) oxyhydroxides (Hanke et al., 2013; Watts, 2000). Organic matter releases organic acids during anaerobic decomposition (Tsutsuki and Ponnamperuma, 1987). These acids form complexes with Ca^{2+} ions and increase the solubility of Ca-P compounds.

2.6.6 Microorganisms

Anaerobic microbes use organic matter as the carbon source for their respiration. The electrons released when organic matter is oxidised are accepted by electron acceptors such as O_2, NO_3^-, Fe(III), Mn(IV). Therefore, reductive dissolution of Fe(III) and Mn(IV) oxy(hydr)oxides and associated P release is microbially mediated. For example, it is evident that *Geobacter spp.* and *Anaeromyxobacter spp.* use Fe(Ш) as a terminal electron acceptor and hence Fe(Ш) reduces to Fe(II) (Hori et al., 2010; Sánchez-Alcalá et al., 2011) releasing associated P (Amarawansha et al., 2015). Other than that, mineralisation of organic P by microbial phosphatases, and microbial decomposition of soil organic matter have positive effects on P release under submergence, as described under section 2.6.5.

2.6.7 Phosphorus sorption capacity

The term P sorption is used generically to explain all processes involved in removing phosphate from soil solution such as adsorption, absorption and precipitation. Phosphorus sorption capacity (PSC) is affected by several soil properties such as pH, Fe and Al oxides, calcium carbonate ($CaCO_3$), and degree of weathering (Antoniadis et al., 2016). Measures of soil P sorption have been identified as promising tools to predict the variability of rice yield response to added P fertilisers under submergence in typical P deficient paddy soils (Nishigaki et al., 2021). This study reported a negative correlation (r=-0.697) of P sorption with increasing rice yield as a response to P fertiliser application (Nishigaki et al., 2021). Further, they identified air-dried soil moisture content mainly regulated by oxalate extractable Al as a parameter to predict soil P sorption. Similarly, anion storage capacity (ASC), a measure of P sorbing Al and Fe oxides of a soil and widely used in New Zealand, is a test used to identify soils with high potential for P loss to water in New Zealand (McDowell and Monaghan, 2015). Allophanic soils have the highest ASC (~90%) out of the fifteen soil orders in New Zealand (Hewitt et al., 2021). Degree of P saturation which is the extractable P concentration expressed as a percentage of PSC of a soil has also proven to be an important parameter in predicting P release upon submergence of soil (Kumaragamage et al., 2019).

Phosphorus sorption in soil can be explained by three possible mechanisms that involve soil pH. Gradual dissolution of Fe and Al oxides occurs at pH values between 2 and 5, and they reprecipitate as phosphates. Phosphate adsorption on clay mineral surfaces occurs at pH values between 4.5 and 7.5 and P precipitation by divalent cations occurs at pH values between 6 and 10 (Hanyabui et al., 2020). Adsorption can happen either physically or chemically. Physical adsorption occurs due to electrostatic attraction between soil colloidal surfaces and negatively charged phosphate ions. Chemical adsorption occurs with soil colloids with variable charges such as Fe and Al oxides and calcites (Zhao et al., 2021). With time, some of the adsorbed P on clay surfaces can diffuse into the colloid (absorbed) and form a specific mineral.

Two opposite effects of submergence on the P availability in paddy soils are documented. Submergence increases P availability temporarily due to reduction dissolution Fe/Mn oxy(hydr)oxides and releasing P sorbed/occluded. Based on the results of a P sorption study on two typical rice-growing soils (Ultisols: pH 6.0 and Entisols: pH 6.5) in China, Zhang et al. (2003) reported that the submergence of paddy soils can also increase PSC and decrease P desorption with time. Under submergence, crystalline Fe and Al oxides transform to amorphous forms (Darke and Walbridge, 2000). Amorphous oxides have higher reactive surface areas compared to their crystalline counterparts (Mayakaduwage et al., 2020). Therefore, P sorption by amorphous compounds of Fe and Al is high.

2.6.8 Soil amendments

Soil amendments alter P release from soil under submergence. A study conducted in Canada in clay soils (pH >7.9) revealed that application of $MgSO_4$ at a rate of 2.5 Mg/ha reduced the P release by 21-75% among the tested soils under snowmelt flooded conditions (Vitharana et al., 2021). The authors suggest a possible reason for this reduction is an increase in Mg concentrations which enhanced P precipitation. Application of alum ($Al_2(SO_4)_3{\cdot}18H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$) and manganese(IV) oxide (MnO_2) was also found to decrease P release under flooding conditions (Dharmakeerthi et al., 2019b; Attanayake et al., 2022; Kumaragamage et al., 2022).

Biochar application increased the PSC in acidic soils and decreased P sorption in alkaline soils (Xu et al., 2014). However, this is not an independent effect of biochar and is likely to occur due to interactions with other organic (organic matter) and inorganic compounds (cations; Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}) in soils. Biochar can act as a P source or a sink under submergence (Dharmakeerthi et al., 2019a). Previous research from the same authors showed that biochar can increase DRP in porewater in clay soils, while it had no effect on sandy loam soils (Dharmakeerthi et al., 2019a).

Organic amendments increase P availability in soil due to several mechanisms as explained in section 2.6.5. Application of organic manure such as poultry and cattle manure has been reported to increase soil available P concentrations under submergence (Chen et al., 2021). Furthermore, organic fertilisers can improve release of residual P in soil (Yang and Yang, 2021).

2.6.9 Temperature

Phosphorus release is higher at warmer temperatures compared to colder temperatures under anaerobic conditions (Sallade and Sims, 1997; Kumaragamage et al., 2020). An incubation study conducted using five agricultural soils in Canada using warm (20±2 °C) and cold (4±1 °C) temperatures revealed that P release in warm temperature under anaerobic condition is significantly higher ($p<0.05$) compared to that of cold temperature (Kumaragamage et al., 2020). The reason for the increasing trend of P release with increasing temperature, could be an increased rate of microbially mediated redox reactions with temperature in the presence of oxidisable organic matter (Heiberg et al., 2012). Contrastingly, another experiment conducted in wetland soils in the USA revealed that cooler temperatures and anaerobic conditions decrease P sorption (Hurst et al., 2022). Similarly, an incubation study conducted by Barrow (1983) also discovered that high temperatures increase P sorption.

2.6.10 Water management

Frequent alternative wetting and drying of a soil can alter pH and Eh of the water-soil system and thereby affects the P release from soil (Chacon et al., 2006). Drying events following wetting can reduce the PSC of soil by increasing the crystallinity of Fe hydroxides which can ultimately lead to increased P release from soil (Schönbrunner et al., 2012). In contrast, a soil column study conducted in China using vegetable and wheat growing soils revealed that the DRP in floodwater after reflooding, following a draining period of 10 days, was 3-25 times less than the DRP recorded in floodwater during a continuous flooding of 17 days (Tian et al., 2017). Furthermore, another study conducted in England and Wales reported that the water-soluble P, especially the organic form of P increased up to 1900% with the process of drying and rapid rewetting, possibly due to release of P from microbial biomass as they die by osmotic shock and cell rupture under rapid changes in soil moisture content (Turner and Haygarth, 2001).

Rainfall characteristics affect the magnitude of P losses from agricultural soils (Ramos et al., 2022). As rainfall infiltrates the previously unsaturated soil profile, water fills up pore spaces and saturates the soil profile. This results in saturation excess overland flow/runoff with continued rainfall (Stewart et al., 2019). In general, surface excess runoff occurs in wet areas near to channels (eg: critical source areas) (Loague et al., 2010). Saturation excess runoff is a mixture of ‘old’ porewater, and ‘new’ rainfall water which has failed to infiltrate (Burt and Pinay, 2005), thereby provisioning to mobilise porewater P to overlying runoff. Saturation condition in soil following a rainfall event can lead to P release from soils (Smith et al., 2023).

2.6.11 Presence/absence of plants and cultivars

The soil rhizosphere provides different environmental conditions relative to the bulk soil. The conditions in the rhizosphere are unique to plant species and even the cultivars of the same species, thereby incurring differences in P availability within that discreet region. Root exudates accumulating in the rhizosphere include low molecular weight (eg: organic acids, amino acids and sugars) and high molecular weight (eg: complex carbohydrates, enzymes etc.) organic compounds (Hinsinger et al., 2009; Pii et al., 2015). The composition of root exudates is influenced by plant cultivar and environmental factors (Aulakh et al., 2001; Pii et al., 2015). This abundance of carbon sources causes migration of microbes within a radius of 50 µm from roots (Dotaniya and Meena, 2015; Pii et al., 2015). Phosphatase enzymes released by microbes mineralise organic P and release orthophosphates (Rodrı et al., 2006). In addition, rhizosphere microbes produce organic acids such as oxalic and citric acids, and release protons to soil that help to decrease rhizosphere pH and compete for adsorption sites (Long et al., 2018). A field study conducted in a historic wetland but later (1940s) converted to a beef cattle pasture (bahia grass- *Paspalum notatumsite*) in Florida, USA revealed a significant correlation (r=0.82; $p \leq 0.01$) between total organic carbon (TOC) and organic-bound P for beef cattle pastures revealing the potential effects of pasture and hydrology on P release (Sigua et al., 2009).

There is a potential of root exposure to high levels of harmful reduced chemical species such as hydrogen sulphide (H_2S) and Fe(II) under O_2 depleted conditions in submerged soils (Larsen et al., 2015). However, an oxygenated zone exists in the rhizosphere due to atmospheric O_2 transfer through aerenchyma tissues (Mongon et al., 2014). This oxygen secretion by roots of rice plant enhances utilisation of P under submergence (Zhang et al., 2004).

2.6.12 Other non-phosphatic fertilisers

Phosphorus fertilisers are applied with other non-phosphatic fertilisers such as N fertilisers (urea or ammonium sulphate) and K fertilisers (muriate of potash) in both rice and pasture cultivations. Although these non-phosphatic fertilisers do not affect the P dynamics directly, they change other soil properties which affect P dynamics. For example, N fertilisers used in rice cultivation such as urea affect soil pH, and electrical conductivity (Park et al., 2023). Two paddy field studies conducted in Inceptisols (sandy clay loam) having an acidic pH ranging from 4.8-5.5, revealed a linear decrease in soil pH with increasing rates of urea, and ammonium sulphate fertilisers (Fageria et al., 2010). Further, application of urea to submerged/saturated soils increases NO_3^- ions to soil solution via hydrolysis of urea, followed by nitrification in the oxidised soil-water interface. Anaerobic microbes use electron acceptors for their respiration in sequential order of NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2 (Sahrawat, 2012; Marschner, 2021) which means usually, microbes do not use less energetically favourable electron acceptors, such as Fe and/or Mn in the presence of NO_3^-. Therefore, the presence of NO_3^- in soil solution can delay the microbially mediated P release under submergence through reductive dissolution of Fe/Mn oxy(hydr)oxides (Smith et al., 2021a). Potassium fertilisers increase the exchangeable K in soil (Volf et al., 2021). Large quantities of K^+ in exchangeable sites can displace divalent cations such as Ca^{2+} and Mg^{2+} from exchange sites (Zaker and Emami, 2019), which can affect P removal from soil solution by precipitation.

2.7 Methods and techniques to identify phosphorus dynamics in submerged soils

Phosphorus release in a submerged soil system is a result of complex biogeochemical reactions in soils mainly influenced by the inherent soil characteristics. It is important to study the behaviour of P under submergence at the P species level to gain a comprehensive understanding of P dynamics under such conditions. There are numerous methods which can be used to study soil P speciation. The P fractionation method introduced by Chang and Jackson (1957) is considered the oldest P fractionation method (Gu and Margenot, 2021). However, the Hedley sequential fractionation which was later developed by Hedley et al. (1982) is the most widely used P fractionation method (Table 2.6). As in any analytical methods, it also has its own drawbacks despite the modifications made by Tiessen and Moir (1993). One of the major limitations of these sequential chemical extraction methods is, they are limited to operationally defined fractions (Schmieder, 2019). For example, the Hedley fractionation separates soil P into resin-P, $NaHCO_3$-P, NaOH-P and HCl-P extractable fractions (Nishigaki et al., 2018). But it does not reveal P species (Gu et al., 2020; McDowell and Burkitt, 2022).

When P fractionation is performed for submerged soils, it is important to collect samples under reduced conditions and handle them appropriately during P fractionation (Condron and Newman, 2011) as P dynamics under submergence is controlled by the redox potential of soil. Redox-driven ions such as Fe^{2+} and Mn^{2+} in submerged soils can be oxidised within a short period of time upon exposure to an aerobic environment and this will lead to an inaccurate interpretation of P concentrations in different soil P fractions. Moore and Coale (2000) considered these conditions and introduced a method for P fractionation in flooded soils and sediments based on the P fractionation methods by van Eck (1982) and Moore and Reddy (1994).

Redox potential measurements have been used as an important parameter in exploring P dynamics in submerged agricultural soils in previous field and laboratory studies (Shenker et al., 2005; Kumaragamage et al., 2019; Zhang et al., 2021). In such studies, the Eh has been measured using oxidation-reduction potential (ORP) sensors (Shaheen et al., 2021) or using half-cell platinum electrodes with an Ag/AgCl or a calomel reference electrode and a voltmeter (Kumaragamage et al., 2019; Vitharana et al., 2021).

Advanced technologies such as molecular analyses have evolved since the 1990's, overcoming the limitations of P fractionation methods. Molecular analyses such as ^{31}P nuclear–magnetic resonance (NMR) spectroscopy and X-ray absorption near-edge structure (XANES) spectroscopy enable an identification of P species in soils (Alam et al., 2021). These techniques have been used to successfully identify changes in P species in submerged soils, including paddy soils (Liu et al., 2014; Attanayake et al., 2022). However, these analyses also have several limitations (Vogel et al., 2016) as outlined in the Table 2.6.

Table 2.6 Commonly employed methods along with their advantages and disadvantages for the identification of phosphorus species in soil

Method/Technique	Advantages	Limitations	Reference
Hedley fractionation and modifications	• Reveal extractable Resin-P, $NaHCO_3$-P, NaOH-P, and HCl-P • Quantify P available for plants (sum of resin P (inorganic), bicarbonate P (inorganic) and P (organic)	• Cannot distinguish Fe-bound, Al-bound, or Ca-bound P	Hedley et al. (1982) Tiessen and Moir (1993) Yang and Post (2011) Gu et al. (2020)
X-ray absorption near-edge structure (XANES) spectroscopy	• Indicate the structure and chemical group of target elements at the molecular level • Distinguish P fractions bound by metal oxides or hydroxides (eg: Fe, Al, and Ca) and adsorbed phases of P • Non-invasive	• Possible substantial matrix interference	Lombi and Susini (2009) Prietzel et al. (2013) Wu et al. (2014) Kruse et al. (2015) Alam et al. (2021)
^{31}P nuclear–magnetic resonance (NMR) spectroscopy	• Non-destructive • Can detect all P species in single analysis • Highly specific to P species	• Interference from paramagnetic ions (Fe, Mn)	Weyers et al. (2016) Rivard et al. (2016) Alam et al. (2021)
Isotope techniques (^{32}P, ^{33}P and $\delta^{18}O_p$)	• Reveal the role of microbes in P cycling ($\delta^{18}O_p$)	• Short half-life • Health risks • Specific safety procedures to apply in soil	Tamburini et al. (2012) Helfenstein et al. (2018) Pfahler et al. (2022)

P: phosphorus, Fe: iron, Al: aluminium, Ca: calcium, Mn: manganese, Resin-P: resin extractable P, $NaHCO_3$-P: Sodium bicarbonate extractable P, NaOH-P: Sodium hydroxide extractable P, HCl-P: hydrochloric acid extractable

However, none of these analytical techniques can successfully identify P species in soil independently because of the complex biochemical processes of P (Liu et al., 2017). For example, for certain soils, XANES spectroscopy may not enable reliable differentiation between organic P and inorganic P adsorbed to a given soil adsorbent under certain soil conditions (Prietzel et al., 2016). Furthermore, subsequent studies have also showed that measures of organic P by P fractionation can be used to complement XANES spectroscopy (Gu and Margenot, 2021). Thus, the combined use of wet chemistry and spectroscopic analytical techniques could provide detailed information on the impacts of management practices on various P species distributions and transformations (Liu et al., 2019; Negassa et al., 2020). Furthermore, the kinetics of the exchanges of P among different P pools of submerged soil can also be incorporated in the analysis to improve the overall understanding of the P dynamics under submergence.

2.8 Summary and research gaps

There is a poor response of rice yield to added P fertilisers in rice paddy soils in Sri Lanka. Several research studies have proved that this response cannot be explained by Olsen P concentrations of soils alone or by factors such as irrigation schemes, soil texture, pH, electrical conductivity, total carbon content, and available Fe and Mg concentrations. However, a mechanistic understanding P transformation in paddy soils under submergence with management practices such as fertiliser addition has not been studied to date. Understanding these connections is important in rational decision making with regards to formulating site specific fertiliser recommendations on rice paddy soils in Sri Lanka. The optimal use of fertilisers will also help to reduce the negative effects on surface freshwater bodies in Sri Lanka.

In New Zealand, previous studies have focused on quantifying DRP loss from pasture soils via surface subsurface runoff and leaching with rainfall rather than on understanding the mechanisms of P release. The need to fully understand the sources, time, and mechanisms of P release from pasture soils has been highlighted in several studies. There are limited research on the effect of different soil types on the P release upon short-term but frequent submergence, caused by saturation excess during rainfall events in agricultural features such as CSAs in New Zealand. Furthermore, the extent and mechanisms of P release by different New Zealand grassland soils to porewater and overlying water during short-term submergence has not previously been studied. A comprehensive understanding of these aspects is important for implementing improved P management strategies in CSAs to minimise P loss to surface waters, specifically when CSAs are located adjacent to freshwater bodies. Furthermore, detainment bunds and constructive wetlands are increasingly being used in New Zealand as an effective method to mitigate nutrient losses from pasture lands. However, it is not known if different soils release P to overlying water during this temporary submergence (eg: 3 days in detainment bunds). Yet, an improved understanding of P release in different CSA soils upon short-term submergence is important when selecting suitable sites/soils to construct detainment bunds and/or constructed wetlands.

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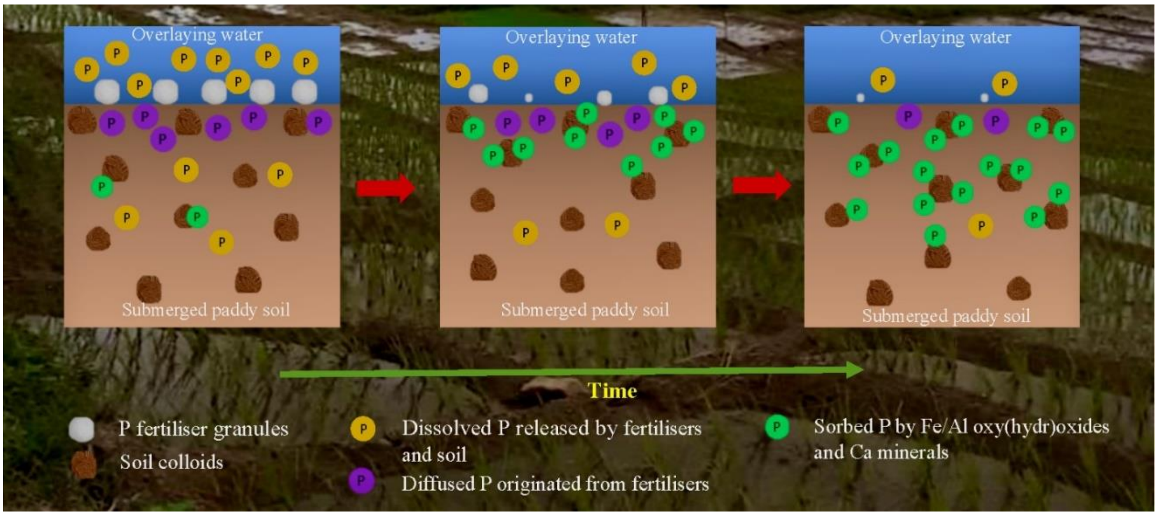
Chapter 3

Phosphorus release and transformations in contrasting tropical paddy soils under fertiliser application

Graphical Abstract



Highlights

- Release of P from TSP and SSP applied to submerged Ultisol, Alfisol and Entisol soils was assessed.
- P fertilisers did not increase DRP in porewater in all soils, except immediately after fertiliser application.
- Calcium phosphates and P associated with ferrihydrite dissolved and released P to porewater during submergence.
- The dissolved P translocated to deeper soil layers and resorbed onto amorphous and crystalline Fe/Al oxy(hydr)oxides and Ca minerals.

Abstract

The driver for inconsistent yield response to applied inorganic phosphorus (P) fertilisers in tropical rice paddy soils is yet to be fully addressed. The contribution of applied P fertilisers to soluble soil P and the P transformation mechanisms of P and nitrogen (N) fertilised soils in rice paddy soils remain unresolved. A laboratory incubation study was conducted aiming to explore the P release and transformations of three rice-growing soils (Ultisol, Alfisol, and Entisol) in Sri Lanka during submergence for 112 days, with and without single superphosphate (SSP) or triple superphosphate (TSP) and urea. Dissolved reactive phosphorus (DRP), pH, dissolved organic carbon, and selected cation and anion concentrations in porewater, and soil Eh were measured. The soil P transformations were assessed using thermodynamic modelling and chemical P fractionation. Phosphorus fertiliser applied soils had significantly higher (1.1-8.0 mg/L) DRP concentrations compared to unfertilised soils only at 7 days after submergence (DAS). Beyond 21 DAS, the DRP concentration in all soils remained low, ranging from 0.024 to 0.300 mg/L. The SSP treatment demonstrated greater efficacy than the TSP treatment in elevating short-term porewater DRP. Urea application did not significantly ($p>0.05$) change porewater DRP in any of the soils. Thermodynamic modelling revealed that calcium (Ca) phosphates and P associated with ferrihydrite potentially dissolved during the submergence. Released P in the soils may be resorbed by the abundant iron (Fe) and aluminium (Al) oxy(hydr)oxides and Ca minerals, as indicated by fractionation results. Further, there is evidence of downward movement of dissolved P and its resorption onto Fe/Al and Ca minerals (moderately labile pool) possibly due to saturation of P sorption sites in the topsoil layer. Inherent soil characteristics such as low organic matter content and high concentration of amorphous Fe and Al oxides may have contributed to the low dissolved P in porewater.

Keywords: Calcium phosphates, dissolved reactive phosphorus, Fe/Al oxy(hydr)oxides, P fractionation, submergence, tropical paddy soils

3.1 Introduction

Rice (*Oryza sativa* L.) is the third most commonly grown cereal crop in the world next to wheat and maize (FAOSTAT, 2022). Rice is cultivated on approximately 165 million ha, covering over 10% of the total arable lands of the world (FAOSTAT, 2022), which makes it a staple food for over half of the world's population. More than 80% of rice is cultivated in the tropical region, mostly in Asia. Among the essential nutrients, phosphorus (P) stands out as a key element applied by farmers, given its key role in regulating rice growth. However, several studies have highlighted the inconsistent rice yield response to applied P fertilisers in tropical rice paddy soils, and it has remained unexplained for a long time (Doberman et al., 2003; Kendaragama et al., 2003; Sirisena and Suriyagoda, 2018; Nishigaki et al., 2021; Palihakkara et al., 2024).

Rice is cultivated in two seasons per year called *Yala* (May to September) and *Maha* (October to January), based on monsoonal rains in Sri Lanka. Many studies reported in the literature have demonstrated that the response of rice yield to applied P fertilisers is inconsistent in paddy soils in Sri Lanka. Short-term field studies of up to four cropping seasons revealed that rice yield did not respond to applied P fertilisers in most of the paddy-growing soils (Kendaragama et al., 2003; Sirisena et al., 2013; Kulasinghe et al., 2020). Long-term field experiments conducted in up to five consecutive seasons showed significant (p<0.05) yield increase with P fertiliser application only in *Yala* season (Kendaragama et al., 2003). Another long-term experiment conducted with different fertiliser rates for ten consecutive seasons showed no significant (p>0.05) yield increase in either *Yala* or *Maha* seasons (Senevirathne Banda et al., 2002). An experiment conducted over a span of 10 years in a field without applied fertilisers revealed no statistically significant increase in rice yield when P fertiliser was applied in the subsequent three consecutive seasons (Kodagoda et al., 2022). Kulasinghe et al. (2020) reported significant spatial heterogeneity in soil P concentrations in rice-growing soils. Further, it has been demonstrated that the yield response to applied P fertilisers in rice paddy soils cannot be explained by common soil P tests (eg: Olsen P concentration), or soil properties such as soil texture (Kendaragama et al., 2003; Sirisena et al., 2013; Kulasinghe et al., 2020).

The cultivation of rice under submerged conditions can influence the dynamics of P in soils (Huang et al., 2014; Jia et al., 2018) by altering soil properties (Ponnamperuma, 1972). For example, under submergence, soil pH typically shifts towards the neutral range (Fageria et al., 2011). In acidic soils, pH increases primarily due to reductive dissolution of Fe(Ш) and Mn(IV)/Mn(Ш) minerals, leading to the release of P (Lu et al., 2022). Conversely, in alkaline soils, pH decreases due to decomposition of organic matter (Fageria et al., 2011), which causes Ca and Mg minerals to dissolve, releasing P into the porewater (Jayarathne et al., 2016). In addition to pH, changes in other soil properties under submergence include redox potential, P sorption capacity, organic matter availability, and crystallinity of minerals which play a significant role in P dynamics (Maranguit, 2017; Marschner, 2021; Nishigaki et al., 2021). Due to the complex interactions between hydrological and biochemical processes, understanding the dynamics of soil P under submergence has proven challenging. Previous attempts to pinpoint the underlying reasons for inconsistencies in yield response by examining individual soil properties have been unsuccessful (Kendaragama et al., 2003; Sirisena et al., 2013; Kulasinghe et al., 2020). Therefore, a mechanistic understanding of P dynamics of paddy soils under submergence is necessary to address this unexplained phenomenon.

Phosphorus release due to submergence is limited in highly weathered tropical soils due to their high P sorption potential (Rakotoson et al., 2015; Andriamananjara et al., 2016; Pierzynski and Hettiarachchi, 2018; Nishigaki et al., 2019). This is mainly due to inherent characteristics of soils, such as having greater concentrations of Fe and Al oxy(hydr)oxides and highly weathered kaolinitic (1:1) clay minerals, which have high affinity to P (Gérard, 2016; Pierzynski and Hettiarachchi, 2018). These inherent soil characteristics could be contributing to the poor/unclear yield response to applied P fertilisers in tropical soils, including those found in rice-growing soils in Sri Lanka. However, there is a lack of studies that offer empirical evidence regarding P release and transformations in fertiliser applied rice paddy soils under submergence.

Phosphate transformation under submerged conditions is often different from that observed in aerobic soil conditions. In submerged conditions, the anaerobic microbes become more dominant than aerobic microbes (Fageria et al., 2011) which changes the P transformation dynamic. The anaerobic microbes use electron acceptors for their respiration in sequential order of NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2 (Marschner, 2021; Sahrawat, 2012). Most commonly, microbes do not use less energetically favourable electron acceptors, such as Fe and Mn in the presence of NO_3^-. Therefore, the presence of NO_3^- in soil solution can buffer or delay the microbially mediated P release under submergence through reductive dissolution of Fe/Mn oxy(hydr)oxides (Smith et al., 2021). Application of urea as a source of nitrogen (N) fertiliser in rice paddy cultivation increases NO_3^- ions to soil solution via hydrolysis of urea followed by nitrification in the oxidised soil-water interface. However, previous studies have not considered the factor of NO_3^- as an important variable that can be examined to explain the inconsistent yield response to applied P fertilisers in rice paddy soils.

Therefore, a study was initiated to investigate the transformation of P in submerged paddy soil in the presence of NO_3^- with the aim of developing effective P management strategies to enhance P use efficiency in rice cultivation. The objectives of this study were to investigate release and transformations of P in three contrasting rice paddy soils fertilised with either TSP or SSP, and to assess how the application of urea influences P release and transformations in the P fertilised soils under submerged conditions. It was hypothesised that the reductive dissolution of Fe/Mn oxy(hydr)oxides during submergence would release sorbed P, consequently elevating the P concentration in the soil solution. In addition, it was hypothesised that urea application would delay the reductive dissolution of Fe/Mn oxy(hydr)oxides by increasing the NO_3^- concentration in soils, thereby impairing P release through reductive dissolution.

3.2 Materials and Methods

3.2.1 Soils used in the incubation study

The present incubation study used three rice-growing soils with contrasting properties collected from three locations in Sri Lanka, namely Hanguranketha (N 7° 08’ 23.57”, E 80° 47’ 34.16”), Mahailluppallama (N 8° 05’ 59.2”, E 80° 26’ 33.2”), and Aranaganwila (N 7° 46’ 30.1”, E 81° 09’ 55.0”). Bulk soil samples from 0 to 30 cm depth of the three locations were classified according to the US Soil Taxonomy as Typic Rhodudults (Ultisol), Typic Haplustalfs (Alfisol), and Typic Udipsamments (Entisol), respectively. The soil samples were air-dried, passed through a 2 mm sieve, homogenised, and stored at room temperature until further analysis. A sub-sample of each soil was analysed for basic soil properties. Soil pH and electrical conductivity were determined in 1:2.5 soil to distilled water suspension using a pH meter (Hanna HI2020-02) and a conductivity meter (Eutech COND 6+), respectively. Organic carbon was determined by Walkey and Black method (Nelson and Sommers, 1996). Available P was extracted by Olsen (Olsen and

Sommers, 1982) and Mehlich-3 (Mehlich, 1984) methods. Water extractable P was extracted by the method introduced by Self-Davis et al. (2000). Phosphorus in the extracts were determined by the molybdate blue colour method by Murphy and Riley (1962). Phosphorus sorption capacity (PSC) was determined by the single point P sorption method by Bache and Williams (1971). Cation exchange capacity (CEC) was determined by the unbuffered salt extraction method (Sumner and Miller, 1996). Bulk density was determined by the core method (Grossman and Reinsch, 2002). Oxalate extractable Al and Fe were determined using the acid ammonium oxalate extractant in the dark (Jackson and Lim, 1986). Mehlich-3 extractable K and Na concentrations were measured using flame emission spectrophotometer (Jenway PFP 7) and Mehlich-3 extractable Ca and Mg concentrations were measured using atomic absorption spectrophotometer (Shimadzu AA-6200). Soil texture was determined by the pipette method (Gee and Bauder, 1986). The X-ray diffraction (XRD) analysis was performed for the initial soil samples of the three soils. The XRD intensities were recorded as a function of 2θ operated at a potential of 40 kV and 34 mA producing Cu Kα radiation (λ=1.5406 Å).

3.2.2 Experiment design and treatments

Plastic incubation vessels (1.5L capacity) were acid cleaned (2% HNO_3) and covered with a dark paper to control photochemical reactions. The incubation vessels were filled with homogenised soil up to a height of 11 cm (approximately 1.2 kg for Ultisol, 1.3 kg for Alfisol, and 1.4 kg for Entisol). Soils were saturated with reverse osmosis (RO) water and a 2 cm waterhead was maintained throughout the experimental period. Porewater samplers (Rhizon-flex – 10 cm in length) were inserted vertically in the middle of each bottle. A platinum (Pt) electrode was permanently installed at the 5 cm depth from the surface of the soils in control soils (no P and no N fertilisers) for Eh measurements. The vessels were placed under room temperature at 30±5 ^{o}C.

Triple superphosphate, SSP and control (no P fertiliser) with and without urea were used in this experiment to formulate six treatments. The P fertilisers were applied at a rate of 3.2 g P/m^2 (equivalent to 32 kg P/ha), 6 days after submergence. Two split applications of urea were applied at the rates of 2.8 and 2.3 g N/m^2 (equivalent to 28 and 23 kg N/ha, respectively) at 20 and 48 days after submergence, respectively. The three fertilisers were applied to the soil surface in granular form, mimicking the farmer practices. The time of fertiliser application was decided based on the fertiliser recommendation for rice by the

Rice Research and Development Institute (RRDI), Sri Lanka (RRDI, 2013). The P rate was three times higher, and the N rates were 50% lower than the recommended rates of the RRDI, Sri Lanka (RRDI, 2013). A higher P rate was employed to define treatment effects and elucidate P transformations, while a lower N concentration was used to offset plant N uptake in the field. Although the RRDI recommends applying urea in four split applications, this experiment adopted two split applications to align with typical farmer practices. The experimental setup was maintained for a duration of 112 days. Four replicates were maintained for each treatment, with one specifically designated for destructive harvesting at 35 days after submergence (DAS) for P fractionation analysis.

3.2.3 Soil and water sampling and analysis

Soil porewater was collected from three replicates, weekly, for the first 70 days and then biweekly for the rest of the 42 days using Rhizon-flex samplers, by applying a vacuum using a 50 ml syringe. The porewater samples were filtered through 0.45 µm nylon membrane filters and analysed for DRP by molybdate blue colour method (Murphy and Riley, 1962) using UV visible spectrophotometer (Shimadzu UV-1900i) within 12 hours after sampling. The pH of porewater samples were measured using a glass pH electrode (Hanna HI2020-02). The soil Eh was measured at each porewater sampling event using a calomel reference electrode (Hanna HI5412). The voltmeter reading was corrected to the standard hydrogen electrode potential by adding +250 mV. Cation concentrations (Ca, Mg, K, Na, Fe, Al, and Mn) of porewater were measured 7, 21, 35, and 70 DAS using inductively coupled plasma optical emission spectroscopy (iCAP 7000 series ICP-OES). Porewater anion concentrations (Cl^-, F^-, NO_3^-, and SO_4^{2-}) were measured 7, 35, and 70 DAS using ion chromatography (Metrohm 930 Compact IC Flex). Dissolved organic carbon concentrations were measured 7, 35, and 70 DAS using a carbon nitrogen analyser (Skalar Primacs SNC 100-IC). Alkalinity of the porewater samples was measured by titrating against 0.1 N H_2SO_4 in the presence of methyl orange indicator.

3.2.4 Soil sampling and analysis for phosphorus fractionation

Phosphorus fractionation was performed using a modified Hedley procedure (Hedley et al., 1982) for the soils collected at 0-2, 2-4 and 4-6 cm depths at 35 and 112 DAS. The soil samples were purged with argon gas, sealed, and stored at -28 ^{0}C until P fractionation analysis were performed. An aliquot of soil (approximately 0.5 g) was subjected to sequential extraction using 30 mL of each of the following solutions in the specified order: distilled water, 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1.0 M HCl. The suspension was shaken for 16 h, centrifuged for 10 minutes at 7500 rpm, and the supernatant was passed through a 0.45 μm nylon membrane filter for each extraction step. The first two extraction steps (using distilled water and 0.5 M $NaHCO_3$) were performed while purging argon gas to have minimum contact with oxygen. A portion of the $NaHCO_3$ and NaOH extracts was acidified using concentrated H_2SO_4 to precipitate extracted organic matter and the supernatant was analysed for inorganic P (Pi), while a portion of H_2O extract was directly analysed for Pi without acidification. Another 10 mL of H_2O, $NaHCO_3$, NaOH, and HCl extracts was digested in a digestion block at 150^{o} for 40–60 minutes until the volume of the digestion tube reduced to 2 mL. Acidified potassium persulfate oxidation was used for the digestion and the residue was analysed for total P (TP). The difference between TP and Pi was estimated to be organic P (Po) (Tiessen and Moir, 1993). The P in the soil residue left after sequential extraction was determined after digestion with aqua regia (Chen and Ma, 2001).

3.2.5 Thermodynamic modelling

To predict the solid P species in porewater samples at 7, 35 and 70 DAS, the thermodynamic modelling software Visual MINTEQ 3.1 (Gustafsson, 2013) was used. The input parameters entered in the software were soil Eh, pH, and concentrations of cations (Ca, Mg, Mn, and Fe), anions (Cl^{-}, F^{-}, NO_3^{-}, and SO_4^{2-}), DOC, alkalinity and DRP in porewater. The Stockholm Humic Model (SHM) was used as the state-of-the-art model to simulate the complexation to natural organic matter, and it was assumed that fulvic and humic acids were present in similar quantities in porewater.

3.2.6 Statistical analysis

Statistical analysis was performed using SAS 9.4 software. Porewater DRP was analysed using Proc Mixed repeated measures analysis to compare soils and treatments (N and P fertiliser effects separately) over DAS. Compound symmetry was used as the covariate structure of the subject effect. Principal component analysis was performed using DRP, Eh, pH, and cations (Fe, Mn, Ca and Mg) to identify the factors governing the porewater DRP.

3.3 Results

Briefly, Ultisols and Entisols had slightly acidic pH (6.81 and 6.15 respectively), whereas Alfisols had a neutral pH (Table 3.1). Entisol had 94% of sand, whereas Ultisol and Alfisol had sandy loam and sandy clay loam texture, respectively. Entisols had the lowest extractable P (Olsen P: 3.2 mg/kg) and PSC (431 mg P/kg) followed by Ultisols (Olsen P: 26 mg/kg, PSC: 493 mg P/kg) and Alfisols (Olsen P: 65 mg/kg, PSC: 506 mg P/kg). Similarly, Entisol had the lowest extractable Ca, Mg and K concentrations. All soils had low organic carbon contents, which ranged from 3.6 to 9.8 g/kg. The mineralogical composition of the clay fraction of the three soils revealed the presence of kaolinite (1:1 type clay), montmorillonite and illite (2:1 type clay) in all three soils and the presence of chlorite (2:1:1 type clay) vermiculite (2:1 type clay) in Ultisols and Alfisols. As metal oxides, gibbsite was present in Ultisols and Entisols and goethite was present in Alfisols. Further, a manganese silicate (bementite) was present in Alfisols and an arsenate mineral (burgessite) was present in Ultisols.

Table 3.1 Initial selected physico-chemical properties of soils

	Ultisol	Alfisol	Entisol
pH	6.81	7.09	6.15
EC (µS/cm)	80.7	29.6	20.8
Sand %	67.7	68.3	93.7
Silt %	17.9	11.3	3.3
Clay %	14.4	20.4	3.0
Textural class	Sandy loam	Sandy clay loam	Sand
OC (g/kg)	7.7	9.8	3.6
CEC ($\text{cmol}_{(+)}$/kg)	8.8	8.0	3.0
Olsen P (mg/kg)	26.0	65.0	3.2
Mehlich-3 extractable P (mg/kg)	35.6	125.8	5.1
Water extractable P (mg/kg)	3.6	7.2	2.1
$\text{Al}_{\text{oxalate}}$ (g/kg)	22.6	22.1	9.7
$\text{Fe}_{\text{oxalate}}$ (g/kg)	340	250	86
Bulk density (g/cm^3)	1.54	1.55	1.38
P sorption capacity (mg P/kg)	493	506	431
Extractable Ca (mg/kg)	1016	1525	405
Extractable K (mg/kg)	296.1	206.0	16.4
Extractable Na (mg/kg)	0.9	1.0	0.9
Extractable Mg (mg/kg)	19.0	31.9	3.3
Clay mineralogy	Kaolinite (48.8%) Montmorillonite/ Illite (32%) Chlorite/ Vermiculite (11%) Gibbsite (3.9%) Quartz (traces) As mineral (4.4%)	Kaolinite (9.8%) Montmorillonite/ Illite (47.4) Chlorite/Vermiculite (25.5%) Mn silicate (17.2%) Goethite	Kaolinite (39%) Montmorillonite/ Illite (34.6%) Gibbsite (6.2%) Quartz (20.2%)

OC: Organic carbon, CEC: Cation exchange capacity, $\text{Al}_{\text{oxalate}}$: Ammonium oxalate extractable Al, $\text{Fe}_{\text{oxalate}}$: Ammonium oxalate extractable Fe. pH and EC were measured in 1:2.5 Soil: Distilled water suspension, Ca, K, Na and Mg were extracted by Mehlich-3 solution. The abundance of the clay minerals in the tested sample is indicated in parenthesis as a percentage.

3.3.1 Variation in porewater pH and soil Eh during submergence

The porewater pH variation of three soils showed a similar pattern during submergence (Fig. 3.1A, 1B and 1C). Overall, the pH in porewater decreased during the submergence from ~8.0 to ~6.5, except at the last sample collection, in which the pH was higher. The pH variation of the six treatments of each soil showed a similar pattern during the submerged period. Statistical analysis performed for separate soils revealed significant ($p<0.05$) effect of urea on pH in Entisol soil. The urea applied Entisol significantly ($p<0.05$) increased pH compared to control at one day after the second urea application which was at 49 DAS (Fig. 3.1C). A significant ($p<0.05$) decrease of pH with time compared to the control treatment was observed in the urea applied Ultisol at 35 DAS, nearly two weeks after the first split application (Fig. 3.1A). Further, TSP plus urea applied treatments of Alfisol and Entisol showed a significant ($p<0.05$) decrease in pH at 42 DAS compared to TSP only applied treatments (Fig. 3.1B and 1C). However, later with time, a significant ($p<0.05$) increase of pH was observed again at 63 DAS in the urea applied Ultisol compared to the control treatment (Fig. 3.1A).

The Eh of the three soils decreased over the submergence period. The Eh were 9 (Ultisol), 164 (Alfisol) and 7 mV (Entisol), at 24 hours after submergence (Fig. 3.1D). At the end of 70 days, the Eh values ranged from -195 to -247 mV in all three soils indicating a highly reduced condition. Both Ultisol and Entisol soils were anoxic from the beginning of submergence until the end of the experiment (Fig. 3.1E). In contrast, Alfisol had relatively higher pe+pH until 28 DAS compared to the other two soils and thereafter it was in the anoxic range. According to XRD results, 17% of the clay fraction of Alfisols was comprised of a Mn mineral (Table 3.1). The remaining two soils did not exhibit any indication of the presence of such a mineral. This discrepancy may account for the extended duration Alfisols required to reduce Eh upon submergence compared to Ultisols and Entisols (Fig. 3.1D).

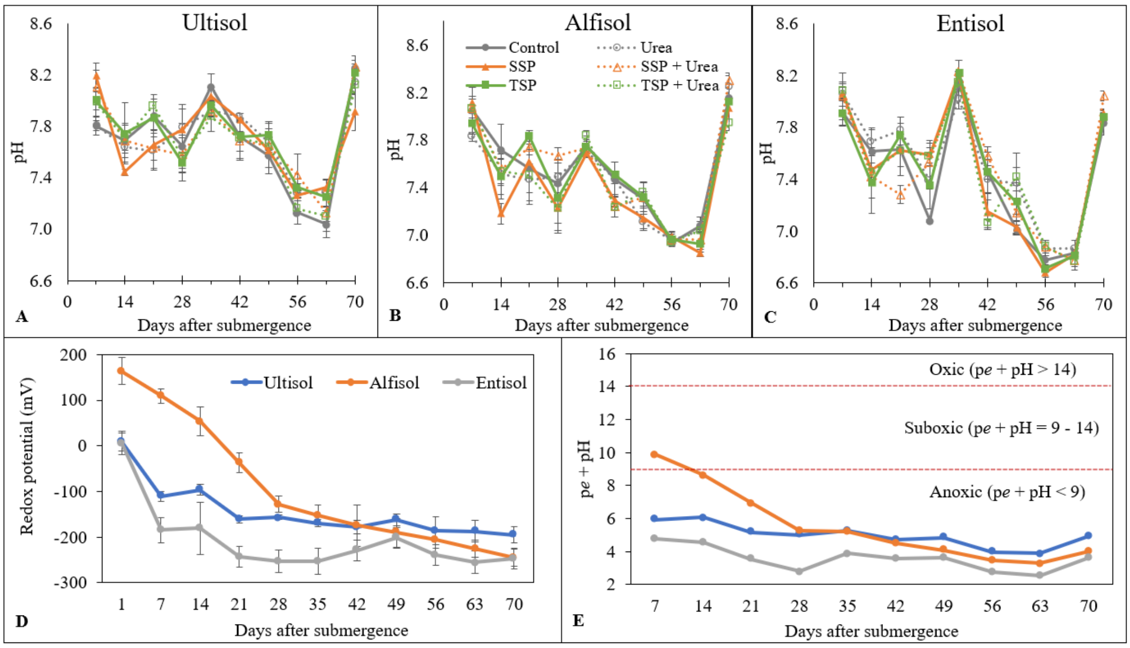


Fig. 3.1 A, B and C: Variation of pH in the three soils during submergence; **D:** Variation of Eh in the three soils during submergence; **E:** p*e*+pH variation in the three soils during submergence Redox zones are indicated by dash lines; oxic (p*e*+pH>14), suboxic (p*e*+pH=9-14), anoxic (p*e*+pH<9). The error bars represent the standard errors of the means.

3.3.2 Phosphorus release during submergence

The DRP release to porewater during submergence was not significant (*p*>0.05) among the three soils. The urea treatment did not significantly (*p*>0.05) influence DRP concentrations in porewater in any of the soils (Appendix I, Supplementary Table 3.S2). Therefore, all six replicates (with and without urea) were combined in each P fertiliser treatment in subsequent analysis (Fig. 3.2). Results in Fig. 3.2 shows that application of both P fertiliser treatments significantly increased (*p*<0.05) the porewater DRP concentration relative to the control only at 7 DAS. In Ultisol, application of the SSP and TSP treatments significantly increased the DRP by 48-fold and 30-fold compared to the control, respectively. Similarly, in the Alfisol, the SSP and TSP increased the DRP values by 54-fold and 11-fold relative to the control, respectively. In the Entisol, the SSP treatment increased the DRP by 3-fold compared to the control. However, the TSP treatment did not significantly (*p*>0.05) increase the DRP at 7 DAS in the Entisol. After day-7, application of SSP and TSP in all three soils did not induce significant (*p*>0.05) changes in DRP concentration compared to the control throughout the experiment.

The porewater DRP concentrations in treatments with applied P fertilisers decreased significantly from 1-8 mg/L at 7 DAS to <0.10 mg/L at 14 DAS across all three soils (Fig. 3.2). Later, around 28 DAS, DRP concentrations slightly increased up to ~0.1 mg/L in all treatments in Alfisols, and P fertiliser applied Entisols (Fig. 3.2B and 2C). Ultisols had the lowest DRP concentration throughout the submergence period and it was always below the detection limit (0.024 mg/L), except on a few occasions in P fertiliser applied treatments, in which the DRP concentrations were slightly ~0.04 mg/L above the detection limit (Fig. 3.2A).

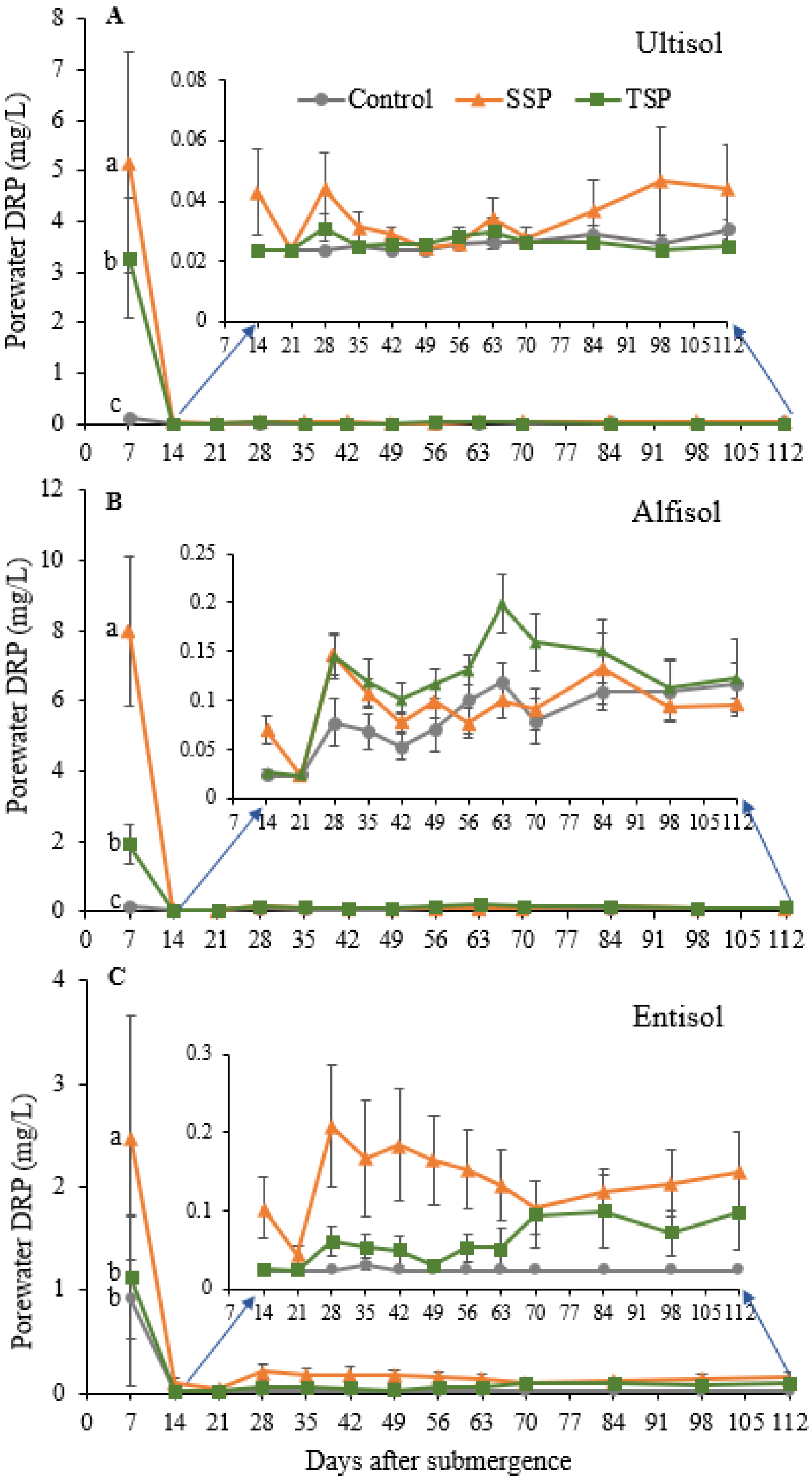


Fig. 3.2 Variation in dissolved reactive P in porewater of Ultisol (**A**), Alfisol (**B**) and Entisol (**C**) soils during submergence. SSP: Single superphosphate, TSP: Triple superphosphate. The error bars represent the standard errors of the means.

3.3.3 Variations of porewater Fe, Mn, Ca and Mg concentrations and their relationship with redox potential and pH

The concentrations of porewater Fe, Mn, Ca and Mg during the submergence were significantly ($p<0.0001$) different among the three soils (Fig. 3.3). Correlation analysis conducted to evaluate the relationship among porewater DRP, pH, Eh, and cation concentrations revealed significant correlations between porewater DRP and Ca concentration (r=0.45, $p<0.01$), and Eh (r=0.35, $p<0.01$) (Appendix I, Supplementary Table 3.S3). Subsequent separate correlation analyses for each soil type revealed relationships among these parameters specific to soil types. In Ultisol, porewater DRP exhibited significant correlations with porewater Ca (r=0.59, $p<0.01$), Mg (r=0.30, $p<0.01$), Mn concentrations (r=0.35, $p<0.01$), and soil Eh (r=0.24, $p<0.05$). In Alfisol, significant correlations were observed between porewater DRP and porewater Ca concentration (r=0.58, $p<0.01$), pH (r=0.27, $p<0.05$), and soil Eh (r=0.45, $p<0.01$). Further, in Entisol, porewater DRP displayed significant correlations with porewater Ca (r=0.46, $p<0.01$), Mg concentrations (r=0.50, $p<0.01$), and soil Eh (r=0.35, $p<0.01$).

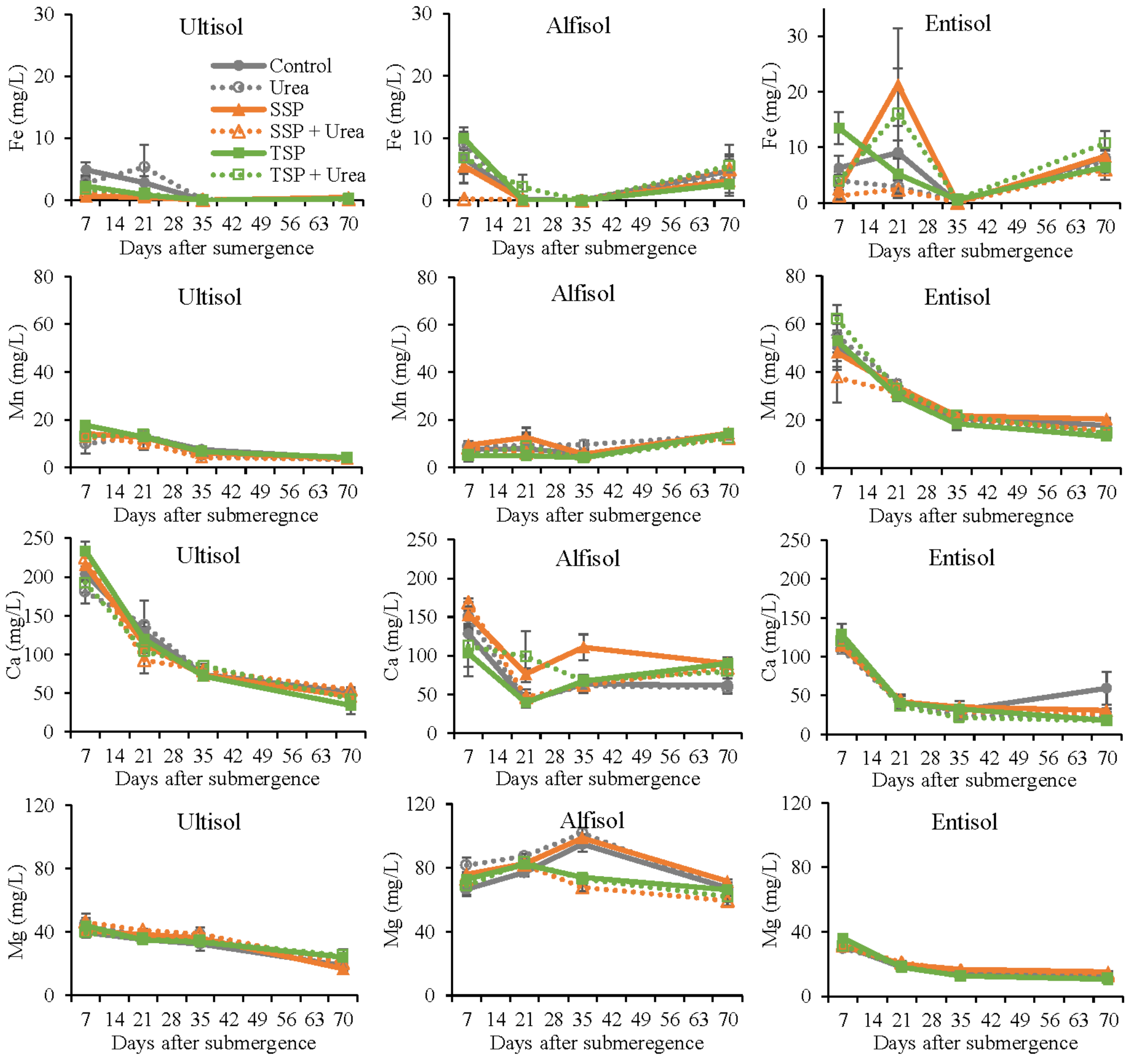


Fig. 3.3 Variation in porewater Fe, Mn, Ca and Mg concentrations of Ultisol, Alfisol and Entisol soils at 7, 21, 35, and 70 DAS. The error bars represent the standard errors of the means.

The principal component (PC) analysis of all three soils reduced the dimensionality of the data set into three principal components (eigenvalue>1). The variability attributed to PC1, which accounted for 33%, highlighting the relationships among DRP, porewater Ca, Mg, Mn concentrations and Eh (Appendix I, Supplementary Fig. 3.S3). The PC2 attributed to 21% variability of the dataset, elucidated the relationships among DRP, porewater Ca, Fe and Mn.

3.3.4 Sequential fractionation of soil phosphorus

The changes in P fractions along the three depth categories (0–2, 2–4 and 4–6 cm) of the soil profile at 35 and 112 DAS are illustrated in Fig. 3.4. The detailed P fractionation results are shown in the supplementary document (Appendix I, Supplementary Fig. 3.S4-3.S6). Phosphorus fractions analysed in this sequential analysis can be divided into three broad categories as labile, moderately labile and stable fractions. Organic and inorganic P fractions extracted by water and 0.5 M $NaHCO_3$ are labile fractions which are readily plant available. Organic and inorganic P extracted by 0.1 M NaOH are moderately labile P which are bound to Fe/Al oxy(hydr)oxides. Inorganic P extracted by 1.0 M HCl are also moderately labile P which are bound to Ca (Niederberger et al., 2019). Residual P is the stable P fraction which is bound to primary and secondary P minerals.

The P fractions varied differently with DAS in the three soils. In the Ultisol, at the 0-2 cm depth, the total P (summation of all the eight fractions) of both SSP and TSP applied treatments decreased from 35 to 115 DAS by 224% and 69% respectively. In the Alfisol, at the 0-2 cm depth, the total P of SSP applied soil increased by 7% with time while it decreased by 59% in TSP applied soil. Comparatively, in the Entisol (0-2 cm depth), the total P of SSP applied treatment decreased with time by 112% and it increased by 34% in TSP applied treatment. In the 0-2 cm depth, the labile P fraction increased by 2-453% compared to the control with P fertiliser addition in all the soils at both 35 and 112 DAS, except for the TSP applied Entisols at 35 DAS. In the same soil layer, the labile fraction deceased with time by 44-86% in the P applied treatments except for SSP applied Alfisols and TSP applied Entisols, where they increased with time by 52% and 39% respectively. The Fe and Al associated P fraction deceased with time by 9-83% in all the three treatments except for SSP applied Alfisol and TSP applied Entisol, where they increased with time by 58% and 64% respectively in the same depth. The Ca bound P fraction also decreased with time by 4-77% in all the three treatments except for the TSP applied Entisol where it increased by 113% at the 0-2 cm depth. In the 2-4 cm depth, the total P increased by 17-30% with time in the TSP applied treatments in all three soils. In the 4-6 cm depth, the total P increased by 19-36% with time, in the P fertiliser applied treatments.

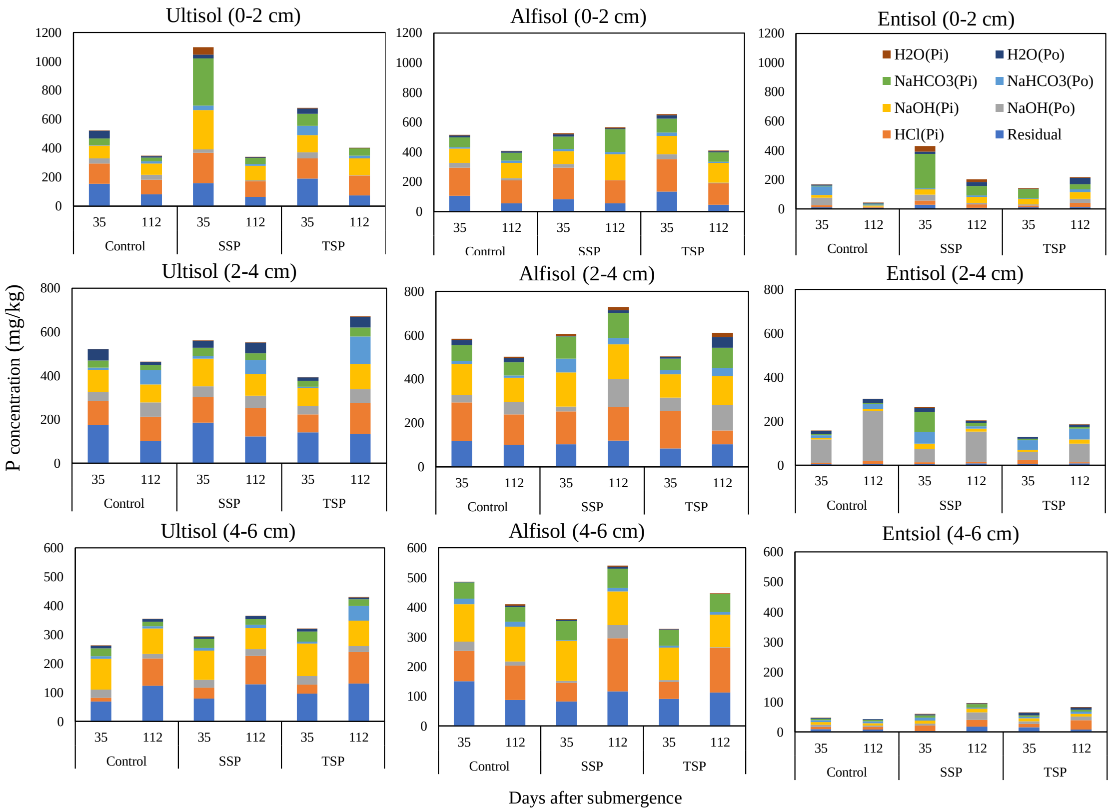


Fig. 3.4 Changes in different P fractions at depths of 0-2, 2-4 and 4-6 cm at 35 and 112 days after submergence of Ultisol, Alfisol and Entisol soils. Pi; inorganic phosphorus, Po; organic phosphorus, H_2O; distilled water extractable P, $NaHCO_3$; 0.5 M sodium bicarbonate extractable P, NaOH; 0.1 M sodium hydroxide extractable P, HCl; 1.0 M hydrochloric acid extractable P, residual; residual P

3.3.5 Changes of phosphorus species during submergence

Tables 3.2-3.4 show the saturation indices (SI) of P minerals, Fe/Mn carbonates and selected Fe and Al oxy(hydr)oxides of the three soils. Positive SI indicates the supersaturation of solution, thermodynamically favouring its formation, while negative SI indicates undersaturation of the solution, thermodynamically favouring its dissolution (or absence). A positive SI may not necessarily mean that the mineral will precipitate from the solution, as the slow precipitation kinetics may inhibit the precipitation, or favour precipitation of another mineral (Voigt et al., 2018).

Table 3.2 Saturation indices of P minerals from MINTEQ for Ultisol soils during submergence

	Control			SSP			TSP		
DAS	**7**	**35**	**70**	**7**	**35**	**70**	**7**	**35**	**70**
Ca phosphates									
Ca$_3$(PO$_4$)$_2$ (am1)	X	X	X	0.70	X	X	0.70	X	X
Ca$_3$(PO$_4$)$_2$ (am2)	0.02	X	X	3.45	X	X	3.45	X	X
Ca$_3$(PO$_4$)$_2$ (β)	0.69	X	X	4.12	X	X	4.12	X	X
Ca$_4$H(PO$_4$)$_3$:3H$_2$O	X	X	X	3.82	X	X	4.01	X	X
CaHPO4	X	X	X	X	X	X	0.13	X	X
FCO$_3$-Apatite	21.98	19.74	16.64	30.76	20.09	13.80	30.49	18.71	14.86
Hydroxyapatite	8.50	7.34	5.51	14.06	7.41	3.46	13.88	6.58	4.47
Fe/Mn phosphates									
Strengite (Fe^{III})	1.08	X	0.14	0.38	X	0.28	0.74	X	0.14
Vivianite (Fe^{II})	3.98	X	X	3.95	X	X	5.84	X	X
MnHPO$_4$ (Mn^{II})	3.37	2.93	2.02	4.55	3.01	1.97	4.87	2.87	2.10
Fe/Mn carbonates									
Siderite (Fe^{II})	X	X	X	X	X	X	X	X	X
Rhodochrosite (Mn^{II})	1.95	1.95	1.78	2.27	1.82	1.57	2.14	1.81	1.80
MnCO$_3$ (am)	1.45	1.45	1.28	1.77	1.32	1.07	1.64	1.31	1.30
Fe/Al oxy(hydr)oxides									
Fe(OH)$_2$.7Cl$_{0.3}$	3.91	0.84	2.20	3.81	0.52	1.72	3.95	0.71	2.10
Ferrihydrite (Fe^{III})	0.89	X	X	0.94	X	X	1.00	X	X
Ferrihydrite (aged)	1.40	X	X	1.45	X	X	1.51	X	X
Goethite (Fe^{III})	3.60	0.67	2.12	3.65	0.34	1.55	3.71	0.53	2.02
Hematite (Fe^{III})	9.59	3.75	6.65	9.70	3.08	5.49	9.82	3.45	6.44
Hercynite (Fe^{II})	8.10	4.10	3.70	7.31	2.16	3.73	6.83	3.00	3.67
Lepidocrocite (Fe^{III})	2.72	X	1.24	2.77	X	0.67	2.83	X	1.14
Maghemite (Fe^{III})	1.79	X	X	1.90	X	X	2.02	X	X
Magnetite (Fe^{III}, Fe^{II})	15.97	7.87	12.51	15.73	6.95	11.12	16.11	7.58	12.25
Al(OH)$_3$	1.61	0.74	0.62	1.38	X	X	1.02	0.18	X
Al$_2$O$_3$	0.15	X	X	X	X	X	X	X	X
Boehmite	1.32	0.45	X	1.10	X	X	0.73	X	X
Diaspore	3.03	2.15	1.08	2.80	1.31	1.21	2.44	1.60	1.10
Gibbsite	2.16	1.29	0.22	1.93	0.44	0.35	1.57	0.73	0.23
Fe sulphides									
Pyrite	X	X	X	X	X	X	X	X	X

DAS: Days after submergence, X: indicates negative saturation indices

Table 3.3 Saturation indices of P minerals from MINTEQ for Alfisol soils during submergence

DAS	**Control**			**SSP**			**TSP**		
	7	**35**	**70**	**7**	**35**	**70**	**7**	**35**	**70**
Ca phosphates									
$Ca_3(PO_4)_2$ (am1)	X	X	X	3.67	X	X	1.34	X	X
$Ca_3(PO_4)_2$ (β)	0.32	X	X	4.34	X	X	2.01	X	X
$Ca_4H(PO_4)_3{:}3H_2O$	X	X	X	4.31	X	X	1.08	X	X
$CaHPO_4$	X	X	X	0.22	X	X	X	X	X
FCO_3-Apatite	21.98	16.86	12.03	31.87	16.45	19.57	25.81	17.59	20.81
Hydroxyapatite	8.10	4.75	1.83	14.22	4.32	6.45	10.47	5.09	7.28
Fe/Mn phosphates									
Strengite (Fe^{III})	X	X	X	1.05	X	X	0.60	X	X
Vivianite (Fe^{II})	2.20	X	1.10	3.51	X	3.15	3.07	X	3.36
$MnHPO_4$ (Mn^{II})	2.87	2.58	1.36	4.78	2.14	2.86	3.83	2.51	3.06
Fe/Mn carbonates									
Siderite (Fe^{II})	0.78	X	1.67	X	X	1.21	0.34	X	1.15
Rhodochrosite (Mn^{II})	1.95	1.74	2.35	2.06	1.70	2.19	1.73	1.63	2.21
$MnCO_3$ (am)	1.45	1.24	1.85	1.56	1.20	1.69	1.23	1.13	1.71
Fe/Al oxy(hydr)oxides									
$Fe(OH)_{2.7}Cl_{0.3}$	7.53	X	2.52	6.86	X	2.08	6.85	X	2.10
$Fe_3(OH)_8$	6.60	X	X	4.55	X	X	4.51	X	X
Ferrihydrite (Fe^{III})	4.70	X	X	4.03	X	X	3.96	X	X
Ferrihydrite (aged)	5.21	X	0.28	4.54	X	X	4.47	X	X
Goethite (Fe^{III})	7.40	X	2.48	6.74	X	2.02	6.67	X	2.06
Hematite (Fe^{III})	17.21	1.63	7.36	15.89	1.39	6.45	15.74	0.15	6.52
Hercynite (Fe^{II})	8.01	0.73	5.97	6.44	1.32	5.62	6.43	X	5.45
Lepidocrocite (Fe^{III})	6.52	X	1.60	5.86	X	1.14	5.79	X	1.18
Maghemite (Fe^{III})	9.40	X	X	8.08	X	X	7.94	X	X
Magnetite (Fe^{III}, Fe^{II})	23.42	4.76	14.50	21.37	4.47	13.23	21.33	2.54	13.28
$Al(OH)_3$	1.64	X	0.16	1.23	X	0.16	1.17	X	0.09
Al_2O_3	0.22	X	X	0.96	0.60	0.61	0.68	0.47	0.65
Boehmite	1.36	X	X	0.92	X	X	X	X	X
Diaspore	3.06	0.96	1.58	2.64	1.29	1.58	2.58	0.40	1.50
Gibbsite	2.19	0.09	0.71	1.78	0.42	0.71	1.72	X	0.64
Fe sulphides									
Pyrite	X	X	X	X	X	0.18	X	X	X

DAS: Days after submergence, X: indicates negative saturation indices

Table 3.4 Saturation indices of P minerals from MINTEQ for Entisol soils during submergence

DAS	**Control**			**SSP**			**TSP**		
	7	**35**	**70**	**7**	**35**	**70**	**7**	**35**	**70**
Ca phosphates									
$Ca_3(PO_4)_2$ (am2)	0.30	X	X	X	X	X	X	X	X
$Ca_3(PO_4)_2$ (β)	0.97	X	X	0.55	X	X	X	X	X
FCO_3-Apatite	22.48	8.87	13.08	21.66	16.58	14.21	19.66	16.32	15.84
Hydroxyapatite	8.92	0.87	3.41	8.43	5.43	3.79	7.20	5.26	5.24
Fe/Mn phosphates									
Strengite (Fe^{III})	X	X	X	X	X	X	X	X	X
Vivianite (Fe^{II})	5.24	X	3.13	3.66	X	4.30	5.07	X	5.68
$MnHPO_4$ (Mn^{II})	4.29	1.79	2.59	3.88	3.14	3.09	3.69	2.42	3.85
Fe/Mn carbonates									
Siderite (Fe^{II})	1.34	X	1.20	1.09	X	1.57	1.59	1.30	1.15
Rhodochrosite (Mn^{II})	2.65	2.41	1.93	2.73	2.47	2.28	2.57	0.59	1.85
$MnCO_3$ (am)	2.15	1.91	1.43	2.23	1.97	1.78	2.07	3.03	1.35
Fe/Al oxy(hydr)oxides									
$Fe(OH)_2.7Cl_{0.3}$	2.97	0.35	1.88	3.00	0.61	2.09	3.42	1.63	1.90
Ferrihydrite (Fe^{III})	0.06	X	X	0.12	X	X	0.45	X	X
Ferrihydrite (aged)	0.57	X	X	0.63	X	X	0.96	X	X
Goethite (Fe^{III})	2.77	0.24	1.75	2.83	0.52	1.98	3.16	1.55	1.78
Hematite (Fe^{III})	7.94	2.88	5.90	8.06	3.45	6.36	8.71	5.50	5.97
Hercynite (Fe^{II})	7.05	2.26	7.19	7.38	2.64	7.06	7.17	4.05	7.11
Lepidocrocite (Fe^{III})	1.89	X	0.87	1.95	X	1.10	2.28	0.67	0.90
Maghemite (Fe^{III})	0.14	X	X	0.26	X	X	0.91	0.17	X
Magnetite (Fe^{III}, Fe^{II})	14.62	7.95	12.70	14.65	8.72	13.31	15.77	1.92	12.74
$Al(OH)_3$	0.94	X	0.94	1.14	X	0.80	0.80	X	0.91
Boehmite	0.65	X	0.65	0.86	X	0.51	0.51	X	0.62
Diaspore	2.35	0.76	2.36	2.56	0.84	2.22	2.22	1.04	2.33
Gibbsite	1.49	X	1.49	1.69	X	1.35	1.35	0.17	1.46
Fe sulphides									
Pyrite	X	X	4.99	X	X	4.86	X	X	5.41

DAS: Days after submergence, X: indicates negative saturation indices

All the three soils were supersaturated with hydroxyapatite, FCO_3-apatite and $MnHPO_4$ throughout the submergence period (Table 3.2-3.4). At 7 DAS, the P fertiliser applied soils were supersaturated with more soluble Ca-P forms (eg: amorphous $Ca_3(PO_4)_2$, β-

$Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3{:}3H_2O$) compared to the control soils, except for Entisols, for which supersaturation with those Ca-P was not observed in P fertiliser applied soils.

All the treatments of Ultisol were supersaturated with vivianite at 7 DAS and later dissolved with time and all the treatments were supersaturated with strengite at 7 and 70 DAS in Ultisols (Table 3.2). Comparatively, all the treatments of Alfisol were supersaturated with vivianite at 7 and 70 DAS (Table 3.3). Further, some applied P precipitated as strengite in both SSP and TSP applied treatments at 7 DAS in Alfisols. In Entisols, all the treatments were supersaturated with vivianite at 7 and 70 DAS (Table 3.4).

Out of the selected Fe/Al oxy(hydr)oxides, hematite, magnetite, diaspore, $Fe(OH)_2.7Cl_{0.3}$, goethite, hercynite, and gibbsite were supersaturated in all the treatments of Ultisols throughout the submerged period (Table 3.2). Comparatively, only hematite, magnetite, and diaspore were supersaturated throughout the submergence of all the treatments of Alfisols (Table 3.3). All the treatments of Entisols were supersaturated with $Fe(OH)_2.7Cl_{0.3}$, goethite, hematite, hercynite, magnetite and diaspore throughout the submergence (Table 3.4). Ferrihydrite and maghemite were supersaturated at 7 DAS in all the treatments of all the three soils and later undersaturated with time. Supersaturation with another Fe/Al oxy(hydr)oxide, namely lepidocrocite, occurred at 7 DAS in all the treatments of Ultisols, then undersaturated at 35 DAS and again supersaturated at 70 DAS. Similarly, supersaturation with $Fe(OH)_2.7Cl_{0.3}$, goethite, lepidocrocite, and $Al(OH)_3$ occurred at 7 DAS in all the treatments of Alfisols and then undersaturated at 35 DAS and again supersaturated at 70 DAS. In Entisols, this pattern was observed for Al oxy(hydr)oxides namely $Al(OH)_3$ and boehmite. Supersaturation with Fe sulphides (pyrite) occurred 70 DAS in all the treatments of Entisols and SSP applied treatment of Alfisols.

3.4 Discussion

3.4.1 Effect of TSP and SSP on P release

Application of P fertilisers increased DRP in soils only at the beginning of the experiment (<14 DAS). The low DRP concentration (0.03-0.10 mg/L) maintained throughout the remaining experimental period (14-112 DAS) did not demonstrate significant differences between the two P fertiliser types and among the three soils. Initially, supersaturation of soils with comparatively more soluble forms of Ca phosphates (ie: amorphous $Ca_3(PO_4)_2$, β-$Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3{:}3H_2O$) in the P fertiliser applied soils and Fe oxy(hydr)oxides (ie: ferrihydrite, maghemite) in the P fertiliser applied and the control treatments and later, undersaturation of soils with those minerals, demonstrated dissolution of these minerals during the submergence. This could potentially increase the DRP concentration during the submergence (Jayarathne et al., 2016; Weerasekara et al., 2021; Attanayake et al., 2022; Kumaragamage et al., 2022). However, "net" DRP concentration in all three soils was not increased, probably due to resorption of P onto Fe and Ca minerals (Amarawansha et al., 2015; Jayarathne et al., 2016; Nishigaki et al., 2021) as described in detail in section 3.4.2. The two P fertilisers used in this experiment were $Ca(H_2PO_4)_2.2H_2O$. This could have resulted in supersaturation of more soluble Ca-P minerals (α- and β-$Ca_3(PO_4)_2$) in fertiliser applied Ultisols and Alfisols at the initial stage of submergence.

3.4.2 Phosphorus release by soils, and fate of dissolved reactive P

Previous studies reported increased dissolved P concentrations in porewater upon submergence (Amarawansha et al., 2015; Jayarathne et al., 2016; Weerasekara et al., 2021; Attanayake et al., 2022; Kumaragamage et al., 2022). However, despite anoxic conditions, exceptions have been reported where soils did not release P to porewater (or floodwater) (Young and Ross, 2001; Shober and Sims, 2009). Those authors attributed that observation to the process of resorbing P into Fe(II) oxy(hydr)oxides and $Al(OH)_2$ phases. The increase of Fe in porewater during the submergence has not been observed in this study as hypothesised (Fig. 3.3). This indirectly explained that the reductive dissolution of Fe oxy(hydr)oxides was not a prominent mechanism of releasing P in these soils. One reason for this could be the low organic carbon content (~4-10 g/kg) of the three soils. The speed of sequential reduction (O_2, NO_3^-, MnO_2, Fe^{3+}, SO_4^{2-} and CO_2) under submergence is affected by the availability of organic matter as it is the main electron donor for the reduction reactions (Marschner, 2021). Therefore, low organic matter content could hinder the reductive dissolution of Fe oxides and consequent P release in these soils. Or else, since the three soils surpassed the Mn and Fe reduction Eh range (Marschner, 2021) at 7 DAS in Ultisols and Entisols and at 28 DAS in Alfisols, the reduction dissolution of Fe and Mn oxy(hydr)oxides might have occurred during the early days of submergence, and elevated porewater Fe concentrations were not observed as the porewater Fe concentrations were measured only at intervals of 7, 21, 35 and 70 DAS.

The positive significant (*p*<0.01) correlation between DRP and porewater Ca concentration in the three soils provides evidence that dissolution of Ca minerals contributed to P release at least at the beginning of the submerged period. The reason for not observing a significant increase of DRP in this study could be due to resorption of P released by the fertilisers onto other solid phases as described below.

Previous studies reported dissolution of P sorbed to Fe/Al oxy(hydr)oxides as a major source of P release to porewater under an anoxic environment (Gérard, 2016; Gu et al., 2019; Queiroz et al., 2021; Attanayake et al., 2022; Shaheen et al., 2022). Several Fe/Al oxy(hydr)oxides, namely $Fe_3(OH)_8$ and boehmite in Alfisols, maghemite and boehmite in Ultsiols and maghemite in Entisols, may have dissolved with time during this study period. However, several other Fe/Al oxy(hydr)oxides had a positive SI throughout the submergence, including hematite, magnetite, and diaspore. Highly weathered tropical soils usually characterised by having high potential to sorb P due to the presence of high amounts of Fe and Al oxy(hydr)oxides (Rakotoson et al., 2016). Both Fe and Al oxides are effective adsorbents of phosphate, but Al oxides are more effective than Fe oxides. For example, oxalate extractable Al oxides adsorb nearly twice as much phosphate as oxalate extractable Fe oxides (Darke and Walbridge, 2000). Therefore, presence of Al oxy(hydr)oxides even in minor quantities in these soils can sorb considerable sums of P released to porewater under submergence. The decreasing porewater Al concentration of the three soils with time (from an average of 0.2 mg/L to below method detection limit) pointed to the possibility of P sorption with Al minerals. The XRD analysis of soil samples revealed gibbsite [$Al(OH)_3$] as a major metal oxy(hydr)oxide in Ultisols and Entiols. Gibbsite was found either as major or trace clay mineral in several soils of Sri Lanka including Ultisols, Alfisols, and Entisols (Indraratne, 2020). Phosphorus sorbed on to gibbsite does not undergo reductive dissolution as P sorbed on to Fe oxy(hydr)oxides. Being a very slow exchanging component (Kyle et al., 1975), the P sorbed to gibbsite does not contribute to P release in submerged soils. The XRD analysis revealed the presence of goethite (a trace mineral) in Alfisols. According to previous XRD analysis, it is known that these soils contain Fe oxy(hydr)oxides too (Indraratne, 2020). The addition of P fertiliser treatments to Ultisols reported high concentrations of P in the Fe associated fraction compared to the other two soils. The released P to porewater by the dissolution of Ca-P and ferrihydrite may be resorbed by the abundantly available Fe and Al oxy(hydr)oxides in all three soils. Conversion of applied P fertilisers to Fe associated P under submergence was previously reported in rice paddy soils in the tropics (Abolfazli et al., 2012). However, this effect may be higher in Ultisols than the other soils, as explained by the comparatively high Fe associated P fraction in Ultisols. Apart from metal oxides, clay minerals such as kaolinite, montmorillonite and illite itself have high phosphate binding capacity (Gérard, 2016) which may have contributed to P sorption in these three soils.

The crystallinity of metal oxy(hydr)oxides affects the PSC of soils. Poorly crystalline and amorphous oxy(hydr)oxides contribute to a stable fixation of P compared to well crystalline oxy(hydr)oxides. Amorphous Fe minerals will not be detected by XRD (Ali et al., 2022). It is possible that paddy soils that are frequently undergoing alternative flooding and drainage during the rice cropping cycle have amorphous Fe oxides that have not been crystallised and can be detected by XRD. The initial soil analyses of the three soils, reported the presence of high concentrations of oxalate extractable Fe and Al (Table 3.1). This suggested that these soils had a high amount of poorly crystalline Fe and Al which have high PSC. Previous research evidenced a trend of forming lower crystallinity Fe(Ш) oxides after reoxidation of Fe(II) minerals in a redox fluctuating system (Chen et al., 2018) or partial transforming of Fe oxides into lower crystalline phases with submergence (Zhang et al., 2003). Further, high concentrations of Fe(II) in soil solution are likely to induce precipitation of Fe(II)/Fe(III) carbonates and hydroxides that limit P release due to sorption or co-precipitation (Amery and Smolders, 2012). Supersaturation of Fe(II) carbonates (siderite) was evident at 7 DAS and/or at 70 DAS in Alfisols and Entisols (Table 3.3 and 3.4). Triple superphosphate applied to Entisols showed supersaturation of siderite throughout the submergence which may be contributing to low P release in the TSP applied Entisol treatment compared to the SSP applied treatment. Changes in the crystallinity of Fe oxy(hydr)oxides also impacts the fate of P as it influences the kinetics of microbial Fe(III) reduction. For example, microbes can rapidly reduce ferrihydrite like minerals (typically within hours), but reduce well-ordered hematite, goethite, and lepidocrocite at slower rates (ie: several months) (Bonneville et al., 2004; Ginn et al., 2017). The differences in crystallinity changes of Fe oxy(hydr)oxides might have caused the changes with supersaturation/undersaturation of different Fe oxy(hydr)oxides in the three soils studied.

Phosphorus fractionation analysis showed that the total P concentration of the P fertiliser applied treatments of the three soils increased with time below the 2 cm depth (2-4 and

4-6 cm depths) with a few exceptions. This indicated that the dissolved P fertilisers translocated down through the soil profile. One reason for this P translocation may be due to some saturation of the P sorption sites of the moderately P buffered soils in the study. Previous research reported decreasing P buffering capacity with long-term P fertiliser application in submerged paddy soils and therefore, subsequent increasing risk of P leaching in such soils (Wang et al., 2014; Long et al., 2023). The increased P concentration in the Ca associated P fraction in the P fertiliser applied Ultisols at both 2-4 and 4-6 cm depths and the 4-6 cm depth of Alfisols and Entisols indicated the possible transformation of translocated P into Ca-P minerals. Further, the increased P concentrations in Fe and Al associated P fractions at these depths in the P fertiliser applied Alfisols and Entisols, hinted that the translocated P may have adsorbed onto Fe and Al oxy(hydr)oxides. Since both Ca associated P and Fe and Al associated P are moderately labile, these will not be detected in DRP concentrations but could be available to rice plants under certain conditions. For example, under submergence, rice roots can resolubilise some of the immobilise P (eg: Fe(II) carbonates and hydroxides) by organic anion excretion and acidification caused by oxidation of Fe(II) by oxygen released from roots and the imbalance between the intake of anions and cations (Huguenin-Elie et al., 2003). Increasing residual P fractions at the soil depths below 2 cm of the P fertiliser applied to the three soils, indicated that a fraction of applied P has been transformed to non-available P pools for plants. However, since the fractionation results were based on a single replicate, there is limited confidence in the observed trends, and therefore, the results were discussed in the context of the modelling results.

3.4.3 Effect of urea application on P release

Soil pH has a significant effect on P release in soils (Penn and Camberato, 2019; Barrow and Hartemink, 2023; Wang, 2023). Application of N fertilisers could indirectly affect P release in soils by changing pH. Change of soil pH due to urea application was not consistent across the three soils and DAS. Previous research has shown significant decrease (Fageria et al., 2010), increase (Michael, 2020), no significant changes or mixed results (Khatiwada et al., 2012) of soil pH when urea is applied under different circumstances. Applied urea granules are dissolved within minutes to hours depending on soil water content and temperature (Kissel and Cabrera, 2008). Urea is rapidly hydrolysed by urease enzyme into NH_4^+ and HCO_3^- ions leading to an increase in soil pH near to the granules (Lasisi and Akinremi, 2021), depending on the pH buffering capacity of soil (Curtin et al., 2020). High pH favours formation of ammonia (NH_3) by NH_4^+ which could be volatilised. The NH_4^+ which is not volatilised may be oxidised into NO_3^- via nitrification. This causes soil acidification (Subbarao et al., 2006) and because of acidification, the rate of nitrification will also be reduced (Zebarth et al., 2015; Hanan et al., 2016). Although in general, SSP or TSP do not affect soil pH, they sometimes cause soil acidification specially in alkaline soils (Pahalvi et al., 2021) due to reaction products being very acidic. The reason for the mixed effects of overall soil pH of the three soils observed in this study may be due to the combined effect of urea hydrolysis, nitrification of NH_4^+ ions, and effect of acidification from TSP or SSP, and pH buffering capacity of soils. The immediate and significant ($p<0.05$) increase of pH with urea application in Entisols may be due to low pH buffering capacity in the soil due to its sandy texture.

It was hypothesised that the increase in NO_3^- following urea application could delay P release by NO_3^- acting as a preferable electron acceptor over Fe and Mn in the sequential reduction process (O_2, $NO_3^–$, MnO_2, Fe^{3+}, $SO_4^{2–}$ and CO_2). However, urea addition did not significantly ($p>0.05$) affect the P release of the soils. One reason for this observation may be the time of urea application. Urea was applied as two split applications at 20 DAS and 48 DAS. A leaching column study conducted in South Korea reported that it takes nearly 6 days to hydrolise the applied urea completely in a sandy loam soil (Seol et al., 2000). Meanwhile, the formed NH_3 gas could be volatilised, and the rate of volatilisation will increase at pH values greater than 7. Since the pH of porewater was higher than 7 in all three soils, especially after the first urea application (Fig. 3.1A, B and C), there can be a considerable loss of applied N as NH_3 gas. This may be another reason for not observing a significant effect of urea addition on P release. The remaining NH_3 which did not volatilise, could be slowly converted to NO_3^- ions via nitrification. Therefore, the NO_3^- formation due to urea application may have occurred after 21 DAS. However, the Eh of the three soils were below 0 mV by this time indicating that they passed the NO_3^- and Mn^{4+}/Mn^{3+} reduction in the redox ladder. Furthermore, NO_3^- ions formed via nitrification will also be subjected to microbially mediated denitrification processes resulting in the loss of N from the system in its gaseous forms such as nitrous oxide (N_2O), nitric oxide (NO) and nitrogen gas (N_2) (Coyne, 2008).

3.5 Implications for rice cultivation

This study presents evidence indicating that the three paddy soils exhibited no significant change in porewater DRP in response to applied P fertilisers during submergence, except immediately after the fertiliser application. The critical level of soil solution P concentration for rice plant growth is 0.1 mg/L (Hossner et al., 1973). In the Alfisol where fertilisers were applied, the DRP concentration remained higher than the critical level. In Entisols, only the treatment with SSP addition showed DRP concentrations surpassing the critical level. In Ultisols, the DRP concentration remained lower than the critical level even in soils where P fertilisers were applied.

The dissolution of Ca-P minerals and ferrihydrites constituted the main source of P release by the three soils. However, the released P appeared to be translocated to deeper soil layers and subsequently resorbed onto the abundantly available Fe and Al oxy(hydr)oxides surfaces and/or clay minerals, and also precipitated as Ca minerals. Further, urea addition did not affect the P release of any of the soils.

This study offers insights into the potential changes in P species following submergence in three different paddy soils of Sri Lanka. For future studies, a direct P speciation method, X-ray absorption near-edge structure spectroscopy, can be used to validate the results obtained through assumptions-based thermodynamic modelling. Although the porewater DRP level was lower than the critical concentration threshold for P in rice plant growth during submergence, particularly in Ultisols, previous studies have indicated no yield response (no significant increase or decrease) to applied P fertilisers across paddy-growing soils in Sri Lanka. Future studies may consider replacing the Olsen P test which extracts P under high soil pH (8.5) compared to the neutral pH found under submerged paddy soils, with another test (ie: Resin P test) that extracts P under field pH condition. The unique micro-environment of the rice plant rhizosphere may play a role in enhancing P release into the porewater under submergence, particularly by tapping the P in moderately labile pools. Hence, future research should prioritise investigating P transformations involving rice plants and rhizosphere soils. Such studies would contribute to a comprehensive understanding of why rice yield could remain unaffected despite the addition or omission of P fertilisers. Further, a proportion of dissolved fertiliser P can be retained in overlying water and so future studies should also focus on analysing dissolved P in both overlying water and porewater after applying inorganic P fertilisers. Since the results indicated a significant increase of porewater DRP concentrations only immediately after P fertiliser application, future research should focus on testing slow-release P fertilisers for rice paddy. Furthermore, this research could be expanded to develop more effective P management strategies, including methods to access sorbed P or legacy P in Sri Lankan paddy soils.

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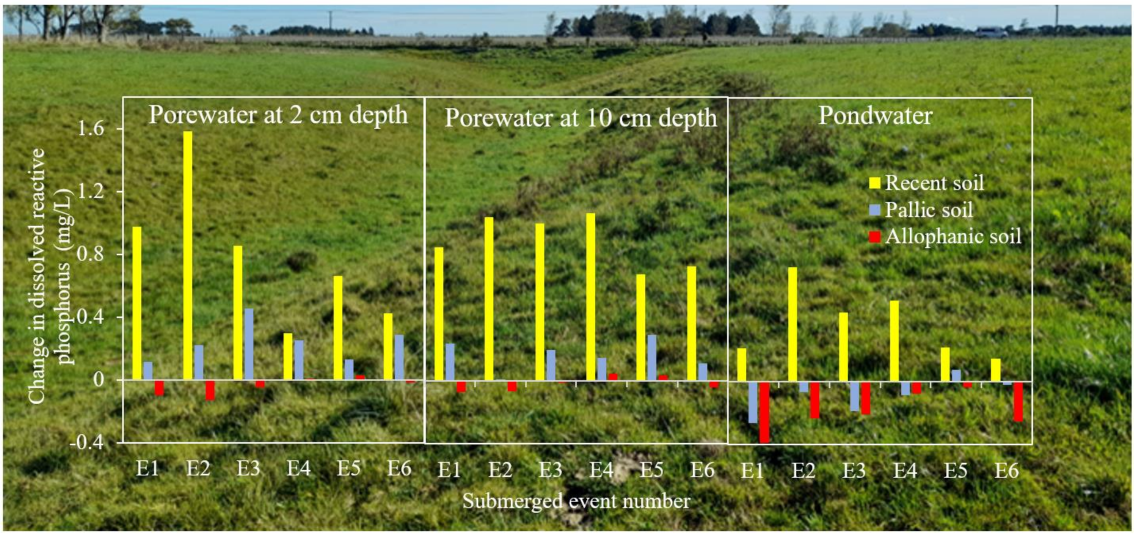
Chapter 4

Phosphorus release under short-term submergence of different pasture soils

Graphical Abstract



Highlights

- Phosphorus release from 3 pasture soils upon 3-day submerged events were assessed.
- Recent and Pallic soils released P and Allophanic soil sorb P during submergence.
- Risk of P loss increased in the order of Allophanic < Pallic < Recent soil.
- Phosphorus release from 2 and 10 cm layers of the three soils were similar.
- Allophanic soil is less likely to be a source of P under sustained periods of submergence.

Abstract

A study was conducted to explore the potential of three contrasting dairy and sheep/beef farm soils (Recent, Pallic and Allophanic soils) to release P to porewater and pondwater P dynamics under short-term and frequent submergence. Five undisturbed soil blocks (20×20×15 cm) were sampled from each soil. Porewater samplers and half-cell platinum electrodes for in-situ redox potential measurements were installed at 2 and 10 cm depths from the soil surface. Six submerged events were created by maintaining a 5 cm waterhead. Porewater and pondwater samples were collected immediately and three days after each submergence event. After three days of submergence, the soil blocks were drained and maintained at 70% of water holding capacity for 10 days before the next submerged event. Dissolved reactive phosphorus (DRP), pH, dissolved organic carbon, cations, anions, and alkalinity of the water samples were measured. Soil chemical P fractions were assessed in initial soils and soils in the middle and end of the experiment. Thermodynamic modelling was used to infer dissolution and formation of P and P-associated minerals. The Recent soil released P to porewater at both depths and to pondwater. The Pallic soil released P to porewater at both depths but did not change pondwater DRP. Allophanic soil sorbed P and did not increase DRP either in porewater or pondwater. The average pondwater DRP of the three soils during submergence were 17 to 65-fold higher than the New Zealand lowland river target DRP concentration (0.01 mg/L). The mechanisms of P release from the Recent and Pallic soils were desorption and reductive dissolution of Mn(II) minerals. Reductive dissolution of Fe(II) minerals was not supported by fractionation or modelling results. Decreases in labile, moderately labile and stable P fractions contributed to P release in the Recent soil, while increases in the labile and moderately labile P fractions contributed to P retention in the Pallic and Allophanic soils. This study highlighted that the Recent soil is riskier than the other two soils in releasing P upon short-term submergence and the Allophanic soil is less likely to be a source of P under short-term submergence compared to the Recent and Pallic soils.

Keywords: Allophanic, dissolved reactive phosphorus, Pallic, Recent, short-term frequent submergence

4.1 Introduction

Non-point source phosphorus (P) contamination originating from agricultural soils is a significant contributor to the degradation of freshwater quality (Yang et al., 2008; Schoumans et al., 2014; Dharmakeerthi et al., 2019). Agricultural soils with elevated P concentrations, exceeding the optimal requirement for plant growth, are prone to P loss via surface runoff and leaching, which is an extensively investigated phenomenon (McDowell and Sharpley, 2001; Djodjic et al., 2004; Tóth et al., 2014). Surface runoff during or following a rainfall event can lose P in two forms: dissolved P and particulate bound P. The loss of dissolved P is critical for eutrophication, as it is bioavailable for the growth of harmful microorganisms and aquatic plant in freshwater bodies (Li and Brett, 2013). Therefore, there is significant interest in transportation of dissolved P from agricultural soils to waterways.

Agricultural soils can be submerged temporarily on frequent occasions either naturally or artificially. For example, short-term submergence of critical source areas (CSAs) (Sharpley et al., 2011; Thomas et al., 2016; Smith et al., 2021) during rainfall events, or temporary flooding of agricultural lands (Kumaragamage et al., 2020) are examples of natural submergence events. Whereas, constructed wetlands, detainment bunds and sediment ponds (Levin et al., 2021; Li et al., 2021; Robotham et al., 2021) are considered to be artificially submerged conditions. Agricultural soils under these situations can be subjected to alternating anerobic and aerobic conditions during rainfall events, especially during winter. These alternative conditions are likely to influence the P transformations and P release to soil porewater. Further, the released P could be diffused into the pondwater overlying the soil and can then be transported to surface waters via flow pathways (Amarawansha et al., 2015; McDowell et al., 2016; Smith et al., 2021), posing a threat of eutrophication of nearby waterways.

Phosphorus is released to porewater under submergence of soil as a combined result of complex hydrological and biogeochemical processes (Jayarathne et al., 2016; Dharmakeerthi et al., 2019). Soil pH changes towards neutrality upon submergence (Ponnamperuma, 1972). The Eh of soil reduces due to the anaerobic condition created in soil by submergence (Maranguit et al., 2017). The redox potential controls the stability of several chemical compounds in soil. For example, reductive dissolution of

Mn(IV)/Mn(Ш) and Fe(Ш) can release P associated with them (Amarawansha et al., 2015).

Continuous alternation of redox conditions such as repeated reductive dissolution and oxidative reprecipitation increase amorphous Fe oxyhydroxides in soil and thereby increase P sorption (Baldwin and Mitchell, 2000). Further, the frequency and duration of soil submergence are known to influence the release of dissolved P into porewater (Gu et al., 2019; Warrinnier et al., 2020). A significant amount of research has been conducted worldwide to explore the P release under prolong submergence (eg: more than two weeks) for a range of land use such as paddy (Hua et al, 2017; Liu et al., 2019), wetlands (Maranguit et al., 2017; Parsons et al., 2017; Rapin et al., 2019) and river valleys/basins (Weerasekara et al., 2021; Kumaragamage et al., 2022). However, the studies on the effect of short-term (eg: less than four days) submergence with alternative wetting and drying of soil, which are experienced during winter and spring seasons, on P release, are limited. Smith et al. (2021) reported an increase in total dissolved P (up to 0.12 mg/L) in the subsoil (below 20 cm) of a Melanic Orthic Gley soil in the South Island of New Zealand during wet periods, but this study did not measure P in overlying water and so has limited applicability to surface runoff associated with CSAs. In addition, the effect of soil type on the release of P upon short-term but frequent submergence during storm events in agricultural features such as CSAs has not been studied previously in New Zealand. Furthermore, the extent and mechanisms of P release by different New Zealand grassland soils to porewater and overlying water has not previously been studied. A comprehensive understanding of these aspects is important for implementing improved P management strategies in CSAs to minimise P loss to surface waters.

The intact soil blocks were subjected to short-term (three days) and frequent (every ten days) submergence (1) to explore the potential of three contrasting soils to release P to porewater and pondwater, (2) to explore the relationships between soil characteristics, and P release and (3) to elucidate the mechanisms of P release in these soils using P fractionation and thermodynamic modelling. It was hypothesised that 1) the reductive dissolution of Fe/Mn oxy(hydr)oxides during submergence would release sorbed P, consequently elevating the P concentration in the soil solution and pondwater and 2) the degree of P release due to submergence would depend on soil characteristics.

4.2 Materials and Methods

4.2.1 Soils used in the glasshouse study

Three soils with contrasting properties were selected from or adjacent to CSAs on three farms belong to Massey University in the Manawatū-Whanganui region of New Zealand, namely Dairy 1 (S 40^{o} 22’ 27”, E 175^{o} 37’ 05”), Dairy 4 (S 40^{o} 23’ 39”, E 175^{o} 36’ 55”), and Tuapaka farm (S 40^{o} 21’ 00”, E 175^{o} 44’ 43”). Five undisturbed soil blocks (20×20×15 cm) with long-term ryegrass/white clover pasture (Dairy 1 and Dairy 4) and ryegrass, white clover and browntop (Tuapaka) were sampled from each site and placed in black-coloured plastic containers. Two extra soil blocks were collected from each site and treated the same as other replicates to reform the damaged soil blocks due to sampling at the middle of the experiment for the P fractionation study (explained in section 4.2.5). Soils from the 0-10 cm depth were sampled from each soil type, immediately adjacent to the location where the blocks were collected, for initial soil characterisation. Soils from Dairy 1, Dairy 4 and Tuapaka farms were classified according to the *New Zealand Soil Classification* as Recent soil (Entisol), Pallic soil (Alfisol) and Allophanic soil (Andisol), respectively.

4.2.2 Initial soil characterisation

The soil samples (0-10 cm depth) were air-dried, passed through a 2 mm sieve, homogenised, and analysed for basic soil properties. Soil pH was determined in 1:2 (v/v) soil:water slurry followed by potentiometric determination of pH. Olsen phosphorus was determined by Olsen extraction (Olsen and Sommers, 1982) followed by molybdenum blue colorimetry (Murphy and Riley, 1962). Anion storage capacity (ASC) was determined by equilibration of 5 g of soil with 1000 mg/L P solution for 16 hours followed by colorimetric analysis (Saunders, 1965). Mehlich-3 P was determined by Mehlich-3 extraction followed by Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Mehlich, 1984). Mehlich-3 extractable cations (Ca, Mg, Fe, Mn, Al and Zn) were also determined using ICP-OES. Cation exchange capacity was determined by 1M neutral ammonium acetate extraction of cations (K, Ca, Mg, Na) followed by ICP-OES (Blackmore et al., 1987). Total organic carbon was determined by thermal conductivity detector (Elementar Analyser) after acid pretreatment to remove carbonates present followed by catalytic combustion (900°C, O_2) and separation (Nelson and Sommers, 1996). Soil texture was determined by sedimentation procedure by hydrometer after organic matter removal (Standards Association of New Zealand,1986). The oxalate extractable Fe, Al and Mn concentrations were determined by acid ammonium oxalate method (McKeague and Day, 1966) followed by Microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4200). The acid ammonium oxalate method was repeated for the soil samples collected at the end of the experiment.

4.2.3 Experimental design

The experiment was set up in a glasshouse at the Massey University Plant Growth Unit. Porewater samplers were prepared using 0.5 cm diameter polytetrafluoroethylene (PTFE) tubes connected to 6 µm pore diameter filter cloth at one end and the other end of the tubes were connected to 50 ml syringes. Two porewater samplers were installed (Fig. 4.1) enabling porewater extraction at specific depths of 2 and 10 cm. The 2 cm depth was selected since it is the soil layer which retains 80% of the P from P fertiliser additions via sorption and also primarily contributes to P runoff via desorption (Vadas et al., 2007a; Vadas et al., 2007b). The 10 cm layer was selected as more than half of the root mass of permanent pasture is generally located within the surface 10 cm depth (Crush et al., 2006). Changes in P chemistry and potential release of P within the root zone would influence plant access to P, therefore this is of great interest agronomically. Platinum half-cell electrodes were installed at the same two depths for in-situ redox potential measurements. The glasshouse experimental set up was arranged in a Complete Randomised Design. The average room day/night temperature ranged between 25 and 17 °C during this period. Each ponding event was created by filling the containers using tap water up to a waterhead of 5 cm above the soil surface. Tap water, with its known background dissolved P concentration was used to represent the typical agricultural P additions sourced under field conditions and as a replenishment to P removal when water was drained after each submergence event. The soil blocks were maintained under submergence for three days and thereafter the water was drained off using two outlets: one just above the surface soil level and the other at the bottom of the container (Fig. 4.1). Soil blocks were maintained at a field capacity of 70% during the experimental period. The submergence events were repeated six times after a 10-day interval between each event.

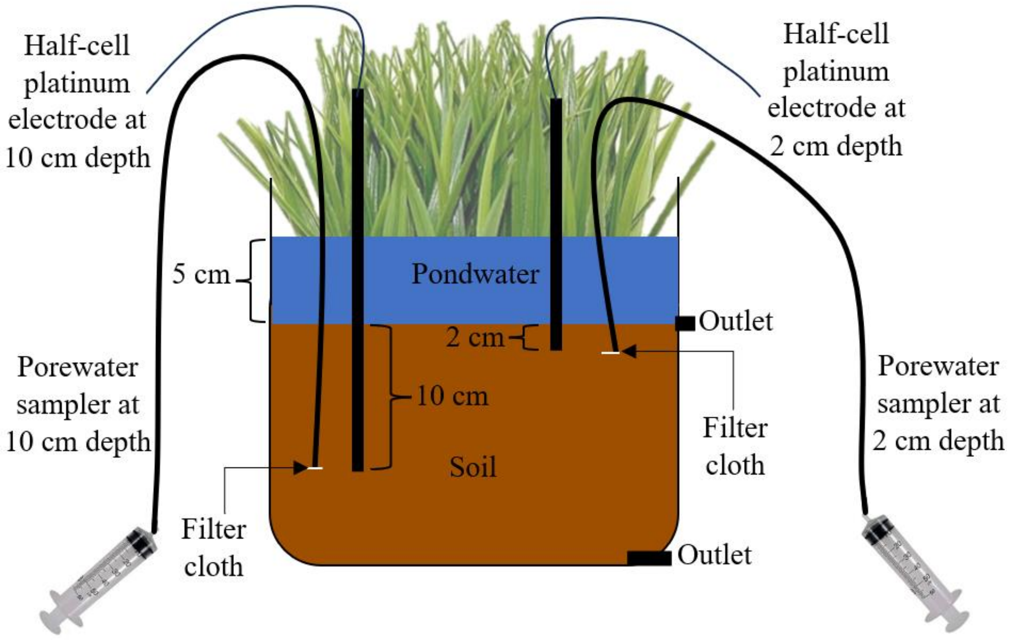


Fig. 4.1 A diagram of the ponded soil block used in the glasshouse experiment. The diagram is not to scale.

4.2.4 Porewater and pondwater sampling and analysis

Porewater and pondwater samples were collected within an hour and three days after submergence, across the six repeated submerged events (referred to as E1, E2, E3, E4, E5 and E6, respectively). Soil porewater was collected by applying a vacuum using the 50 ml syringe attached to the sampler. Pondwater was collected near to the soil surface using a 50 ml syringe. The porewater and pondwater samples were filtered through 0.45 µm cellulose membrane filters and analysed for DRP by the molybdate blue colour method (Murphy and Riley, 1962) using UV visible spectrophotometer (JENWAY 7315) within 12 hours of sampling. The pH of porewater and pondwater samples were measured using a glass pH electrode (ORION STAR A214). The soil Eh was measured in-situ at each porewater sampling event using an Ag/AgCl reference electrode (ORION). The voltmeter reading was corrected to the standard hydrogen electrode potential by adding +200 mV. Cation concentrations (Ca, Mg, K, Na, Fe, Al, and Mn) of porewater were measured using microwave plasma atomic emission spectroscopy (Agilent 4200). Porewater anion concentrations (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}) were measured using ion chromatography (Dionex™ Aquion™). Dissolved organic carbon (DOC) concentrations of porewater were measured using a carbon nitrogen analyser (Shimadzu TOC-LCSH). Alkalinity of the porewater samples was measured by titrating against 0.1 N H_2SO_4 in the presence of methyl orange indicator.

4.2.5 Phosphorus fractionation study

Phosphorus fractionation was undertaken using a modified Hedley procedure (Hedley et al., 1982) for the soils collected for initial soil characterisation (0-10 cm) and then soil sampled at the middle of the third submergence event and at the end of the sixth event, just before draining off the pondwater. Three replicates from each of the 0-2, 2-8 and 8-10 cm depths were collected from each soil block and were bulked to make a composite sample. The three soil depths (0-2, 2-8 and 8-10 cm) were selected to represent and cover the whole depth of the initial two soil depths (2 and 10 cm depths). Three replicates from three soil blocks were used for the fractionation study for each soil type. The gaps created by soil sampling were filled with soil cored at the same depths from the additional two soil blocks maintained under similar experimental conditions as the main ponded blocks. The soil samples taken under submerged conditions were purged with nitrogen gas, sealed, and stored at -28 ºC in a freezer until P fractionation analyses were performed.

An aliquot of soil (approximately 0.5 g) was extracted sequentially using 30 mL distilled water, 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1.0 M HCl by shaking the suspension for 16 h, centrifuging for 10 minutes at 5000 rpm, and passing the supernatant through a 0.45 μm cellulose membrane filter for each extraction step. The first two extraction (distilled water and $NaHCO_3$ extraction) steps were conducted while purging with nitrogen gas. Acidified potassium persulfate oxidation was used for the digestion of distilled water, $NaHCO_3$ and NaOH extracts, and the residue was analysed for total P (TP). The difference between TP and Pi was estimated to be organic P (Po) (Tiessen and Moir, 1993). The P in the soil residue left after sequential extraction was determined after digestion with aqua regia (Chen and Ma, 2001).

Phosphorus fractions analysed were grouped into three broad categories as labile, moderately labile and stable fractions. The labile P fraction is a summation of both organic and inorganic P fractions extracted by water (H_2O-P) and $NaHCO_3$ ($NaHCO_3$-P). Organic and inorganic P extracted by NaOH are moderately labile P which are bound to Fe and Al oxy(hydr)oxides (Fe/Al-P). Inorganic P extracted by HCl are also grouped as moderately labile P which are bound to Ca (Ca-P). Residual P is the stable P fraction bound to primary and secondary P minerals (Niederberger et al., 2019).

4.2.6 Phosphorus speciation study by thermodynamic modelling

The thermodynamic modelling software Visual MINTEQ 3.1 (Gustafsson, 2013) was used to predict the changes of P species in soils based on the composition of porewater samples across the six submerged events collected at the 2 cm depth. The input parameters entered in the software were soil Eh, pH, DOC, alkalinity, concentrations of cations (Ca, Mg, Na, K, Mn, Al and Fe), anions (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}), and DRP in porewater. The Stockholm Humic Model (SHM) was used as the state-of-the-art model to simulate the complexation to natural organic matter, and it was assumed that fulvic and humic acids were present in similar quantities (50% each) in porewater.

4.2.7 Overall redox status

The overall redox status of the soil solution during each ponding event was calculated by summing up p*e* and pore water pH values (p*e*+pH). p*e* is a measure of electron activity calculated using the Nernst equation (Lindsay, 1979);

$$\mathrm{p}e = \frac{\mathrm{Eh} \times \mathrm{F}}{2.303 \times \mathrm{R} \times \mathrm{T}}$$

where, the Eh is the redox potential measured at 2 or 10 cm depth (V), F is the Faraday constant (96,485 Coulombs), R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and the T is the absolute temperature in Kelvin (298.15 K, as the average daytime temperature was 25 °C).

4.2.8 Statistical analysis

Statistical analysis was performed using SAS 9.4 software. Porewater DRP, pH, Eh and cations were analysed for the six repeated submerged events separately using three-way ANOVA to 1) compare soils, 2) two depths (2 and 10 cm), and 3) point of submergence (the beginning and the end of submergence). A two-way ANOVA was performed to compare the pondwater DRP of the soils at the beginning and at the end of submergence separately for each submerged event. To identify the factors governing the porewater DRP principal component analysis and correlation analysis were performed. Principal component analysis was performed separately for the three soils using DRP, DOC, Eh, pH, p*e*+pH, and cations (Fe, Al, Mn, Ca and Mg). Correlation analyses were performed separately for each soil between DRP concentrations in porewater and pH, Eh, p*e*+pH, DOC, porewater Fe, Mn, Ca, Mg and Al concentrations at the end of submergence.

4.3 Results

4.3.1 Basic soil properties

The three soils were acidic and varied in their P fertility and texture (Table 4.1). Anion storage capacity was highest in the Allophanic soil followed by the Pallic and Recent soil, respectively. The sum of oxalate extractable Fe and Al was three times and two times higher in the Allophanic soil compared to the Recent and Pallic soils, respectively. The Allophanic soils had the highest total organic carbon (TOC) content at 8.2 g/100g, surpassing the Recent soil by more than 4-fold (2 g/100g) and the Pallic soil by nearly 2-fold (4.7 g/100g).

Table 4.1 Initial physico-chemical properties of the Recent, Pallic and Allophanic soils

	Recent soil	Pallic soil	Allophanic soil
pH	6.5	5.8	5.9
Sand %	39	14	8
Silt %	43	54	57
Clay %	18	32	35
Olsen P (mg/L)	69	66	32
Mehlich-3 P (mg/L)	147	133	65
Anion storage capacity %	19	29	56
CEC (cmol$_{(+)}$/kg)	12	22	23
Total organic C (g/100g)	2.0	4.7	8.2
Fe $_{\text{oxalate}}$ (mg/kg)	3200	4910	6010
Al $_{\text{oxalate}}$ (mg/kg)	725	1210	6455
Mn $_{\text{oxalate}}$ (mg/kg)	80	315	485
Mehlich-3 extractable cations (mg/L)			
Ca	1233	1735	1555
Mg	170	254	216
Fe	681	545	180
Mn	46	75	43
Al	568	800	1278
Zn	2.9	10.7	2.9

pH was measured in 1:2 soil: water slurry. Anion exchange capacity was determined by soil equilibration with 1000 mg/L P solution. CEC: Cation exchange capacity, Al $_{\text{oxalate}}$: Ammonium oxalate extractable Al, Fe $_{\text{oxalate}}$: Ammonium oxalate extractable Fe, Mn $_{\text{oxalate}}$: Ammonium oxalate extractable Mn. Ca, Mg, Fe, Mn, Al and Zn were extracted by Mehlich-3 solution.

4.3.2 Variation of porewater and pondwater pH and soil Eh

Overall, the average porewater and pondwater pH of the six submergence events of the three soils (Appendix II, Supplementary Fig. 4.S1) varied within the neutral pH range (6.7–7.7). The porewater and pondwater pH were similar in the three soils. Immediately after submergence of the first event, soil pH of the three soils increased up to ~7.5. During the submergence events the porewater pH change was minute and the porewater pH change ranged from <0.1 to 0.8.

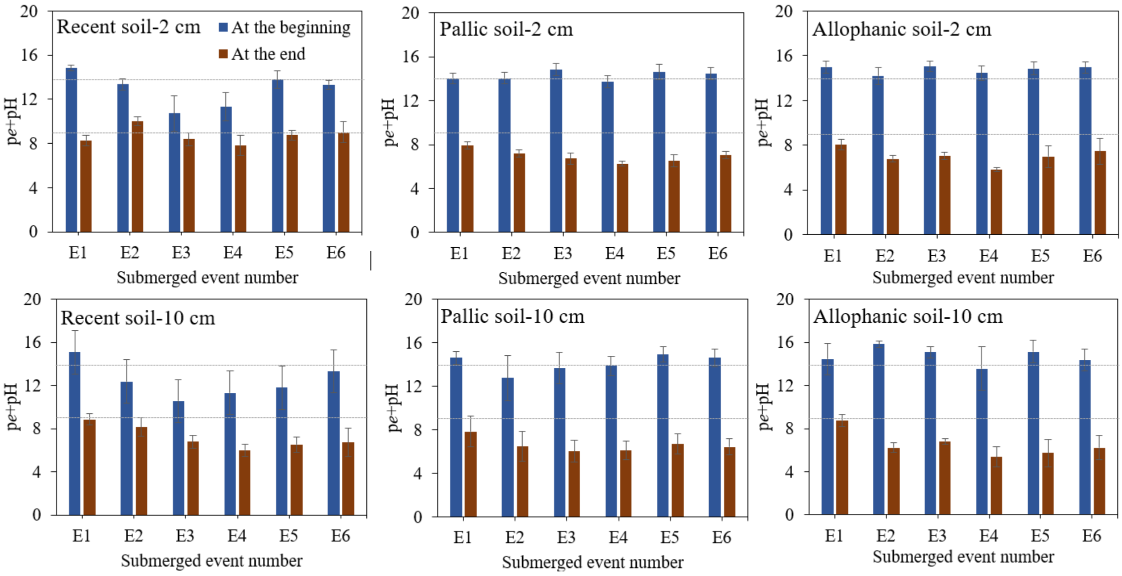


Fig. 4.2 Variation of pe+pH measured from the 2 and 10 cm depths at the beginning and end of six submergence events (E1-E6). Redox zones are indicated by dashed lines: oxic (pe+pH>14), suboxic (pe+pH=9-14), anoxic (pe+pH<9). The error bars represent the standard errors of the means (n=5).

Soil Eh decreased significantly (*p*<0.0001) during the submergence events (Appendix II, Supplementary Fig. 4.S1). The Eh of the two soil depths were not significantly (*p*>0.05) different in any soil at a given submergence event. The average of Eh of the six submergence events at the beginning of submergence were 315 (Recent soil), 398 (Pallic soil) and 443 mV (Allophanic soil) (Appendix II, Supplementary Fig. 4.S1). At the end of submergence, the average Eh were 30 (Recent soil), -25 (Pallic soil) and -4 mV (Allophanic soil).

The redox zones are defined as oxic (pe+pH>14), suboxic (pe+pH=9-14), and anoxic (pe+pH<9). After 1 hour of submergence, the overall redox status of the Recent Soil was suboxic except in the E1 where it was oxic while the other two soils were in the oxic range with few exceptions (Fig. 4.2). At the end of three days of submergence, all three soils were in the anoxic range except the 2 cm depth of the Recent soil at the E2 (Fig. 4.2). The pe+pH values varied from ~11 to ~15 across the six submergence events at the two soil depths of the Recent soil at the beginning and it varied from ~6 to ~10 at the end of submergence. Comparatively, the pe+pH values of both depths of the Pallic and Allophanic soils changed from ~13 to ~16, respectively at the beginning and ~5 to ~9, respectively at the end of submergence (Fig. 4.2).

4.3.3 Variation of porewater and pondwater DRP during submergence

The interaction effect between the two factors “soil” and “point of submergence” was significant ($p<0.05$) for porewater DRP for all the submergence events, indicating that the change in porewater DRP concentrations due to submergence varied among soils. In the Recent soil, porewater DRP concentration at the end of submergence was 2.4 to 5.1-fold higher than that at the beginning of submergence for all six events, indicating the release of soil P during submergence. In the Pallic soil, the magnitude of P release was ~2.3-fold less than that in the Recent soil. In the Allophanic soil, submergence did not result in a release of soil P as indicated by the statistically similar DRP concentrations at the beginning and end of submergence for all of the events. The three way interacton (soil×point of submergence×depth) or two-way interaction with depths (point of submergence×depth) were not signifcant for any submergence events. Porewater DRP concentrations were significantly ($p<0.05$) different in the 2 and 10 cm depths only for three of the submergence events (E1, E2, and E5.) Porewater DRP concentrations were 1.5, 1.6 and 1.4-fold higher at 2 cm than at 10 cm for the E1, E2 and E5, respectively.

The interaction effect between the two factors “soil” and “the point of submergence” was not significant for pondwater DRP for all the submergence events, except E4. The pondwater DRP among the three soils were significantly ($p<0.05$) different from each other in the six submergence events. The tap water dissolved P concentrations at the beginning of the six submergence events were 0.17, 0.22, 0.08, 0.07, 0.03, 0.16 mg/L, respectively. Since the same source of tap water was used for all replicates of the three soils, the effect of tap water was consistent across the soils types and among replicates. The average pondwater DRP at the beginning and at the end of submergence across the six submergence events were 0.72, 0.52 and 0.19 mg/L for the Recent, Pallic, and Allophanic soils, respectively. The DRP concentration in porewater at both the 2 and 10 cm depths showed significant positive correlations ($p<0.01$) with pondwater DRP both at the beginning and at the end of submergence, except for the Allophanic soils where only the DRP at 2 cm and pondwater at the end of submergence was not significantly correlated (Appendix II, Supplementary Table 4.S1).

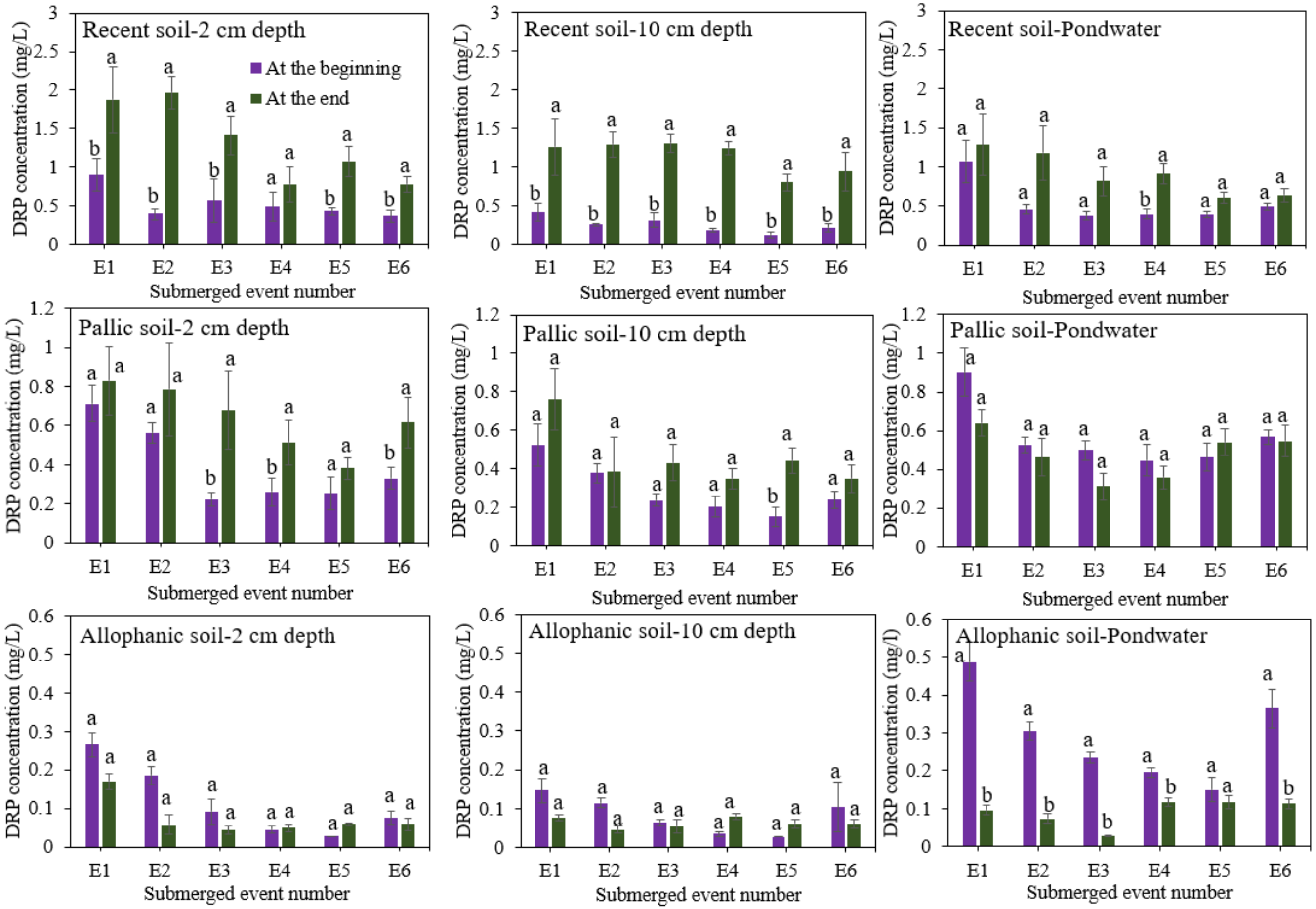


Fig. 4.3 Variations of dissolved reactive phosphorus in porewater measured from the 2 cm and 10 cm soil depths and pondwater measured from the Recent, Pallic and Allophanic soils at the beginning and at the end of six submergence events. The error bars represent the standard errors of the means (n=5). Different scales are used for the DRP concentration (Y axis) of the three soils.

4.3.4 Variations in porewater ion concentrations and the relationship of porewater ion concentrations with porewater DRP and soil redox status

The average porewater NO_3^- concentration measured from the two depths from the three soils ranged from 0.06 to 0.50 mg/L at the beginning of the submergence in the first ponding event (Appendix II, Supplementary Fig. 4.S3). Thereafter, the porewater NO_3^- concentrations decreased throughout the events in all depths of the three soils, with few exceptions. In the Recent soil, porewater Mn concentration at the 2 and 10 cm depths increased with submergence, but a significant ($p<0.05$) increase was recorded only in E1, E2 and E4 (Fig. 4.4 and 4.5). The porewater Mn concentration increased significanly ($p<0.05$) with submergence in both depths of the Pallic soil, with exceptions in E4 and E6 where the increase was not significant (Fig. 4.4 and 4.5). In Allophanic soil, Mn concentration was significantly ($p<0.05$) increased only at 2 cm depth in E2 and Mn concentration during the other submergence events were not changed. Porewater Fe concentration at the two depths of the three soils increased with submergence (Fig 4.4 and 4.5). A significant ($p<0.05$) increase of Fe concentration was observed at the last two submergence events of the three soils compared to the Fe concentration at the beginning of submergence (Fig. 4.4 and 4.5). The increase of porewater Fe concentration in the Recent soil was significant ($p<0.05$) in both the 2 and 10 cm depths in E1, E2, E5 and E6. The porewater Ca and Mg concentrations measured from both depths of the three soils increased significantly ($p<0.05$) with submergence, with few exceptions in the Recent soil (Fig. 4.4 and 4.5). The Allophanic soil showed the highest average porewater Al concentration among the three soils after submergence which were 0.06 mg/L (2 cm) and 0.03 mg/L (10 cm). The average DOC concentration of the 2 cm depth across the six submergence events of the three soils varied from 37 (Pallic soil) to 48 mg/L (in both Recent and Allophanic soils) (Fig. 4.4 and 4.5).

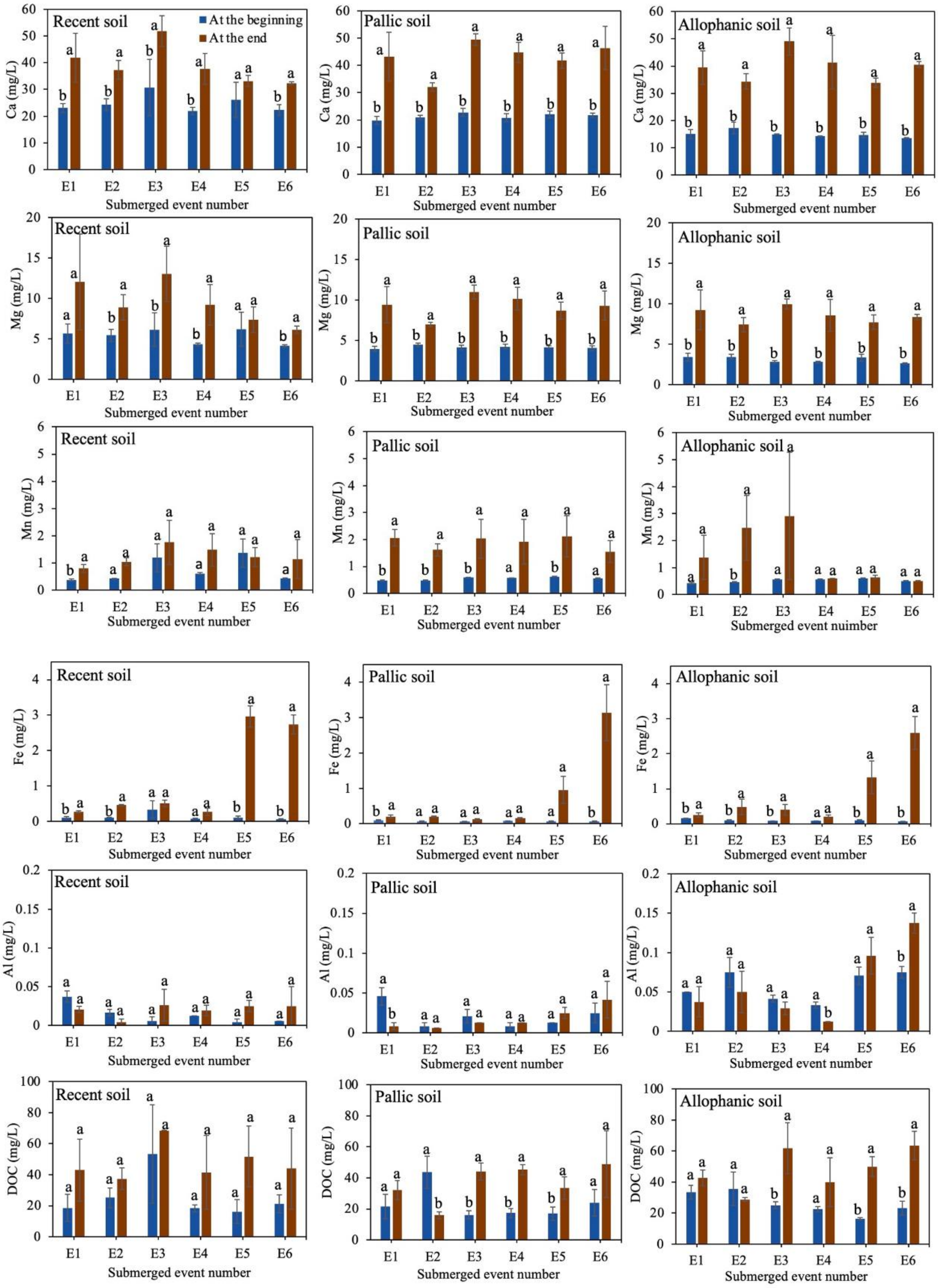


Fig. 4.4 Porewater concentrations of selected cations (Mn, Fe, Ca, Mg and Al) and dissolved organic carbon (DOC) measured from the 2 cm depth following six submergence events in the Recent, Pallic and Allophanic soils. The error bars represent the standard errors of the means.

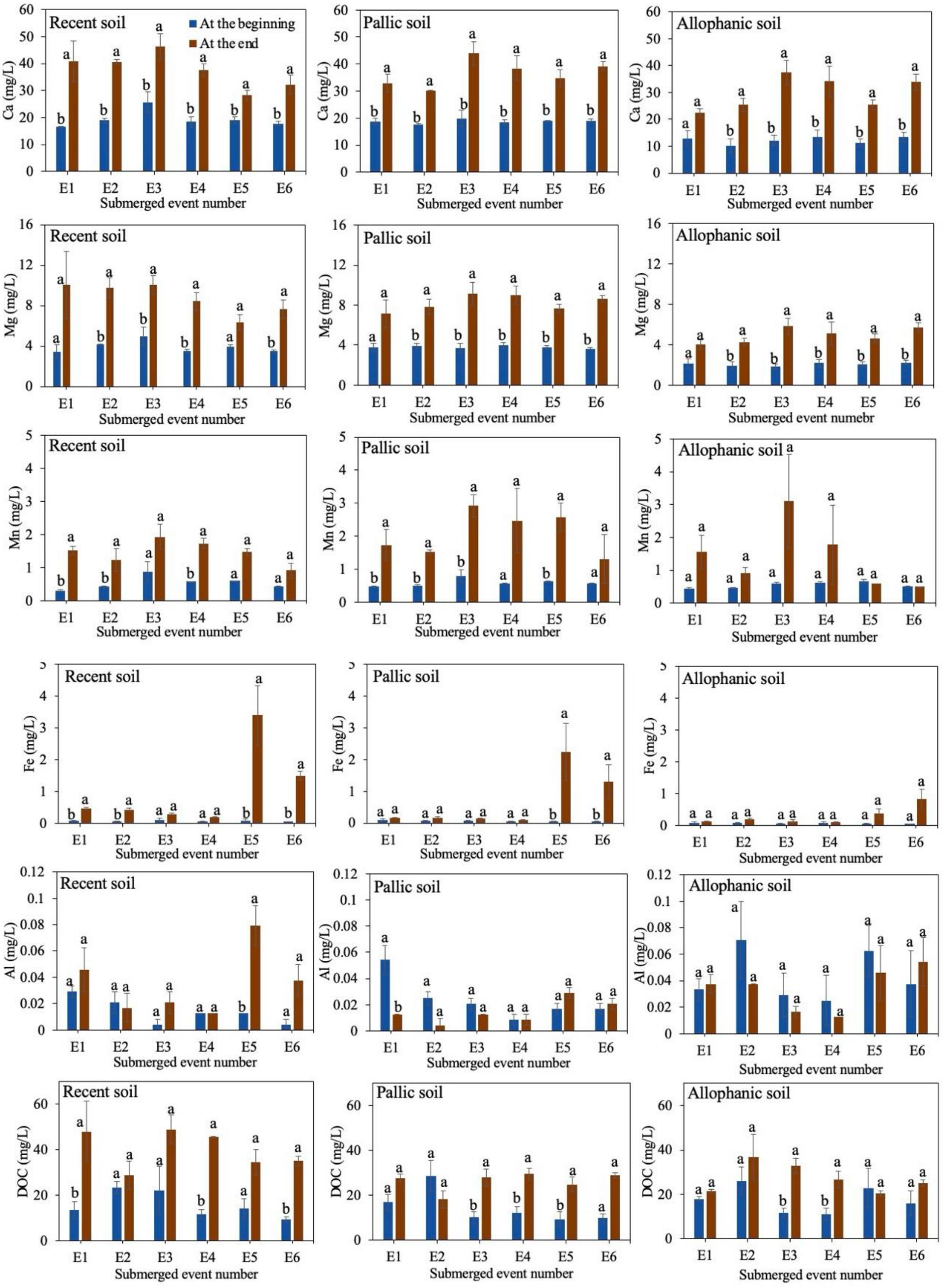


Fig. 4.5 Porewater concentrations of selected cations (Mn, Fe, Ca, Mg and Al) and dissolved organic carbon (DOC) measured from the 10 cm depth following six submergence events in the Recent, Pallic and Allophanic soils. The error bars represent the standard errors of the means.

The porewater DRP concentrations showed significant correlations with several soil parameters. The porewater DRP of the Recent soil and Pallic soil showed significant negative correlations with Eh and p*e*+pH and significant positive correlations with porewater Ca and Mg (Table 4.2). Additionally, in the Recent soil, porewater DRP was positively correlated (r=0.497, $p<0.01$) with DOC and in the Pallic soil, porewater DRP was positively correlated (r=0.235, $p<0.05$) with porewater Mn. In contrast, the porewater DRP of the Allophanic soil showed significant positive correlations with pH, Eh and p*e*+pH and significant negative correlations with porewater Ca and Fe (Table 4.2).

Table 4.2 Correlation coefficients between porewater DRP and pH, Eh, p*e*+pH, DOC and selected cations at the end of submergence

Soil	Recent soil	Pallic soil	Allophanic soil
pH	0.049	0.009	0.474^{**}
Eh	-0.528^{**}	-0.340^{**}	0.498^{**}
p*e*+pH	-0.496^{**}	-0.319^{**}	0.528^{**}
DOC	0.479^{**}	0.185	-0.229
Ca	0.528^{**}	0.327^{**}	-0.331^{**}
Fe	0.153	0.130	-0.262^{*}
Mn	0.235^{*}	0.180	-0.201
Mg	0.450^{**}	0.380^{**}	-0.125
Al	0.171	0.194	-0.196

** $p< 0.01$; *$p< 0.05$

The principal component (PC) analysis of the Recent, Pallic and Allophanic soils including both depths reduced the dimensionality of the data sets into 2, 3 and 3 principal components (eigenvalue>1), respectively (Appendix II, Supplemeatry Table 4.S2). In the Recent soil, the variability attributed to PC1, which accounted for 45%, highlighted the relationships among DRP, DOC, porewater Ca, Mg, and Mn concentrations, Eh and p*e*+pH. While the PC2 attributed to 17% variability of the dataset, elucidating the relationship among p*e*+pH, pH, Eh, porewater Fe, and Al. In the Pallic soil, PC1 attributerd to 54% of the variance highlighting the realtionships among pH, Eh, p*e*+pH, DOC, porewater Ca, Mn and Mg. The PC2 and PC3 of the Pallic soil attributed to 15 and 11%, respectively. In the Allophanic soil, the variability attributed to PC1 was 42% which highlighted the relationships among Eh, p*e*+pH, DOC, porewater Ca, Mn, and Mg. The PC2 and PC3 attributed to 18 and 13% of the variability of the data set, respectively.

4.3.4 Transformation of soil P fractions during submergence

In the Recent soil, P in the $NaHCO_3$-P, Ca-P, and stable-P fractions significantly (p<0.05) changed, while in the Pallic soil, the changes in P occurred only in H_2O-P and stable P fractions (Fig. 4.6). In the Allophanic soil, significant (p<0.05) changes in P occurred in the H_2O-P, $NaHCO_3$-P, Fe/Al-P and stable P fractions (Fig. 4.6). In the Recent soil, the $NaHCO_3$-P fraction reduced by 42% in the 2-8 cm depth, Ca-P fraction reduced by 12% at the 0-2 cm depth and the stable P fraction reduced by 66 and 69% at the 0-2 and 8-10 depths, respectively. In the Pallic soil, the H_2O-P fraction increased by 203% at the 0-2 cm depth and again decreased by 42% towards the end of the experimental period. In addition, in the Pallic soil, the stable P fraction decreased by 38% at the 2-8 cm depth. In the Allophanic soil, at the 0-2 cm depth, H_2O-P, $NaHCO_3$-P and Fe/Al-P fractions increased by 172, 66 and 47-78%, respectively. Comparatively, in the Allophanic soil, the $NaHCO_3$-P fraction at the 2-8 and 8-10 cm depths decreased by 48 and 64%, respectively. In addition, in the Allophanic soil, the stable P fraction at the 8-10 cm depth decreased by 32% (Fig. 4.6).

The total organic P fraction (summation of water, $NaHCO_3$ and NaOH extractable organic P fractions) of the 0-2 cm depth of the Recent soil decreased by 32% at the middle of the third submergence event and it increased by 26 and 83% in the Pallic and Allophanic soils, respectively (Appendix II, Supplementary Fig. 4.S7). The increase in total organic P in the Allophanic soil was significant (p<0.05).

Supplementary tables 4.S3-4.S5 (Appendix II) show the saturation indices (SI) of P minerals, Fe/Mn carbonates and selected Fe and Al oxy(hydr)oxides of the three soils. The SI is an index which shows if porewater will tend to dissolve or precipitate a particular mineral. Positive SI indicates the supersaturation of solution, thermodynamically favouring its formation, while negative SI indicates undersaturation of the solution, thermodynamically favouring its dissolution or absence. A positive SI may not necessarily mean that the mineral is present in soil, as the slow precipitation kinetics may intervene the precipitation (Voigt et al., 2018).

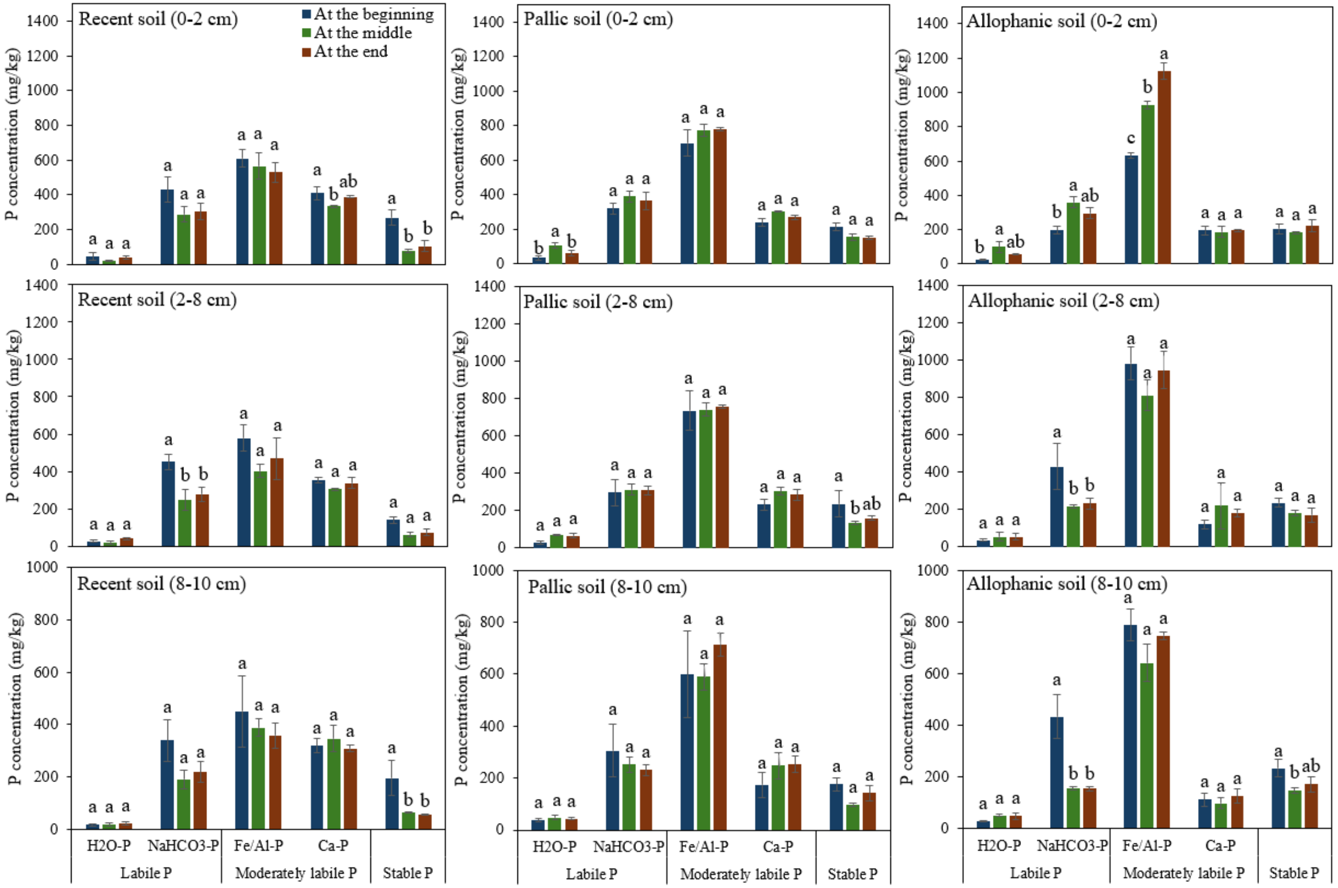


Fig. 4.6 Labile (water extractable (organic and inorganic) P: H_2O-P, sodium bicarbonate extractable (organic and inorganic) P: $NaHCO_3$-P), moderately labile P (Fe/Al (organic and inorganic)-P, Ca-P) and stable P fractions of the 0-2, 2-8 and 8-10 cm depths in the Recent, Pallic and Allophanic soils at the beginning, at the middle and at the end of the experimental period. The error bars represent the standard errors of the means (n=3).

Porewater was supersaturated with FCO_3-Apatite and $MnHPO_4$ in all three soils throughout the submergence period (Appendix II, Supplementary Tables 4.S3-4.S5). In addition, porewater was supersaturated with hydroxyapatite in both Recent (Appendix II, Supplementary Table 4.S3) and Pallic soils (Appendix II, Supplementary Table 4.S4) throughout the submergence period, but became undersaturated with time in the Allophanic soil (Appendix II, Supplementary Table 4.S5). Formation of vivianite and siderite (Fe(II) minerals) was observed in the Recent and Pallic soils and siderite in the Allophanic soil towards the last submergence events (Appendix II, Supplementary Tables 4.S3-4.S5). Supersaturation with some other common Fe/Al oxy(hydr)oxides, namely, hematite, and magnetite occurred in all the three soils throughout the submergence period. Undersaturation with β-$Ca_3(PO_4)_2$ with submergence event was observed in the Recent soil.

4.4 Discussion

The magnitude of P release across the submergence events of the three contrasting soils under short-term frequent submergence were different. The Recent soil released P to porewater at both depths and to overlying pondwater during the 3-day submergence. The Pallic soil released P to porewater at both depths but did not change pondwater DRP during submergence. In contrast to the Recent and Pallic soils, the Allophanic soil sorbed P in pondwater as well as in porewater with submergence, suggesting this soil was effective at mitigating P loss to water.

4.4.1 Effect of pH and Eh on DRP release

The pH and Eh are two factors governing P release in submerged soils. The pH of most soils tends to change toward the neutral range (6.5-7.5) upon submergence (Patrick and Reddy, 1978). Comparably, in this study, the average pH of porewater and pondwater of the three soils varied within a neutral pH range (Appendix II, Supplementary Fig. 4.S1). Marschner (2021) stated that in neutral soils (pH=7), in the presence of equal concentrations of oxidant and reductant, Mn(IV) ions reduce to Mn(II) ions within the redox range of 200 to 100 mV, and Fe(Ш) ions reduce to Fe(II) ions within the redox range of 0 to -100 mV. At the end of three days of submergence, the three soils had surpassed the Mn(IV) reduction redox stage (Appendix II, Supplementary Fig. 4.S1). In further support of this, the three soils showed significant (p<0.05) increases in dissolved Mn in porewater with submergence (Fig. 4.4 and 4.5). Further, the Recent soil showed a significant positive correlation (r=0.235, *p*<0.01) between Mn and porewater DRP, suggesting the possible contribution of Mn reduction and subsequent release of P associated with Mn minerals to porewater, resulting in an increase in the DRP.

Although the Eh of the three soils reduced with submergence, no significant amount of Fe bound P had released due to the short-term submergence period as evidenced by P fractionation (Fig. 4.6) and modelling results (Appendix II, Supplementary Table 4.S3-4.S5). The soils were back to oxidised status after the 3-day submergence (Appendix II, Supplementary Fig. 4.S1), which might have prevented significant reductive dissolution of Fe minerals. The Eh reduction rate of a submerged soil depends on several factors. For example, soils with low contents of reducing Fe and Mn and high organic matter content can lead to a rapid decline in Eh (Fageria et al., 2011). On the contrary, the presence of NO_3^- or Mn(IV)/(Ш) which are preferable by microbes can prevent the redox potential declining further (Smith et al., 2021). Further, abundance of Fe reducing bacteria affects Fe reduction (Li et al., 2021) which affect the rate of Eh reduction under submergence. The decreasing porewater Mn concentration and increasing Fe concentration towards the last two submergence events (E5 and E6), suggested the initiation of Fe(Ш) reduction, possibly due to exhausting the reducible Mn ion pool in soils (Fig. 4.4 and 4.5). This was further evidenced by a tendency towards the formation of vivianite and siderite at the last two submergence events for the three soils (Appendix II, Supplementary Table 4.S3-4.S5).

In most redox-related mineral transformations in soil (eg: Fe and Mn mineral transformations), the redox is poised at characteristic/fixed p*e*+pH values (Lindsay and Sadiq, 1983). Therefore, those values are used to identify mineral transformations in soil. The first redox poise of the Fe minerals starts at p*e*+pH of 14.04 and the transformation of Mn minerals happens even at p*e*+pH value of 16.62 (Lindsay and Sadiq, 1983). Since the p*e*+pH values of the three soils across the submergence events were below 10 at the end of the submergence, it can be stated that there was a favourable condition in soils for both Mn and Fe mineral transformations.

4.4.2 Phosphorus release under short-term and frequent submergence

The magnitude of DRP release to porewater and subsequently to pondwater increased in the order of Allophanic < Pallic < Recent soils. Previous studies suggested that algal growth requires total P concentrations > 0.02 mg/L, and DRP concentrations beyond 0.01

mg/L, when other growth requirements are met (Owens and Shipitalo, 2006). The average pondwater DRP of the three soils across the six submergence events during submergence were 17 to 65-fold higher than the New Zealand lowland river target for DRP concentration; 0.01 mg/L (ANZG, 2018) which is a significant elevation. In this study, the released P from soil accumulated in the overlying water (~2L of volume), but this does not necessarily represent the field condition where a continuous surface flow would be present. However, under field conditions, soil will not be the only source of dissolved P as there will be other P sources such as inorganic P from recent fertiliser application and dissolved organic P from manure (Reid et al., 2018). Therefore, these significant releases of dissolved P from both the Recent and Pallic soils have to be considered in CSA management.

There was no significant difference between the porewater DRP change during submergence and soil depths of any of the soils. Phosphorus translocation through the soil profile (0-10 cm) was also not evident by the P fractionation analysis (Fig. 4.6). Therefore, the results suggested that the 10 cm layer is releasing P upon submergence in both the Recent and Pallic soils at similar concentrations as the 2 cm layer. These results suggested that although the 0-2 cm soil depth is generally considered as the primarily contributing layer to P runoff via desorption (Vadas et al., 2007a; Vadas et al., 2007b), the 10 cm layer is equally important in releasing P upon submergence at least for the Recent and Pallic soils. Similarly, Smith et al. (2021) previously recorded a maximum total dissolved P concentration of 0.12 mg/L at a depth of 20 cm in a Melanic Orthic Gley soil from a dairy farm in New Zealand during winter. Although there will not be a direct interaction of porewater DRP at 10 or 20 cm depths with the surface runoff, the porewater DRP at those depths contribute to the subsurface lateral flow and ultimately transporting DRP to lowland freshwater bodies (McDowell et al., 2004).

Partial drying of previously submerged soils and alternative oxic-anoxic conditions exhibited due to water management processes in this experiment may have influenced P release in these soils as reported in previous studies (Schönbrunner et al., 2012; Kraal et al., 2015). For example, the dissolved Fe during the reduction process under submergence is precipitated as amorphous Fe minerals during re-oxidation. Before those minerals undergo crystallinity, the following reduction event dissolves them. Therefore, alternative oxidation and reduction increase the amorphous Fe oxyhydroxides in soil which have a high affinity to bind P and thus can affect P release (Baldwin and Mitchell, 2000). In support with this, it was evident that the oxalate extractable (amorphous) Fe, Al, and Mn concentrations increased with submergence (Table 4.1 and Appendix II, Supplementary Table 4.S6) in this experiment. This may be one reason among other reasons such as removal of P with draining water, for the significant ($p<0.05$) decrease in DRP concentration recorded in the Recent soil in the later submergence events (Fig. 4.3).

Over the long-term, the dissolution of P species will be the rate limiting step in P release in soil while in the short-term, desorption processes are likely to dominate (McDowell and Sharpley, 2003). However, differentiation of P release by the two processes would be difficult. Adsorption and desorption of P from minerals is pH and redox sensitive (Schönbrunner et al., 2012; Oxmann and Schwendenmann, 2015). Phosphorus sorption/desorption process in soil can be influenced by several factors. Phosphorus can be associated with Fe and Al in the mineral form or can sorbed onto Fe and Al oxides by exchange with hydroxyl groups or associated with Ca or adsorbed onto calcium carbonate minerals (McDowell and Condron, 2001). Phosphorus can also be associated with organo-mineral complexes (Gerke, 2010) or sorbed onto clay mineral surfaces such as illite and montmorillonite (Gimsing and Borggaard, 2002). In this study, although porewater Ca and Mg concentrations of three soils significantly ($p<0.05$) increases with submergence and they showed significant positive correlations (Table 4.2) with porewater DRP (especially in the Recent and Pallic soils), neither the P fractionation or modelling data supported the dissolution of Ca and/or Mg-P and subsequent release of P. Since there was no clear evidence of reductive dissolution of Fe and subsequent release of P as explained in 4.4.1 section, the most probable mechanism of P release of the three soils under 3-day submergence may be sorption/desorption other than the reductive dissolution of Mn.

4.4.3 Risk of P release to runoff

The soil water extractable P fraction is commonly used as a measure of labile P susceptible to risk of P loss via runoff (Castillo and Wright, 2008; Pietrzak et al., 2020). Given the 0-2 cm layer of soil is a critical depth in terms of contributing to P runoff via desorption (Vadas et al., 2007a), it is important to measure the changes of P fractions in that layer upon short-term submergence. The decrease in the H_2O-P and other fractions with submergence in the Recent soil suggests that P in all the fractions (labile, moderately labile, and stable P) is released from this soil upon submergence and this coincides with increased P release to porewater and pondwater in the Recent soil. Similarly, the reduction of the H_2O-P fraction was evident in other two depths (2-8 and 8-10 cm) of the Recent soil indicating the potential risk of subsurface P loss. Therefore, in combining the fractionation results with the porewater and pondwater DRP concentrations, it was clear that having Recent soil in CSAs is riskier under short-term frequent submergence.

In contrast, the Pallic and Allophanic soils, significantly ($p<0.05$) increased the water extractable P suggesting the retention of P in the most labile P fraction rather than releasing them to porewater. According to literature, the clay mineralogy of the Pallic soil is dominated by illite (Hewitt et al., 2021). Therefore, clay minerals and the presence of high amounts of Fe and Al minerals might have controlled P sorption/desorption in the Pallic soil. The increase in the H_2O-P fraction at the 0-2 cm depth of the Allophanic soil may be attributed to the sorption of P from the added tap water. Further, the increases of the same fraction in the deeper soil depths (2-8 and 8-10 cm) of the Allophanic soil may be attributed to the transformation of P from the $NaHCO_3$-P fraction which reduced (Fig. 4.6). However, in the Allophanic soil, the significant ($p<0.05$) increase of Fe/Al-P at the 0-2 cm depth with time suggests that the possible transformation of the labile P into moderately P fraction decreased the risk of P release to runoff (Fig. 4.6). However, it was observed that both labile P and Fe/Al-P fractions decreased with submergence in soil layers below 2 cm in the Allophanic soil (Fig. 4.6). This may be an indication that P present below 2 cm may have migrated to the top layer due to a concentration gradient (high concentration in the deep soil and low concentration in the shallow soil) and accumulated (resorbed) in the top layer.

Allophanic soils are dominated by allophane and also imogolite or ferrihydrite and aluminium or iron humus complexes (Hewitt et al., 2021). Supersaturation of Al oxides such as $Al(OH)_2$, boehmite, diaspore and gibbsite, may be contributed to low dissolved P concentration in the Allophanic soil by sorbing or precipitating phosphates in porewater (Appendix II, Supplementary Table 4.S5). The high amounts of amorphous Fe and Al might have played a significant role in sorbing P in the Allophanic soils as evidenced in previous studies (Hashimoto et al., 2012; Hosokawa et al., 2022). The significantly ($p<0.05$) increased total organic P fraction recorded in the Allophanic soils (Appendix II, Supplementary Fig. 4.S6) upon submergence in the present study might be due to the high TOC (8.2%) content of the soil and the presence of alumino-silicates which allows retention of large quantities of soil organic P (Redel et al., 2016).

In contrast to the Recent soil, volcanic soils (eg: Allophanic soils) usually have a high ASC and have the ability to sorb high amounts of P, minimising losses (Hewitt, 2010). The sum of oxalate extractable Fe and Al is known to be a good predictor of P sorption in soils (Blomback et al., 2021). Here, the P sorption ability (sum of oxalate extractable Fe and Al) of the Allophanic soil was 2-4-fold higher than that of the Pallic and Recent soils, respectively (Table 4.1 and Appendix II, Supplementary Table 4.S6). Further, sorption of P added with the tap water by the Allophanic soil was evident in each submergence event. Therefore, owing to the presence of Al, this study suggests that Allophanic soils were less likely to be a source of P under sustained periods of submergence, compared to the Recent and Pallic soils.

4.5 Limitations and implications

This submergence study differed in some ways to a field CSA as water was not flowing over the soil, submergence events occurred in frequent fixed intervals and overlying tap water was not being replenished with sources of P like it would in a field surface runoff situation (ie: dissolved P fertilisers, organic P from manures and dissolved P from runoff water). However, the current design allowed some control over field soil heterogeneity by maintaining five replicate field soil blocks with actively growing pasture.

This study revealed that three soils located from or adjacent to CSAs with contrasting soil characteristics showed three different P releasing patterns and magnitudes upon short-term frequent submergence. The risk of P loss increased in the order of Allophanic < Pallic < Recent soil. The significant positive correlations between porewater Ca and DRP concentrations of the Recent and Pallic soils suggested that soils with high Ca concentrations might have high risk of P loss during submergence. The finding of this study can be applied to edge of farm mitigation practices such as wetlands and detainment bund constructions, especially in selecting suitable sites/soils. Use of Allophanic soils as a P sorbing material was proved to be advantageous in this study, considering the P sorbing capacity of such soils. The main mechanisms of P release in the Recent and Pallic soils under 3-day submergence may be desorption of P sorbed to minerals (eg: Ca, Mg, Fe, Al and Mn minerals) and reductive dissolution of Mn-P minerals. According to literature, the reduction of Fe and consequent phosphate release starts after the reduction of the entire nitrate pool which was completed three days after the submergence of soils (Reddy and DeLaune, 2008). There is a possibility of an occurrence of iron reduction and concomitant P release under field condition in CSAs during rainfall induced submergence events. Therefore, it is important that further research focusses on the collection of field data and verification of the findings of this study.

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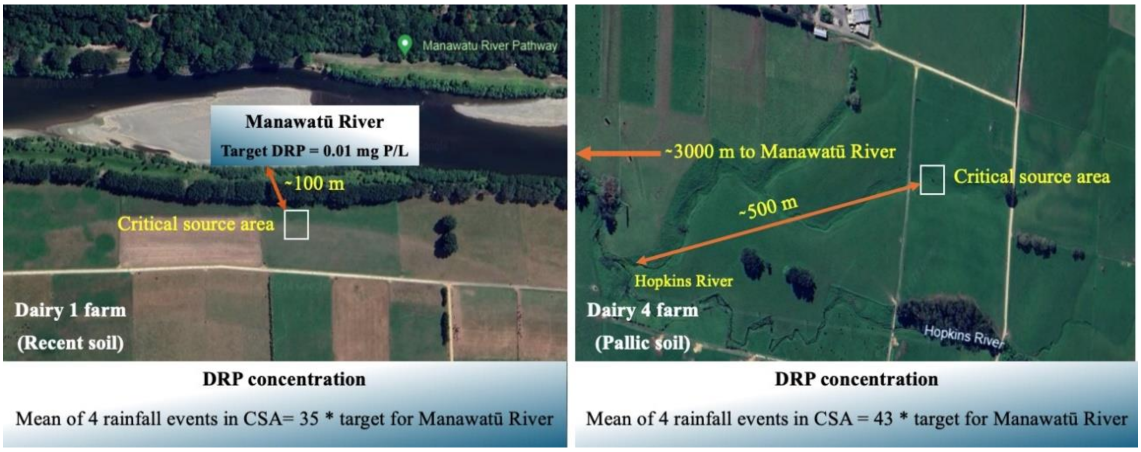
Chapter 5

Redox-induced phosphorus release from critical source areas following rainfall events in New Zealand

Graphical abstract



Highlights

- Phosphorus release from two critical source areas were measured during five intermittent rainfall events.
- Recent and Pallic soils released P to porewater during short-term submergence.
- Average floodwater DRP concentrations of the CSAs were 35-43-fold higher than the target DRP concentration for the Manawatū River.
- Risk of P loss to the Manawatū River was higher in the Recent soil.

Abstract

Critical source areas (CSAs) can act as a source of phosphorus (P) during intermittent rainfall events and contribute to dissolved P loss via runoff. Dissolved forms of P are readily accessible for plant and algal uptake; hence it is a concern in terms of the eutrophication of freshwater bodies. The potential of CSAs to release dissolved P to surface runoff upon intermittent short-term submergence caused by different rainfall events has not been studied at a field-scale in New Zealand previously. A field study was conducted to investigate the potential of two different pastoral soil CSAs (Recent and Pallic soil) to release soil P over five rainfall events during winter and to explore the mechanisms of P release in these soils. Ten sampling stations were installed within each CSA in an area of 6×2 m^2. Each sampling station had two porewater samplers installed at two depths (2 and 10 cm) below the soil surface. Two platinum half-cell electrodes were installed at the same two depths. Porewater and floodwater samples were collected following five rainfall events. Redox potentials were measured in-situ. Dissolved reactive phosphorus (DRP), pH, dissolved organic carbon, cations, anions, and alkalinity of the water samples were measured. Soil chemical P fractions were assessed at the beginning, middle and end of the experiment. Thermodynamic modelling was used to infer dissolution and formation of P and P-associated minerals. The average porewater DRP at the two depths during the rainfall events of the Recent and Pallic soils were 0.32-1.3 mg/L and 0.26-2.31 mg/L, respectively. The average floodwater DRP concentrations of the Recent and Pallic soils were 35 and 43-fold higher than the target DRP concentration (0.01 mg/L) for the Manawatū River. Considering the proximity of the two CSAs to freshwater bodies; ~100 m (Recent soil) and ~500 m (Pallic soil), the elevated floodwater concentrations pose a eutrophication risk. The main mechanism of P release from the two soils upon submergence was P release associated with the reductive dissolution of Mn and Fe oxy(hydr)oxides as evidenced by modelling results and the redox status of the soils. There was a lack of significant changes in chemical P fractions of the two soils, probably due to the short scale of time of the experiment. Significant effects of rainfall characteristics were visible only with the floodwater DRP of the Recent soil and the porewater DRP of the Pallic soil. This implied the effect of other factors such as hydrology, and landscape position on P release under natural field condition. The method established to measure the changes in soil porewater P and redox conditions within CSAs under submergence can be used to monitor such changes in other high-risk CSAs in the future.

Keywords: Critical source areas, dissolved reactive phosphorus, phosphorus, submerge

5.1 Introduction

Agricultural non-point source phosphorus (P) pollution is a major concern in maintaining freshwater quality worldwide. Significant attention has been paid overtime to managing critical source areas (CSAs) within agricultural landscapes to mitigate P loss to freshwater bodies (Sharpley et al., 2011; Doody et al., 2012; Shore et al., 2014; Lou et al., 2016). Critical source areas generally contribute a disproportionately large amount of P loss (~80%), despite representing a small area (~20%) of the landscape (Pionke et al., 2000; Dahlke et al., 2012; Smith et al., 2021). In CSAs, P sources coincide with flow pathways which connect to waterways (McDowell and Srinivasan, 2009; Sharpley et al., 2011). Therefore, CSAs act as a pathways of P transportation from agricultural land to freshwater bodies, thus contributing to eutrophication.

The CSAs often saturate/submerge following rainfall events due to the accumulation of water as a result of topography, to create hydrologically sensitive areas. These areas are often subjected to water table fluctuations, surface runoff and drying and rewetting due to rainfall events with different intensities and durations. Since there can be no infiltration in saturated soils, P is mobilised in such soils and can generate surface P losses due to moving P to surface water (Smith et al., 2021). For example, microbial cell lysis due to osmotic shock and subsequent large fluxes of P release caused by rewetting of soil has been recorded previously (Turner et al., 2003; Blackwell et al., 2010).

Phosphorus is released from soil to porewater (dissolved P) when a soil is submerged depending on inherent soil characteristics such as clay mineralogy, P sorption capacity, presence of Fe, Al, Ca and Mg minerals, and organic matter content (Palihakkara et al., 2024). When the soils of CSAs remain saturated long enough to deplete oxygen in soil solution due to microbial respiration, it creates a unique anaerobic environment. Besides inherent soil characteristics, external factors such as duration of saturation (eg: length of a rainfall event and subsequent water flow over soil), air temperature (Kumaragamage et al., 2020), and the presence of vegetation (Zhang et al., 2016) also affect anaerobic conditions and subsequent dissolved P release. The overall redox status of soil changes upon submergence. For example, the soil pH shifts towards neutrality (Ponnamperuma, 1972) and the redox potential (Eh) of soil reduces under submergence (Maranguit et al., 2017). As a result of this, in calcareous soils, dissolution of Ca and Mg phosphates increase the P concentration in soil solution upon submergence (Amarawansha et al., 2015). In acidic to neutral soils, where Fe, and Mn are mainly responsible for P sorption, reductive dissolution of Mn and Fe oxy(hydr)oxides influences P release (Kröger et al., 2012; Scalenghe et al., 2012; Amarawansha et al., 2015). Although Mn reduction occurs at an early stage of the reduction sequence (~200 mV), Fe reduction occurs at a later stage below 0 mV (Marschner, 2021).

The dissolved forms of P are associated with increased growth of aquatic plants in freshwater bodies as they are readily accessible for uptake. Hence, significant attention has focused on dissolved P losses from agricultural landscapes worldwide, including in New Zealand (Thomas et al., 2016; King et al., 2017; Thomas et al., 2017; Smith et al., 2021; Ross et al., 2022). Field-scale studies have been conducted in New Zealand to quantify subsurface P losses and/or associated mechanisms of P release in several soil types including Melanic Orthic Gley soil (Smith et al., 2021), and Recent and Brown soils (Smith et al., 2016). However, the potential of CSAs to release dissolved P to surface runoff upon intermittent short-term submergence caused by different rainfall events (eg: different durations and intensities) has not been studied at a field-scale in New Zealand previously.

Therefore, the objectives of this study were (1) to investigate the potential of two different pastoral soil CSAs to release P to overlying floodwater over intermittent rainfall events, (2) to explore the relationships between different soil and rainfall characteristics with P release, and (3) to elucidate the mechanisms of P release in these soils under submergence using thermodynamic modelling and P fractionation. It was hypothesised that the reductive dissolution of Fe/Mn oxy(hydr)oxides during temporarily submergence would release sorbed P, consequently elevating the P concentration in the soil solution and that the magnitude of P release due to submergence would depend on soil characteristics and the duration and intensity of rainfall events.

5.2 Materials and Methods

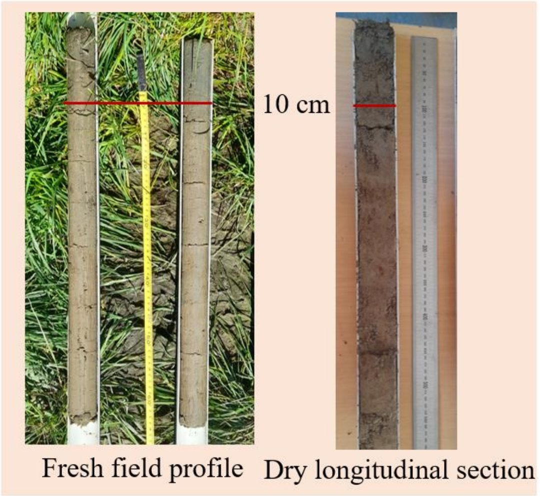
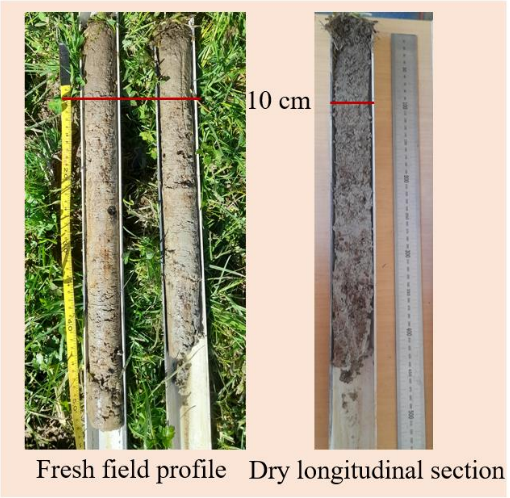
5.2.1 Experimental sites

Critical source areas (Fig. 5.1) were identified on two Massey University farms located in the Manawatū-Whanganui region of New Zealand, namely Dairy 1 (S 40° 22’ 27”, E 175° 37’ 05”), and Dairy 4 (S 40° 23’ 39”, E 175° 36’ 55”). According to the *New Zealand Soil Classification*, the soil types were a Recent and Pallic soil, respectively. These sites were selected considering the fact that floodwater was retained for a sufficient amount of time to allow sample collection. A brief comparison of the two sites is given in Table 5.1. The CSA site at the Dairy 4 (~16.4 ha) had a relatively large catchment area compared to Dairy 1 (~5.4 ha) site. The Dairy 1 site directly connected to the Manawatū River (~100 m distance) while the Dairy 4 site connected to the Manawatū River via the Hopkins River and the Turitea Stream (~3000 m distance). Both CSAs experienced surface runoff and had natural drainage while the Dairy 4 site also had subsurface tile drainage. The runoff water collected by the tile drainage system was discharged to the Hopkins River downstream from the sampling location.

5.2.2 Experimental setup

Ten sampling stations were installed within each CSA in an area of 6×2 m^2 (Fig. 5.1). Each sampling station comprised of two porewater samplers installed at two depths: 2 and 10 cm below the soil surface. Porewater samplers were made using 0.5 cm diameter polytetrafluoroethylene (PTFE) tubes connected to 6 µm pore diameter filter cloth at one end and the other end of the tubes were connected to 50 ml syringes. Two platinum half-cell electrodes were installed at the same two depths. Previous studies suggest that the 0-2 cm soil layer retains around 80% of the P from P fertiliser additions via sorption and therefore disproportionally contributes to P runoff via desorption (Vadas et al., 2007a; Vadas et al., 2007b), hence the focus on the 2 cm depth in the current study. Electrodes were also installed at a depth of 10 cm depth as this is where more than half of the root mass of pasture is generally located (Crush et al., 2006) and is a potential source of P release from soil. The sampling arrangement at the two experimental sites are shown in Fig. 5.1. Five samplers (the middle line in Fig. 5.1) were always submerged during rainfall events, while the rest of the samplers were submerged only in heavy rainfall events.

Table 5.1 Comparison of the two experimental sites at Dairy 1 and Dairy 4 farms

	Dairy 1 farm site	Dairy 4 farm site
New Zealand Soil Classification	Recent soil	Pallic soil
Local soil name	Manawatū loamy gravel	Tokomaru silt loam
USDA Classification (Sub Order)	Fluvents	Aqualfs
Soil profile		
Catchment area (ha)	~5.4	~16.4
Altitude (meters above sea level)	35	80
Nearest freshwater body	Manawatū River	Hopkins River (Hopkins River flows to the Turitea Stream which flows to the Manawatū River)
Distance (m) to the nearest freshwater body	~100	~500
Drainage	Free draining	Naturally poorly drained soils, artificial draining- tile drainage 60 cm below the soil surface
Predominant pasture species	Perennial ryegrass / white clover species	Perennial ryegrass / white clover species
Sources of P	Mineral P fertiliser, organic P (eg: cow dung and plant debris)	Mineral P fertiliser residue, organic P (eg: cow dung and plant debris), effluent runoff from higher in catchment

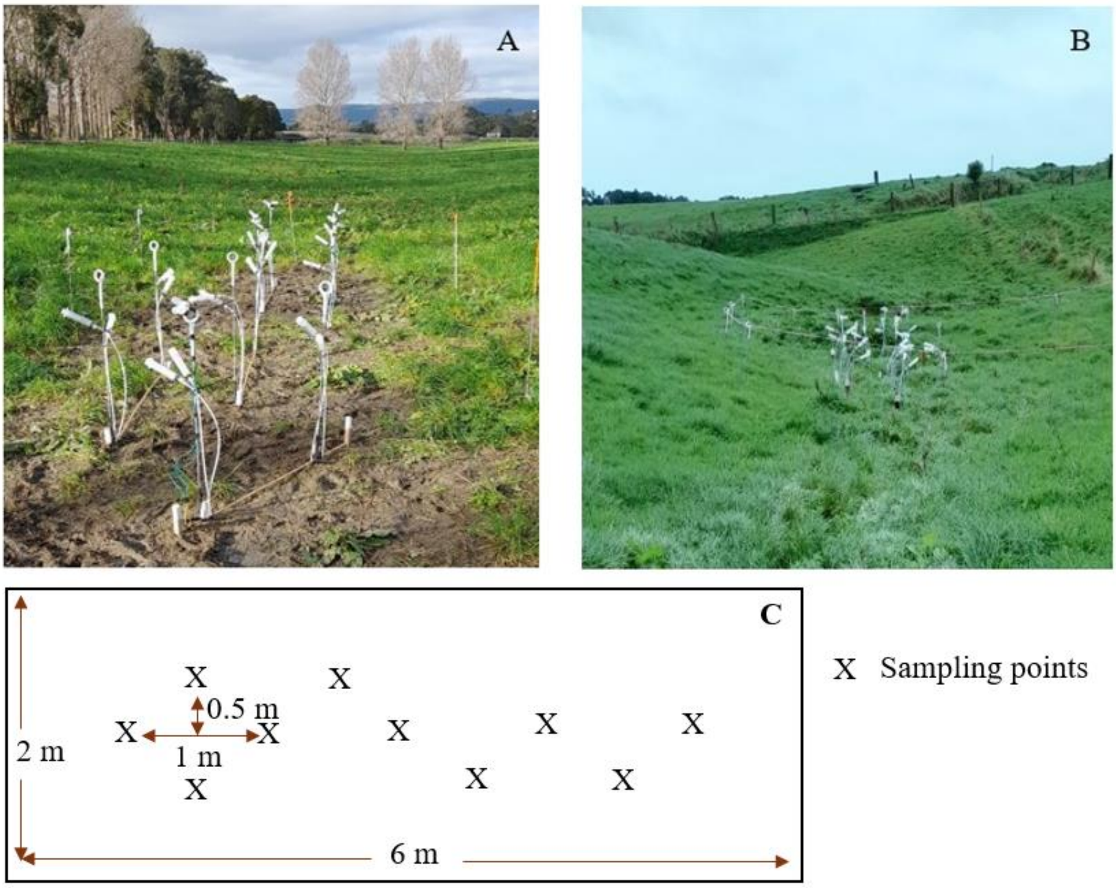


Fig. 5.1 The experimental sites located within critical sources areas at Massey University dairy farms, Palmerston North, New Zealand **A**: Dairy 1 farm site (Recent soil), **B**: Dairy 4 farm site (Pallic soil), **C**: A diagram of sampling point arrangement at the two sites (this diagram is not to scale)

5.2.3 Soil, porewater, floodwater and in-situ data collection

Representative bulk soil samples (0-10 cm depth) were collected from both CSAs for initial soil characterisation. Porewater samplers were placed under suction in the morning via attached syringes and porewater was collected after 12 pm, following five rainfall events between July and August 2022. Although each field had ten sampling stations, porewater could not be collected from all ten stations in each rainfall event, due to issues with clogging and suction. Hence, there were a number of missing data. The five rainfall events will be referred as event 1, 2, 3, 4 and 5 in the manuscript. Surface flow was collected close to the soil surface using a syringe. The surface flow drainage pattern at the two sites were different. Surface runoff accumulated at the CSA site with time following a rainfall event at Dairy 1 farm, whereas it drained off quickly following a rainfall event at Dairy farm 4. Therefore, a sufficient amount of porewater was collected only in four out of the five events at each site.

In-situ redox potential was measured using an Ag/AgCl reference electrode (ORION) and a voltmeter. The voltmeter reading was corrected to the standard hydrogen electrode by adding the potential of the reference electrode (+200 mV). Redox status was expressed as p*e* which is the negative logarithm of electron activity calculated using the Nernst equation (Lindsay, 1979). Rainfall and climate data were collected from the Palmerston North Ews NIWA weather station 21963 (S 40⁰ 22’ 52”, E 175⁰ 36’ 32”) located adjacent to Dairy 1 farm and ~2 km from Dairy 4 farm. Representative soil samples from 0-2, 2-8 and 8-10 soil depths were collected from both sites at the beginning, at the middle (the third rainfall event) and at the end of the last rainfall event, for P fractionation. The soil samples taken under submerged conditions were purged with nitrogen gas, sealed, and stored at -28 ⁰C until P fractionation analyses were performed. Representative soil samples were also taken from both sites from the 0-10 cm depth at the end of the experiment to measure the oxalate extractable Fe, Al and Mn concentration.

5.2.4 Initial soil characterisation

The soil samples (0-10 cm depth) were air-dried, passed through a 2 mm sieve, homogenised, and analysed for basic soil properties. Soil pH was determined in 1:2 (v/v) soil:water slurry followed by potentiometric determination of pH. Olsen phosphorus was determined by Olsen extraction (Olsen and Sommers., 1982) followed by molybdenum blue colorimetry (Murphy and Riley, 1962). Anion storage capacity (ASC) was determined by equilibration of 5 g of soil with 1000 mg/L P solution (pH 4.6) for 16 hours followed by colorimetric analysis (Saunders, 1965). Mehlich-3 P was determined by Mehlich-3 extraction followed by Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Mehlich, 1984). Mehlich-3 extractable cations (Ca, Mg, Fe, Mn, Al and Zn) were also determined using ICP-OES. Cation exchange capacity (CEC) was determined by 1M neutral ammonium acetate extraction of cations (K, Ca, Mg, Na) followed by ICP-OES (Blackmore et al., 1987). Total organic carbon (TOC) was determined by thermal conductivity detector (Elementar Analyser) after acid pretreatment to remove carbonates present followed by catalytic combustion (900°C, O_2) and separation (Nelson and Sommers, 1996). Soil texture was determined by sedimentation procedure by hydrometer, after organic matter removal (Standards Association of New Zealand, 1986). The oxalate extractable Fe, Al and Mn concentrations were determined by acid ammonium oxalate method (McKeague and Day, 1966) followed by Microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4200). The acid ammonium oxalate method was repeated for the soil samples collected at the end of the experiment. Phosphorus fractionation was undertaken using a modified Hedley procedure (Hedley et al., 1982) as explained in detail in section 5.2.6.

5.2.5 Porewater and floodwater sample analysis

The porewater and floodwater samples were filtered through 0.45 µm cellulose membrane filters and analysed for DRP by molybdate blue colour method (Murphy and Riley, 1962) using UV visible spectrophotometer (JENWAY 7315) within 12 hours of sampling. The pH of porewater and floodwater samples were measured using a glass pH electrode (ORION STAR A214). Cation concentrations (Ca, Mg, K, Na, Fe, Al, and Mn) of collected porewater were measured using MP-AES (Agilent 4200). Porewater anion concentrations (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}) were measured at each event using ion chromatography (Dionex™ Aquion™). Dissolved organic carbon (DOC) concentrations of porewater were measured using a carbon nitrogen analyser (Shimadzu TOC-LCSH). Alkalinity of the porewater samples was measured by titrating against 0.1 N H_2SO_4 in the presence of methyl orange indicator.

5.2.6 Phosphorus fractionation study

Phosphorus fractionation was undertaken using a modified Hedley procedure (Hedley et al., 1982). Three replicates from each of the 0-2, 2-8 and 8-10 cm depths at the beginning, at the middle (rainfall event 3) and at the end of the experimental period were analysed from both sites. The three soil depths were selected to represent the entire depth measured by the samplers (2 cm and 10 cm depth). During the sequential extraction, the soil aliquot (~0.5 g) was first transferred to a 50 mL centrifuge tube filled with 30 ml of distilled water, while purging with nitrogen gas. The next two steps involved transferring the supernatant of distilled water extract and adding 0.5 M $NaHCO_3$, while purging nitrogen gas. A portion (2 ml) of the $NaHCO_3$ and NaOH extracts was acidified using concentrated H_2SO_4 to precipitate extracted organic matter, and the supernatant was analysed for inorganic P (Pi). The distilled water and HCl extracts were directly analysed for Pi. A portion (1 ml) of distilled water, $NaHCO_3$ and NaOH extracts were digested in a digestion block at 150° for 20–30 minutes until the vigorous boiling subsided. Acidified potassium persulfate oxidation was used for the digestion and the residue was analysed for total P

(TP). The difference between TP and Pi was estimated to be organic P (Po) (Tiessen and Moir, 1993). The P in the soil residue left after sequential extraction was determined after digestion with aqua regia (Chen and Ma, 2001).

5.2.7 Phosphorus speciation study by thermodynamic modelling

The thermodynamic modelling software Visual MINTEQ 3.1 (Gustafsson, 2013) was used to predict the solid P species based on the composition of porewater samples across the rainfall events. The input parameters entered in the software were soil Eh, pH, DOC, alkalinity, concentrations of cations (Ca, Mg, Na, K, Mn, Al and Fe), anions (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}), and DRP in porewater. The Stockholm Humic Model (SHM) was used as the state-of-the-art model to simulate the complexation to natural organic matter, and it was assumed that fulvic and humic acids were present in similar quantities (50% each) in porewater. The data collected from the 2 cm depth was used for this modelling.

5.2.8 Statistical analysis

Statistical analysis was performed using IBM SPSS Statistics 28.0.0 software. Porewater DRP, pH, Eh, cations (Ca, Mg, Fe, Mn) were analysed using two-way ANOVA to compare different depths (two depths; 2 and 10 cm), over five rainfall events for each soil separately. One-way ANOVA was performed to compare the floodwater DRP over rainfall events of the two soils separately. Pearson correlation analyses were performed separately for each soil to explore relationships between DRP concentrations in porewater at both depths (together and separately) and floodwater DRP, pH, Eh, p*e*+pH, DOC, porewater Fe, Mn, Ca, Mg and Al concentrations. Regression analyses were performed to explore the relationships between rainfall characteristics (previous 24 hr precipitation, previous 24 hr dry period, previous four-day precipitation, and previous four-day dry period) and floodwater DRP and porewater DRP of the two depths of the two soils.

5.3 Results

5.3.1 Initial soil characteristics

The Recent soil was slightly acidic (6.5), whereas the Pallic soil (5.8) was moderately acidic at the beginning of the experiment (Table 5.2). The clay % of the Recent and Pallic soils were 18 and 32%, respectively. The total organic carbon and CEC of the Pallic soil were 2.4 and 1.8-fold higher than that of the Recent soil (Table 5.2). The Olsen P concentration of both the Recent (69 mg/L) and Pallic (66 mg/L) soils were high. Anion storage capacity was low in the Recent soil (19%) and nearly moderate in the Pallic soil (29%). Compared to the Recent soil, in the Pallic soil, the sum of oxalate extractable Fe and Al was 1.3-fold higher at the beginning of the experiment.

5.3.2 Rainfall and temperature variations

There were 36 rainfall events totalling 277.9 mm of rainfall over the experimental period. Rainfall events were defined as events with a minimum rainfall of 1 mm with at least a 1-hour interval. However, out of the 36 rainfall events, only 5 were selected for sampling based on the timing of the rainfall event (morning hours) and the characteristics of the rainfall event and associated climatic conditions, which created temporary flooding conditions in the CSA sites. The rainfall event characteristics were analysed to examine the rainfall amount in the previous 24 hr before sample collection, the number of dry hr within 24 hr before sample collection, the previous four-day rainfall amount and the dry hr within four days before sample collection (Appendix Ш, Supplementary Table 5.S1). The previous 24 hr rainfall amounts for the 5 events were 33.5, 16.1, 7.1, 15.8 and 34.8 mm, respectively. The highest rainfall intensity recorded during this experimental period was 7.3 mm/hr at the last day of sample collection (Appendix Ш, Supplementary Fig. 5.S1). Average air temperatures on the sample collection days were 13, 12, 13, 17 and 12 ^{0}C for events 1, 2, 3, 4 and 5, respectively (Appendix Ш, Supplementary Table 5.S1).

Table 5.2 Initial physico-chemical properties of the two study site soils sampled to a depth of 0-10 cm at the start of the experiment

	Recent soil	Pallic soil
pH	6.5	5.8
Textural class	Loam	Silty clay loam
Clay%	18	32
Sand%	39	14
Total organic carbon (g/100g)	2.0	4.7
CEC (cmol$_{(+)}$/kg)	12	22
Mehlich-3 P (mg/L)	147	133
Olsen P (mg/L)	69	66
Anion storage capacity %	19	29
Oxalate extractable cations (mg/kg)		
Fe	3642	4645
Al	833	1312
Mn	88	231
Mehlich-3 extractable cations (mg/L)		
Ca	1233	1735
Mg	170	254
Fe	681	545
Mn	46	75
Al	568	800
P fractions (mg/kg)		
H_2O-P	16.8	21.2
$NaHCO_3$-P	300.2	346.6
Fe/Al-P	420	781
Ca-P	309	230
Stable P	53	235

pH was measured in 1:2 soil: water slurry. CEC: Cation exchange capacity. H_2O-P: Organic and inorganic P extracted by distilled water. $NaHCO_3$-P: Organic and inorganic P extracted by $NaHCO_3$. Fe/Al-P: Organic and inorganic P extracted by NaOH. Ca-P: Inorganic P extracted by HCl. Stable P: Residual P

5.3.3 pH, Eh and overall redox status of soils during submergence

The initial soil pH of the two soils increased into the neutral pH range with submergence (Appendix Ш, Supplementary Fig. 5.S2). The average pH of the 2 cm depths of the Recent soil and Pallic soils were 7.4 and 7.2, respectively. The average pH of the 10 cm depths of those soils were slightly higher at 7.6 and 7.5, respectively. The average floodwater pH of the Recent and Pallic soils were 7.3 and 7.4, respectively. The interactions between event×depth of the porewater pH of two soils were not significant. The porewater pH at the 10 cm depth of the Recent soil was significantly ($p<0.05$) higher compared to that of event 1 and 4. In the Pallic soil, the porewater pH at the 10 cm depth measured in events 2 and 5 were significantly ($p<0.05$) higher than the other two events.

The overall redox status of soil can be categorised as oxic (>14), sub-oxic (9–14) or anoxic (<9) based on the p*e*+pH values. Both depths of the two soils examined in the current study were in an anoxic condition during the five rainfall events (Fig. 5.2). The p*e*+pH value of the 2 cm depth varied from 6.32 to 7.37 across the four rainfall events in the Recent soil, while it varied from 4.72 to 6.27 in the Pallic soil. At the 10 cm depth, this value varied from 7.38 to 8.23 in the Recent soil and 7.06 to 7.52 in the Pallic soil (Fig. 5.2). The average Eh recorded for any depths of any of the rainfall events of the two soils were below 33 mV (Appendix Ш, Supplementary Fig. 5.S2). The Eh of the 10 cm depth of both soils showed high Eh values (more oxidised) compared to the 2 cm depth (Appendix Ш, Supplementary Fig. 5.S2). The Eh of the 10 cm depth soil was significantly ($p<0.05$) higher compared to the 2 cm depth in rainfall events 2 and 4 in the Recent soil. A relatively oxidised layer was observed in the Recent soil below ~4 cm, compared to the soils above this depth when the soil profile was sampled at the end of the experiment (Table 5.1). This may be due to a trapping of oxygen below the 2 cm layer due to a fine silt layer on the soil surface, preventing/delaying infiltration. This observed fine silt layer might have developed due to the constant deposition of silt particles as water often flows in these CSAs. However, the increase of the p*e*+pH value at the 10 cm depth compared to 2 cm depth, was not significantly different except for event 2 in the Recent soil ($p<0.05$).

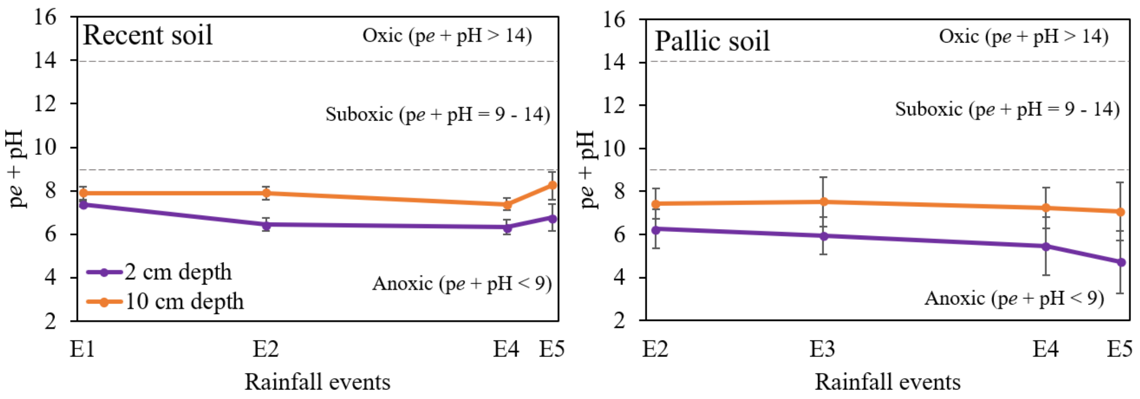


Fig. 5.2 Overall redox status of the soil solution during each event as p*e*+pH varied in the 2 and 10 cm depths of the two soils at different rainfall events. Redox zones are indicated by dashed lines. The error bars represent the standard errors of the means. The rainfall events (Y axis) are spaced based on the days between the events.

5.3.4 Variation of porewater and floodwater DRP following rainfall events and relationship with rainfall characteristics

The interaction between event and depth was not significant for porewater DRP in either of the soils. Further, the porewater DRP concentrations measured at two soil depths were not significantly different in either of the soils. The porewater DRP concentrations measured at different rainfall events from the two soils were not significantly different except during rainfall event 3 for the Pallic soil, which reported significantly ($p<0.05$) higher DRP concentration than the other events. The porewater DRP concentrations from the 2 cm depth varied from 0.65 to 1.03 mg/L and it varied from 0.32 to 0.98 mg/L at the 10 cm depth of the Recent soil across four rainfall events (Fig. 5.3). In the Pallic soil, the porewater DRP concentrations varied from 0.26 to 2.31 mg/L at the 2 cm depth and 0.27 to 1.02 mg/L at the 10 cm depth.

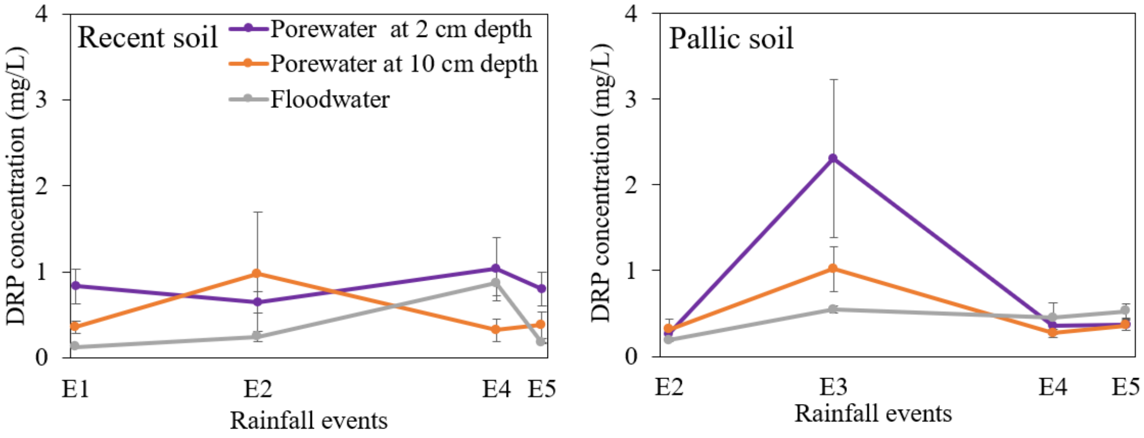


Fig. 5.3 Variations in dissolved reactive phosphorus in porewater at the 2 and 10 cm depths and in floodwater measured from a critical source area on a Recent and Pallic soil across five rainfall events. The error bars represent the standard errors of the means. The rainfall events (Y axis) are spaced based on the number of days between the events.

The floodwater DRP concentrations measured from the two soils were not significantly different among the rainfall events, except in rainfall event 4 in the Recent soil, which was significantly ($p<0.05$) higher than the DRP concentrations measured from the other three rainfall events (Fig. 5.3). The floodwater DRP concentrations during the experimental period varied from 0.13 to 0.87 mg/L and 0.19 to 0.54 mg/L in the Recent and Pallic soils, respectively. The porewater DRP concentrations measured from neither depth of the two soils were significantly correlated with floodwater DRP concentrations (data is not shown).

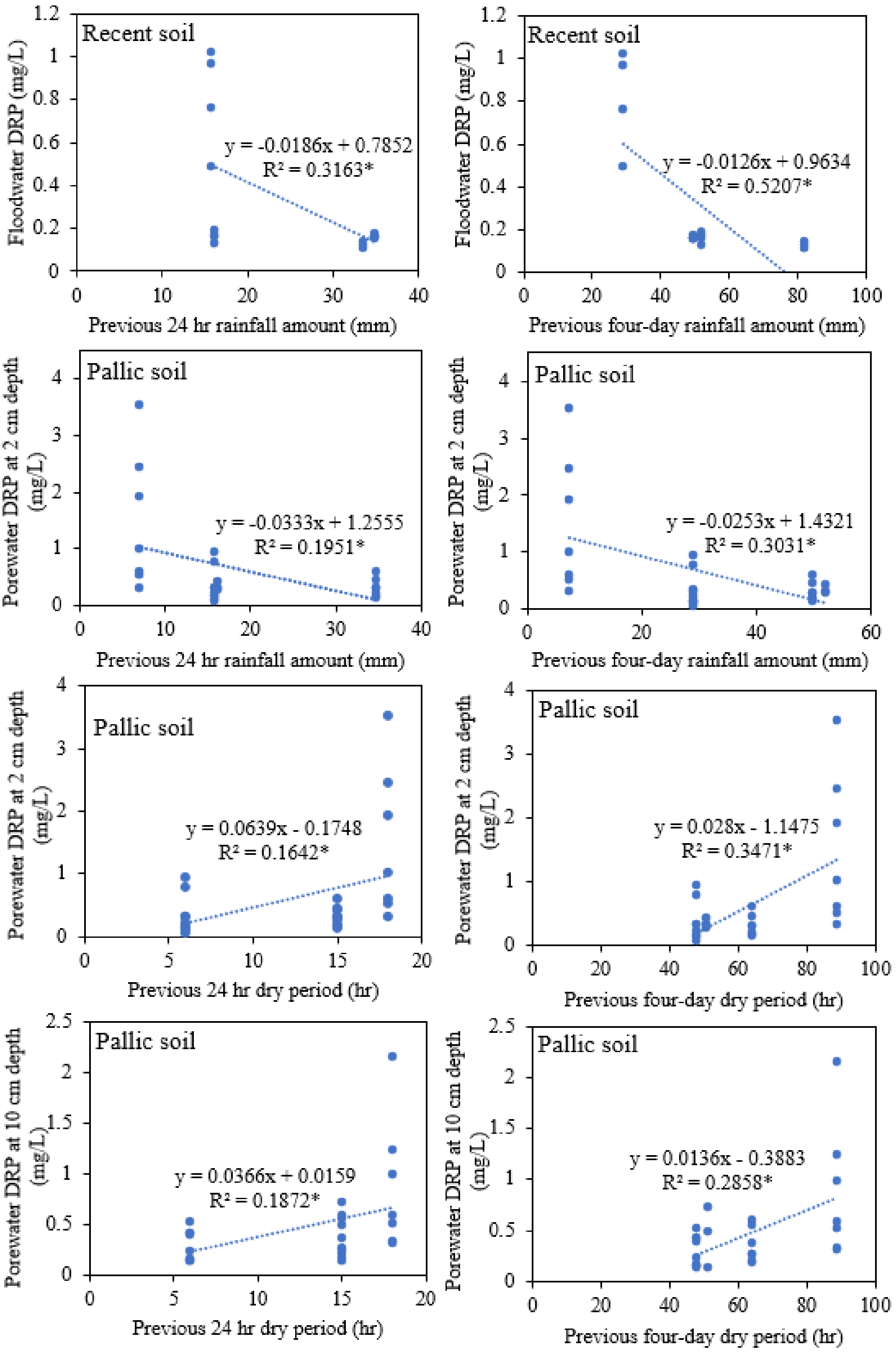


Fig. 5.4 Regression relationships between rainfall characteristics and floodwater DRP of the Recent soil and porewater DRP at the 2 and 10 cm depths of the Pallic soil. * Indicates statistically significant regression (p<0.05) relationships. Statistically non-significant regression relationships are not shown.

The floodwater DRP of the Recent soil showed significant negative relationships (range of $R^2=0.32-0.52$, $p<0.05$) with the previous 24 hr and four-day rainfall amounts (Fig. 5.4). However, the porewater DRP at any of the depths of the Recent soil showed no significant regression relationship with rainfall characteristics. Comparatively, the porewater DRP at the 2 cm depth of the Pallic soil showed significant negative regression relationships (range of $R^2=0.20-0.30$, $p<0.05$) with both previous 24 hr and four-day rainfall amounts, while both depths showed significant positive relationships (range of $R^2=0.16-0.35$, $p<0.05$) with the previous 24 hr and four-day dry periods (Fig. 5.4). The floodwater DRP measured from the Pallic soil did not show a significant relationship with any of the rainfall characteristics. However, since these relationships were derived from only 5 rainfall events out of 36, there is a possibility that they may be biased or not representative of other rainfall events.

5.3.5 Variations in porewater ion concentrations and the relationship with porewater DRP and other parameters

The interaction between event and depth was not significant for any of the porewater cations (Mn, Fe, Ca and Mg) of the two soils. The average porewater Mn, Fe, Ca and Mg concentrations of the 10 cm depth of both the Recent and Pallic soils were 1.9 to 3.9-fold higher compared to that of the 2 cm depth (Fig. 5.5). However, only the Pallic soil showed significant ($p<0.05$) increases in porewater cation concentrations at the 10 cm depth compared to the 2 cm depth, with few exceptions (Fig. 5.5). There was no significant difference in the porewater cations among the events, except the Mg concentration measured in event 2 of the Recent soil, which were significantly ($p<0.05$) higher than the other three events. The Fe concentration measured from the same event for the Pallic soil, was significantly ($p<0.05$) lower than the rest of the events. The porewater NO_3^- concentrations of the two depths of the Recent and Pallic soils were below 2 mg/L and 1 mg/L, respectively (Appendix III, Supplementary Fig. 5.S3).

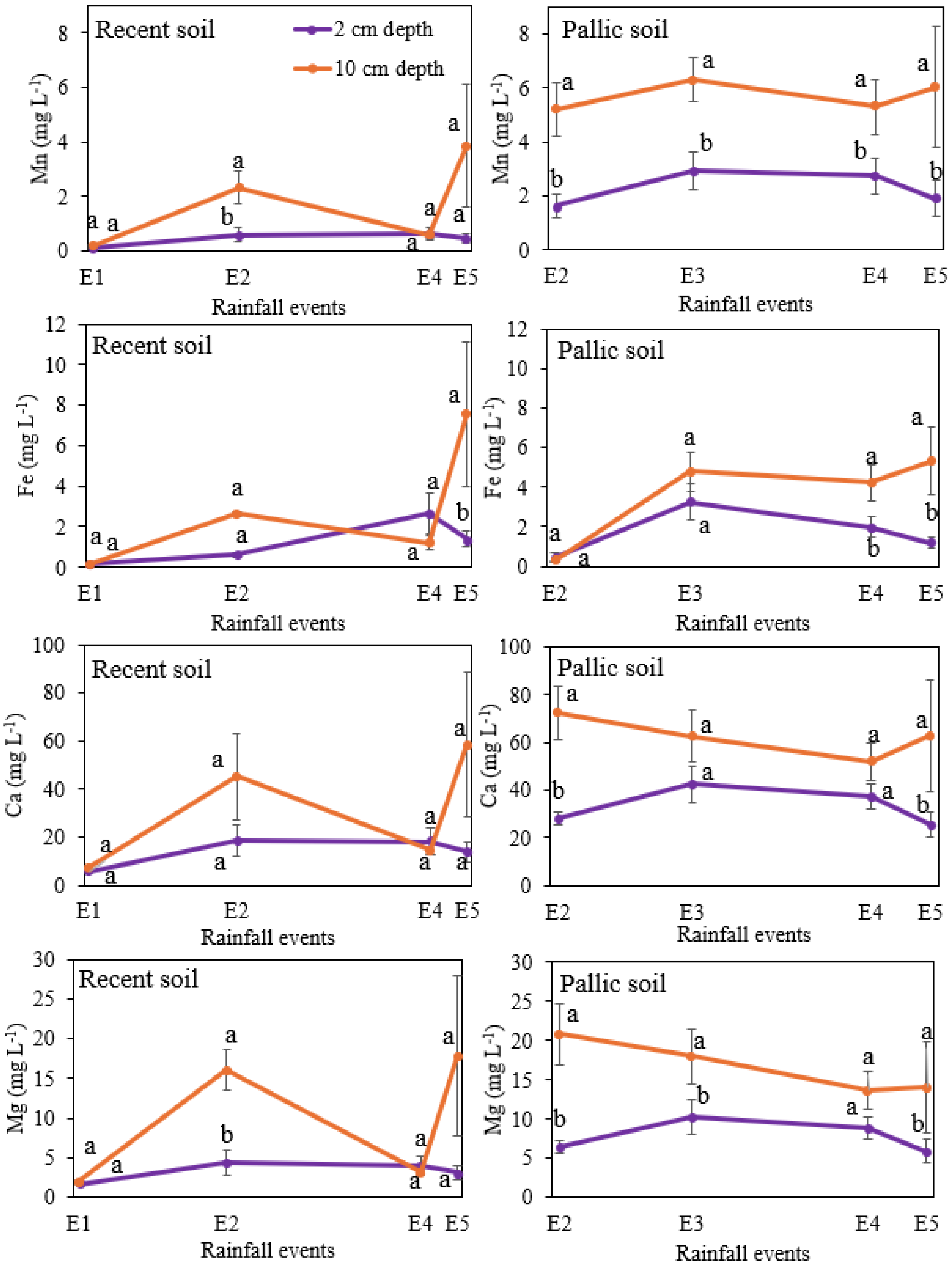


Fig. 5.5 Porewater concentrations of selected cations (Mn, Fe, Ca, and Mg) measured at the 2 cm and 10 cm depths following five rainfall events on the Recent and Pallic soils. The error bars represent the standard errors of the means. Different scales are used for different cation concentrations (Y axis). Significant (*p*<0.05) differences indicate comparison between depths only.

Pearson correlation analysis showed no significant correlation among porewater DRP in the Recent soil (both depths combined) and any of the porewater cation concentrations (Ca, Mg, Mn, Fe) or with DOC, Eh, pH and p*e*+pH (Appendix Ш, Supplementary Table 5.S2). The porewater DRP concentration measured in the Pallic soil (both depths combined) showed significant correlations with only DOC (r=0.41, $p<0.01$) and pH (r=-0.36, $p<0.05$), but not with any of the cations. However, the Pearson correlation analysis conducted for separate depths for the two soils revealed significant positive correlations between porewater Fe concentration and DRP at the 10 cm depth for the Recent soil (r=0.77, $p<0.05$) and porewater DRP at the 2 cm depth for the Pallic soil (r=0.76, $p<0.001$).

5.3.6 Changes in phosphorus fractions

The total water extractable P fraction (H_2O-P) of the Pallic soil (21.2 mg/kg) was slightly higher than the Recent soil (16.8 mg/kg) at the beginning of the experiment. This fraction increased by 1.2-fold at both the 0-2 and 2-8 cm depths and by 0.4-fold at the 8-10 cm depth in the Recent soil towards the end of the experiment (Appendix Ш, Supplementary Fig. 5.S4). The H_2O-P fraction of the Pallic soil remained the same at the 0-2 and 2-8 cm depths and increased by 0.3-fold at the 8-10 cm depth towards the end of the experiment (Appendix Ш, Supplementary Fig. 5.S4). None of these changes were significant.

The labile P fraction (sum of H_2O-P and $NaHCO_3$ extractable P ($NaHCO_3$-P) fractions) in the Recent and Pallic soils ranged from 317-368 mg/kg at the beginning of the experiment (Table 5.2). This fraction increased at all of the three depths in the Recent soil with time, but the changes were significant ($p<0.05$) only at the 2-8 cm depth (Fig. 5.6). In the Pallic soil, the labile P fraction decreased by ~0.3-fold at the 0-2 cm depth, remained unchanged at the 2-8 cm depth and increased by ~0.4-fold at the 8-10 cm depth with time (Fig. 5.6). None of these changes were significant. There were no significant changes in the moderately labile P fractions of the three depths of the Recent and Pallic soils with time (Fig. 5.6).

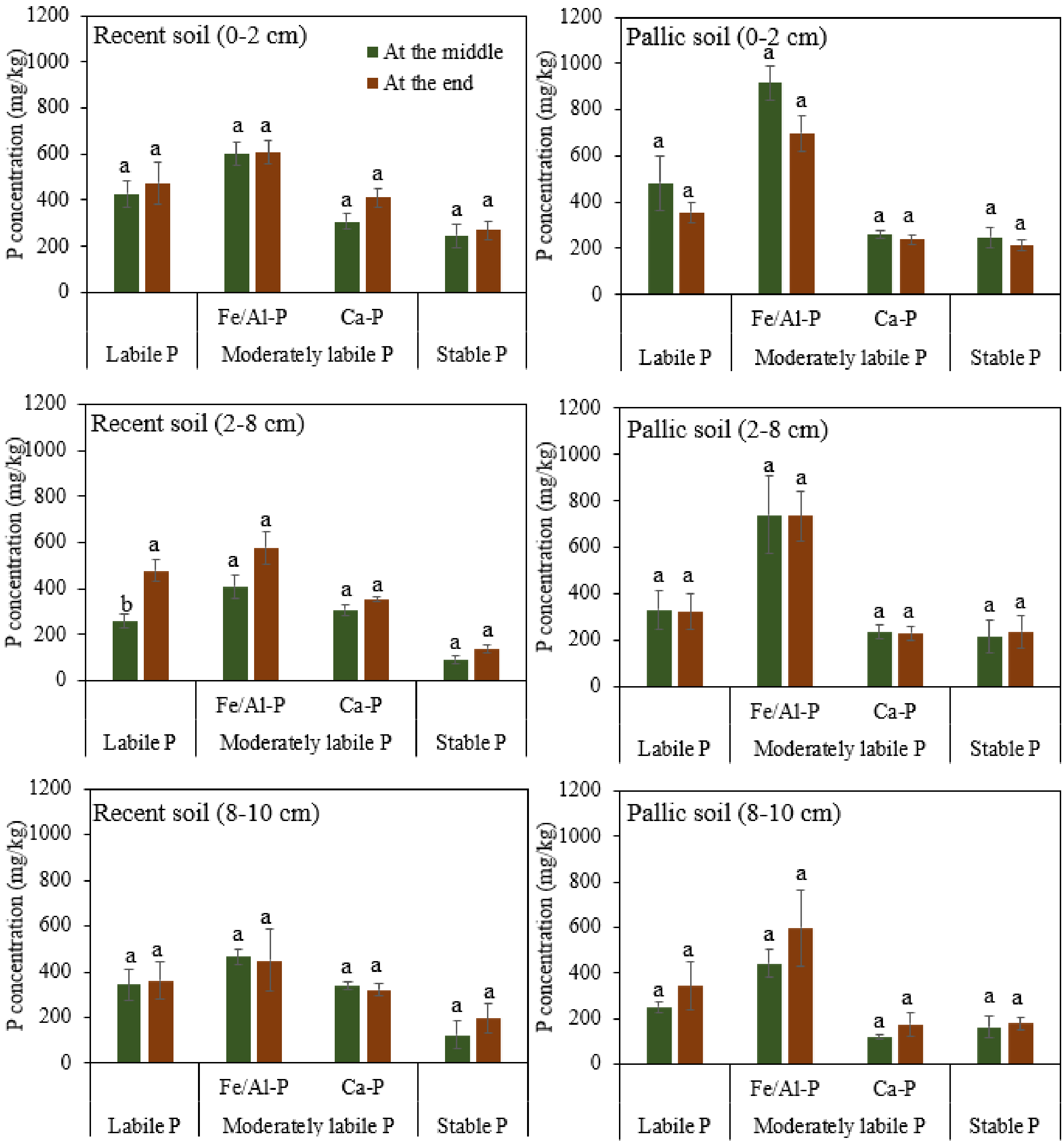


Fig. 5.6 Labile, moderately labile (NaOH extractable P: Fe/Al-P, and HCl extractable P: Ca-P) and stable P fractions of 0-2, 2-8 and 8-10 cm depths of the Recent and Pallic soils at the middle and at the end of the experimental period. The error bars represent the standard errors of the means (n=3).

The total P (sum of all the eight fractions) concentration increased by 0.1 and 0.5-fold at the 0-2 and 2-8 cm depths and remained unchanged at the 8-10 cm depth in the Recent soil, with time (Fig. 5.6). Only the increase in total P concentration at the 2-8 cm depth in the Recent soil was significant (p<0.05). In the Pallic soil, although the changes were not significant, the total P concentration decreased by 0.2-fold at the 0-2 cm depth, remained unchanged at the 2-8 cm depth and increased by 0.3-fold at the 8-10 cm depth over time (Fig. 5.6).

5.3.7 Changes in phosphorus species during rainfall events - thermodynamic modelling

The two depths (2 and 10 cm) of the Recent and Pallic soils were supersaturated with Ca, Mn phosphates, namely FCO_3-Apatite, and $MnHPO_4$, and with several Fe/Al oxy(hydr)oxides namely $Fe(OH)_{2}.7Cl_{0.3}$, goethite, hematite, hercynite, lepidocrocite, magnetite and diaspore in all rainfall events (Table 5.3 and 5.4). In addition, the Pallic soil was supersaturated with hydroxyapatite, siderite, rhodochrosite, $MnCO_3$ and gibbsite in all the rainfall events. The Recent soil was supersaturated with Fe(II) phosphates (vivianite) and carbonates (siderite) and Mn(II) carbonates (rhodochrosite) towards the middle and the end of the experiment (Table 5.3). The Pallic soil was supersaturated with Fe(Ш) oxy(hydr)oxides such as ferrihydrite, maghemite and magnesioferrite only at the 10 cm depth (Table 5.4).

Table 5.3 Saturation indices of P minerals from Visual MINTEQ at the 2 and 10 cm depths in the Recent soil during four rainfall events

	Event 1		Event 2		Event 4		Event 5	
	2 cm depth	10 cm depth	2 cm depth	10 cm depth	2 cm depth	10 cm depth	2 cm depth	10 cm depth
Ca phosphates								
$Ca_3(PO_4)_2$ (β)	X	X	X	0.38	X	X	X	X
FCO_3-Apatite	6.76	5.03	12.92	20.48	11.64	10.12	11.50	17.47
Hydroxyapatite	X	X	2.54	7.40	1.94	1.01	2.22	5.18
Fe/Mn phosphates								
Vivianite (FeII)	X	X	0.99	4.43	2.52	1.13	2.37	4.13
$MnHPO_4$ (MnII)	1.51	1.39	2.11	2.63	2.20	1.90	2.20	2.66
Fe/Mn carbonates								
Siderite (FeII)	X	X	0.20	1.48	0.82	0.29	0.22	1.11
Rhodochrosite (MnII)	X	X	0.62	1.64	0.63	0.46	0.19	1.31
$MnCO_3$ (am)	X	X	0.13	1.16	0.13	X	X	0.82
Fe/Al oxy(hydr)oxides								
$Fe(OH)_{2.7}Cl_{0.3}$	2.14	2.64	2.53	6.02	2.37	3.55	3.11	5.57
Ferrihydrite (FeШ)	X	X	X	2.48	X	0.38	X	1.90
Ferrihydrite (aged)	X	X	X	2.99	X	0.89	X	2.41
Goethite (FeШ)	1.45	1.90	1.93	5.50	1.93	3.28	2.50	4.93
Hematite (FeШ)	5.24	6.14	6.19	13.35	6.23	8.93	7.34	12.19
Hercynite (FeII)	0.47	0.51	4.37	5.67	3.00	5.94	4.62	7.02
Lepidocrocite (FeШ)	1.01	1.46	1.53	5.11	1.34	2.69	2.11	4.53
$Fe_3(OH)_8$ (FeШ, FeII)	X	X	X	4.32	X	X	X	2.88
Maghemite (FeШ)	X	X	X	6.57	X	1.75	0.57	5.42
Magnesioferrite (FeШ)	X	X	X	6.69	X	0.63	X	4.86
Magnetite (FeШ, FeII)	8.50	9.18	10.44	19.47	10.91	13.54	11.89	18.04
$Al(OH)_3$	X	X	0.91	0.61	X	1.47	0.88	1.43
Boehmite	X	X	0.52	0.23	X	1.12	0.49	1.04
Diaspore	0.87	1.00	2.34	2.05	1.39	2.90	2.31	2.87
Gibbsite	X	0.12	1.46	1.16	0.52	2.02	1.43	1.98

X: indicates negative saturation indices

Table 5.4 Saturation indices of P minerals from Visual MINTEQ at the 2 and 10 cm depths in the Pallic soil during four rainfall events

	Event 2		Event 3		Event 4		Event 5	
	2 cm depth	10 cm depth	2 cm depth	10 cm depth	2 cm depth	10 cm depth	2 cm depth	10 cm depth
Ca phosphates								
$Ca_3(PO_4)_2$ (β)	X	X	X	X	X	X	X	X
FCO_3-Apatite	11.61	17.58	15.17	15.94	10.63	12.96	11.50	17.39
Hydroxyapatite	1.95	5.40	3.87	4.16	1.37	2.62	1.87	5.16
Fe/Mn phosphates								
Vivianite (FeII)	X	X	3.17	3.23	1.13	2.22	1.17	3.72
$MnHPO_4$ (MnII)	2.11	2.53	3.19	3.16	2.43	2.55	2.36	2.69
Fe/Mn carbonates								
Siderite (FeII)	0.14	0.12	0.63	0.89	0.40	1.06	0.35	1.47
Rhodochrosite (MnII)	1.05	1.83	1.03	1.44	0.96	1.56	0.97	1.84
$MnCO_3$ (am)	0.57	1.34	0.54	0.96	0.47	1.07	0.49	1.36
Fe/Al oxy(hydr)oxides								
$Fe(OH)_2.7Cl_{0.3}$	2.23	3.79	2.44	4.34	1.71	4.35	1.41	4.68
Ferrihydrite (FeШ)	X	X	X	0.46	X	0.76	X	1.01
Ferrihydrite (aged)	X	0.51	X	0.97	X	1.27	X	1.52
Goethite (FeШ)	1.54	3.03	1.58	3.46	1.03	3.66	0.69	4.04
Hematite (FeШ)	5.42	8.40	5.50	9.26	4.42	9.68	3.72	10.41
Hercynite (FeII)	6.22	3.10	1.73	4.31	3.31	4.92	2.57	5.82
Lepidocrocite (FeШ)	1.14	2.63	1.15	3.02	0.44	3.07	0.29	3.64
$Fe_3(OH)_8$ (FeШ, FeII)	X	X	X	X	X	X	X	1.00
Maghemite (FeШ)	X	1.62	X	2.40	X	2.50	X	3.63
Magnesioferrite (FeШ)	X	1.20	X	1.00	X	1.88	X	2.97
Magnetite (FeШ, FeII)	9.52	12.80	9.80	13.98	8.73	14.73	8.05	16.15
$Al(OH)_3$	1.90	0.19	X	0.63	0.30	0.74	X	0.88
Boehmite	1.51	X	X	0.25	X	0.39	X	0.49
Diaspore	3.33	1.63	0.98	2.06	1.73	2.17	1.40	2.32
Gibbsite	2.45	0.74	0.10	1.18	0.85	1.29	0.51	1.43

X: indicates negative saturation indices

5.4 Discussion

5.4.1 Impact of rainfall characteristics on DRP release

In the present study, the release of dissolved P from the Recent soil was not influenced by rainfall amount or duration. The significant negative regression relationships between floodwater DRP of the Recent soil and previous 24 hr and four-day rainfall amounts (Fig. 5.4) implies the effect of dilution on the floodwater DRP. This may be related to the drainage pattern of the Dairy 1 site having Recent soil. At Dairy 1, floodwater accumulated at the sampling site with time following a rainfall event, which may have diluted the floodwater DRP concentration. The significant negative correlations which existed between the previous 24 hr and four-day rainfall amounts and porewater DRP at the 2 cm depth in the Pallic soil, may be due to a dilution effect. Considering the larger catchment area of the CSA at Dairy 4 (Pallic soil) farm site (~16.6 ha), there is a possibility that a high volume of runoff in floodwater increased lateral waterflow below the soil surface diluting the porewater DRP concentration. However, the same effect of rainfall amount on the porewater DRP of the Pallic soil was not observed at the 10 cm depth. Further, floodwater DRP of the Pallic soil did not significantly correlate with any of the tested rainfall characteristics. In contrast with the Dairy 1 CSA site, floodwater at Dairy 4 (Pallic soil) drained off quickly following rainfall. The tile drainage system underlaying subsurface soil and slope on this CSA might have also aided the draining of runoff in this site (Table 5.1). The significant positive regression relationships between the porewater DRP measured on the Pallic soil in the previous 24 hr and four-day dry period (Fig. 5.4) may be due to the concentration of the released dissolved P in the soil pore spaces. Previous simulated rainfall studies have revealed positive relationships between DRP in runoff and rainfall intensity in different soils including mesic Aquic Fragiudalfs (Kleinman et al., 2006) and mesic Typic Hapludults (Shigaki et al., 2007), which is the opposite to findings of the present study. However, it is likely that the effect of rainfall characteristics on the porewater and floodwater DRP may have been influenced by other factors in this case, such as hydrology and landscape position (Buda et al., 2009).

5.4.2 Effect of overall redox status on DRP release

Although previous laboratory incubation studies with soil monoliths on pH, Eh, p*e*+pH variations under submergence of various soils observed significant correlations/linear relationships between those parameters and porewater DRP (Vitharana et al., 2021;

Weerasekara et al., 2021), significant correlations between those parameters and porewater DRP were not observed in this experiment, except for pH in the Pallic soil (Appendix Ш, Supplementary Table 5.S2). A glasshouse study (discussed in Chapter 4), using the same two soils from the same catchment revealed significant negative correlations (r=-0.32 to -0.53, $p<0.01$) among porewater DRP and Eh and p*e*+pH. The complex field conditions and soil heterogeneity resulting in a contribution of different sources for DRP and dilution effect, may be one reason for the lack of significant correlation between porewater DRP and these parameters. The Eh values below 33 mV and the p*e*+pH values below 8.2 imply that Mn and Fe reduction has already begun in these two soils. The increasing porewater Mn and Fe concentrations measured in the two soils with time, suggested the reductive dissolution of Fe and Mn minerals (Fig. 5.5). Similarly, this was evident via significant ($p<0{,}05$) correlations among Eh, porewater DRP, Fe and Mn concentrations in previous incubation studies conducted under submergence (Amarawansha et al., 2015; Kumaragamage et al., 2020). The P release occurred through soil biogeochemical transformations and its relationship to soil pH and Eh may have been masked by the dilution effect (McDowell et al., 2001; McDowell et al., 2004) from rainfall under field condition.

5.4.3 Risk of P release from the Recent and Pallic soils

Both the Recent and Pallic soils released DRP to porewater at both the 2 and 10 cm depths. There can be a diffusion of DRP from porewater to overlying floodwater of the two soils as there is a concentration gradient where the porewater concentrations of the soils were 1.5 to 1.9-fold higher than the floodwater DRP concentrations. Floodwater DRP depends on both DRP release from porewater and efficient diffusion of dissolved P to overlying floodwater (Kumaragamage et al., 2000). A glasshouse experiment conducted using field soil blocks of these same two soils demonstrated significant positive correlations (r=0.49-0.66, $p<0.01$) between porewater DRP measured at the 2 and 10 cm depths with overlying pondwater under submergence (Chapter 4). However, since the glasshouse experiment had stagnated overlying water which did not represent the constantly flowing water observed in this field study, the results/observations from the glasshouse study cannot be directly related to this current field study. The reason for not observing significant correlations between porewater DRP and floodwater DRP from the two soils during submergence, may be because of other factors influencing floodwater DRP. For example, floodwater DRP concentrations could be the result of upslope sources of P and may not be related to porewater DRP concentrations or the diffusion of porewater DRP to overlying floodwater may have been diluted due to the large volume of runoff flowing through the CSA. However, the stagnated floodwater following a rainfall event at the Dairy 1 farm site (Recent soil) may have given the necessary/more time for DRP diffusion to overlying floodwater, compared to the Pallic soil.

The average floodwater DRP concentrations of the Recent and Pallic soils were 35 and 43-fold higher than the targeted DRP concentration (0.01 mg/L) for the Manawatū River (lower Manawatū sub zone) declared by the Manawatū-Wanganui Regional Council (One Plan, 2024). Considering the proximity of the two CSAs to freshwater bodies; ~100 m (Recent soil) and ~500 m (Pallic soil), the elevated floodwater concentrations pose eutrophication risk. For example, minor increases in P even at picomolar concentrations can potentially stimulate algal production under the right conditions (Hudson et al., 2000) and dissolved P can be absorbed quickly (Barlow-Busch et al., 2006). The floodwater from the CSA located at Dairy 1 farm (Recent soil) is directly connected to the Manawatū River, while the floodwater from the other CSA (Pallic soil) connects to the Manawatū River via two other streams/rivers (Table 5.1). Due to its proximity to the Manawatū River, there is a possibility of ground water table rise in the Dairy 1 CSA site, especially during winter. This could lead to associated P release due to redox induced processes. Therefore, although both soils showed a similar magnitude of risk of releasing DRP from soils, DRP release from the Recent soil to floodwater is riskier in this case. However, the ultimate magnitude of DRP concentration which passes to a water body will depend on flow path length (McDowell and Sharpley, 2002; Doody et al., 2006), dilution (Shigaki et al., 2007), and landscape processes such as land use practices (Sharpley et al., 2002).

The H_2O-P fraction is important not only within the topsoil but also the subsoil layers. This is because, water infiltrates the soil following rainfall, then percolates and from there, can be subject to lateral movement according to slope gradient (Tarboton, 2003). Therefore, H_2O-P in both the surface and subsoil depths can easily be mobilised by runoff following a rainfall event. An increasing H_2O-P and labile P fraction at all depths in the Recent soil with time, confirmed that the Recent soil was more susceptible to P release upon submergence in this study. However, attention must be paid to the increasing H_2O-P concentration in the 8-10 cm depth of the Pallic soil, as subsurface loss of DRP can still have significant impacts on freshwater quality, especially when the soil P sorption capacity is low (King et al., 2015), which is not the case for the Pallic soil.

Apart from the P release from soils, several other sources are likely to have contributed to elevated DRP concentrations in floodwater in this study. For example, P sources such as organic manure (McDowell et al., 2004; McDowell et al., 2007), unutilised inorganic fertilisers (Hart et al., 2004), and effluent spray in the upper catchment areas (Che et al., 2022) can be mobilised in runoff during rainfall events. Application of effluent at Dairy 4 (Pallic soil) in the upper catchment, might have contributed to the floodwater DRP concentrations measured in the current study. In contrast, soil properties such as degree of P saturation affects P loss risk from soil (Pradhan et al., 2021). In this experiment, the Recent soil reported low ASC and low concentrations of oxalate extractable Fe and Al compared to the Pallic soil (Table 5.2), further implying a higher risk of P loss from this soil.

5.4.4 Mechanisms of P release

The major P releasing mechanism for the two soils is most likely to be reductive dissolution of Mn and Fe oxy(hydr)oxides and subsequent release of P. High porewater DOC and low NO_3^- concentrations, together with moderate air temperature (>12 ºC) also implied the possibility of reductive dissolution of Mn and Fe minerals as recorded previously (Smith et al., 2021). This was supported by severe reduced status in soils, with low Eh values (<33 mV) and elevated porewater Mn and Fe concentrations (Fig. 5.5). In neutral soils (pH=7), Mn(IV) ions reduce to Mn(II) ions within the redox range of 200 to 100 mV, and Fe(Ш) ions reduce to Fe(II) ions within the redox range of 0 to -100 mV (Marschner, 2021). Supersaturation of both Recent and Pallic soils with Fe(II) and Mn(II) phosphates towards the middle and the end of the experiment and undersaturation of soil solution with several Fe(III) oxy(hydr)oxides (ferrihydrite, maghemite, $Fe_3(OH)_8$, magnesioferrite) throughout the experiment (Tables 5.3 and 5.4), suggested that the reductive dissolution of Fe(Ш) and Mn(IV)/Mn(Ш) minerals may have occurred, potentially contributing to P associated with them. Previous studies reported significant correlations between porewater Mn and Fe with porewater DRP (Smith et al., 2021a; Amarawansha et al., 2015). Although significant correlations between porewater Mn and DRP were not observed for any of the soils in this study, significant correlations with porewater Fe concentrations were observed for porewater DRP from the 10 cm depth for the Recent soil (r=0.77, $p<0.05$) and the 2 cm depth for the Pallic soil (r=0.76, $p<0.001$). Elevated porewater Mn and Fe concentrations do not necessarily represent reduced Fe(Ш)-P and Mn(IV)/Mn(Ш)-P minerals. In contrary, significant changes in the Fe/Al-P fraction during the experiment in any of the soils were not observed, probably because the changes occurred in those P fractions were not great enough to detect by the P fractionation procedure (Attanayake et al., 2022) or due to the short time frame of the experiment (~2 months).It is possible that dissolution of Ca and Mg phosphates contributed to the porewater DRP elevation in these soils, as suggested by the increasing porewater Ca and Mg concentrations (Fig 5.5). However, the fractionation analysis did not show any significant decreases in Ca-P fraction with time, in any of the soils corresponding to dissolution of Ca-P.

5.5. Limitations and implications for P management in CSAs

Several factors were uncontrollable in this study given the nature of a field experiment. For example, although elevated floodwater DRP concentrations were reported for both soils in this experiment, DRP release from soils were not the sole source of P in floodwater, as there could have been contributions from other sources such as organic manure, inorganic fertiliser and effluent. Although the DRP release from the 2 cm depth was reported, under field conditions, this depth can be slightly variable due to depositions with runoff or the erosion of the surface soil layer. Although a considerable number of studies have been conducted under simulated rainfall conditions at the field and laboratory scale, limited studies have been conducted in actual field conditions to quantify DRP loss from CSAs under natural rainfall. The associated complexity due to combining numerous factors such as soil heterogeneity, landscape, hydrology, and climate, made it difficult to detect significant correlations between factors affecting DRP release. Therefore, field data should be combined with laboratory or controlled environment studies to help explain the processes of DRP loss.

This current study revealed both Recent and Pallic soils release DRP to porewater upon submergence, following intermittent rainfall, mainly due to the reductive dissolution of Mn and Fe oxy(hydr)oxides. Elevated DRP concentrations were recorded in floodwater collected from two CSAs in close proximity to the Manawatū River. Further, the effect of rainfall characteristics such as intensity and duration can be masked by other factors such as hydrology, and landscape position under field conditions. The method established in this study to measure changes in soil porewater P and redox conditions within CSAs under submergence can be used to monitor similar changes in other high-risk CSAs in the future. Further, the study has enhanced current understanding of the mechanisms of P release under short-term submergence of CSAs. This knowledge can be further extended to identifying and verifying P species using advanced techniques, such as X-ray absorption near-edge structure (XANES) spectroscopy (Palihakkara et al., 2024). Future research should be focused on mitigating P loss from these CSAs during periods of high-risk for surface runoff, such as during winter. This study highlighted the occurrence of redox-induced P release from CSAs during short-term submergence; therefore, future research should investigate the effect of seasonal variations in soil nitrate abundance on P release, to develop targeted P management strategies.

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Chapter 6

General Discussion

6.1 Introduction

Phosphorus (P) dynamics in soil under submerged anaerobic condition differs from that of an aerobic condition. Submergence generally leads to soil P release due to complex hydrological and biogeochemical reactions and this depends on inherent soil characteristics (Jayarathne et al., 2016; Dharmakeerthi et al., 2019; Palihakkara et al., 2024). Hence, efficient management of soil P in crop and pasture land use under submergence is challenging. The objective of this thesis was to investigate soil P dynamics under two submergence scenarios, focusing on enhancing P availability for plants and mitigating P loss from the soil. In this thesis, P release from tropical soils under long-term (>2-3 continuous months) submergence was studied, aiming to gather in-depth knowledge associated with inconsistent rice yield response to added inorganic P fertilisers in paddy soils with contrasting soil properties in Sri Lanka (Chapter 3). Further, P release from temperate pasture soils in critical source areas (CSAs) under short-term (hours to few days) submergence was also studied to investigate the potential of soils with contrasting soil properties to release P upon temporary submergence experienced during rainfall events under simulated and field conditions in New Zealand (Chapters 4 and 5).

This chapter aims to synthesise the findings of these studies (Chapters 3, 4 and 5) and compare P release from tropical and temperate soils under both long-term and short-term submergence. It also explores the implications of these findings for broader P management practices and highlights opportunities for future research in this area.

6.2 Current understanding

Short-term (< 2 ½ years) and long-term (> 2 ½ years) yield response studies have reported inconsistent rice yield responses to applied P fertilisers in paddy soils in Sri Lanka and this inconsistency cannot be adequately explained by soil available P (eg: Olsen P), irrigation schemes, soil texture, pH, electrical conductivity, total carbon content, and available iron and magnesium concentrations (Kendaragama et al., 2003; Sirisena et al., 2013; Kulasekara et al., 2020). Prior to the current study in this thesis, there was no mechanistic understanding of the changes in P species of paddy soils under submergence and different management practices (eg: fertiliser application). This knowledge is important for making site specific P fertiliser recommendations for rice cultivation in Sri Lanka and for understanding the potential for P build up and P release in paddy soils.

A significant number of research studies have been undertaken to quantify P loss from agricultural catchments in New Zealand over the last decade. These studies encompass various methods of P loss assessments, including the evaluation of dissolved P losses via surface, subsurface runoff, and leaching from contrasting soils in laboratory experiments (Smith et al., 2021; Smith et al., 2023), simulated rainfall studies (Simmonds et al., 2017), and field studies (Gray et al., 2022; McDowell and Smith, 2023). While Smith et al. (2021) demonstrated the release of dissolved P from subsoil (below 20 cm) of a Melanic Orthic Gley soil under field conditions in New Zealand, there has been no research on the potential of different surface soils to release dissolved P upon short-term but frequent submergence during storm events in agricultural features, such as CSAs, in New Zealand. Given that CSAs represent relatively small fractions of farm land area yet account for a disproportionate quantity of P loss, it becomes evident that there is a critical gap in understanding that warrants urgent attention and investigation.

6.3 Comparison of phosphorus release from submerged tropical and temperate soils

The selected soil types of Sri Lanka and New Zealand examined in this thesis had contrasting physico-chemical characteristics (Table 6.1). The soils from the two countries were also different in terms of land use, climate, management, and submergence purpose and duration. The three soil types (Ultisol, Alfisol and Entisol soils) from Sri Lanka selected for sample collection were from long-term (>20 years) paddy fields in a region characterised by a tropical climate. Farmers in Sri Lanka generally grow rice in paddy soils twice a year (*Maha* season: October-January, *Yala* season: May-September). These soils are generally submerged for periods lasting 4-6 months per year (2-3 months per season). Comparatively, the soils selected from New Zealand were from grazed pastoral farms with long-term (>5 years) ryegrass/white clover pasture mixture (Recent and Pallic soils) and with ryegrass, white clover and browntop mixture (Allophanic soil). These soils are from a temperate region. Unlike in paddy cultivation where submergence is created artificially, the New Zealand soils experience natural, relatively short-term (hours to a few days) submergence due to intermittent rainfall events, most commonly occurring during winter.

Table 6.1 Selected initial soil physico-chemical characteristics of the contrasting soils from Sri Lanka and New Zealand representing tropical and temperate regions

Local soil classification	Soil order (USDA classification)	Textural class	pH	Olsen P (mg/kg)	Fe oxalate (g/kg)	Al oxalate (g/kg)	P sorption capacity (%)	Ca (mg/kg)	Mg (mg/kg)	OC (g/kg)	CEC (cmol$_{(+)}$/kg)
Sri Lanka											
Reddish Brown Latosol	Ultisol	Sandy loam	6.8	26	340	22.6	56	1016	296	7.7	8.8
Reddish Brown Earth	Alfisol	Sandy clay loam	7.1	65	250	22.1	55	1525	206	9.8	8.0
Non-Calcic Brown	Entisol	Sand	6.2	3	86	9.7	60	405	16	3.6	3.0
New Zealand											
Recent soil	Entisol	Loam	6.5	50	3.2	0.7	19	900	124	20.0	12
Pallic soil	Alfisol	Silty clay loam	5.8	55	4.9	1.2	29	1458	213	47.0	22
Allophanic soil	Andisol	Silty clay loam	5.9	38	6.0	6.5	56	1851	257	82.0	23

Results obtained from Chapters 3 and 4. Olsen P, Ca and Mg concentrations of the Recent, Pallic and Allophanic soils were converted from the unit of mg/L to mg/kg by assuming the bulk densities of the three soils as 1.37, 1.19 and 0.84 g/cm^3, respectively. Fe oxalate: ion extracted by 0.1 M acid ammonium oxalate (pH =3); Al oxalate: aluminum extracted by 0.1 M acid ammonium oxalate (pH =3). Ca and Mg: Mehlich-3 extractable calcium and magnesium ions. P: phosphorus. OC: organic carbon. CEC: Cation exchange capacity

Phosphorus release from soils during submergence were different in soils from the two countries. The P fertiliser (triple superphosphate: TSP and single superphosphate: SPP) applied to the Ultisol, Alfisol and Entisol soils of Sri Lanka showed significantly (p<0.05) higher (1.1-8.0 mg/L) DRP concentrations compared to unfertilised soils only up to one week after P application. About 3 weeks after P application, the DRP concentration in all soils remained low, ranging from below the detection limit (0.024) to 0.300 mg/L. Results from the control soils (no fertiliser application) indicated that there was a slight P release (0.03-0.09 mg/L) upon submergence, and the addition of P did not significantly increase DRP in these soils. Application of urea did not affect P release from paddy soils. Comparatively, the New Zealand glasshouse experiment indicated that during short-term submergence due to simulated rainfall events, the Recent soils released P to pondwater, whereas the Pallic and Allophanic soils did not. Although the Pallic soil released soil P to soil porewater, the extent of P release was not adequate to increase the P concentration in the overlying pondwater. The Allophanic soil acted as a sink for P due to the greater sorption capacity of the soil. Similarly, under field conditions with intermittent rainfall events, both the Recent and Pallic soils released porewater P, while the floodwater concentrations of the two soils were 0.13 to 0.87 and 0.19 to 0.54 mg/L, respectively.

6.4 Key findings

In topical soils, irrespective of different initial Olsen P concentrations (3-65 mg/kg) of the three paddy soils, there was no significant increase in porewater DRP concentrations in soils that had P fertiliser applied compared to control soils throughout the submergence, except immediately after the P fertiliser application. This result supported the previous findings that the inconsistent rice yield response could not be explained by Olsen P concentrations in rice paddy soils in Sri Lanka (Sirisena et al., 2013; Kulasekara et al., 2020). Urea application did not delay P release from paddy soils, probably due to the time of urea application. The fertiliser applied to Alfisols (both TSP and SSP) and Entisols (only SSP) maintained at least the critical concentration of soil solution P concentration needed for rice growth (0.1 mg/L) throughout the submergence. Comparatively, Ultisols failed to maintain this critical level even when P fertilisers were applied. These observations together with P fractionation data and modelling revealed that the released/dissolved P was resorbed to abundantly available Fe and Al oxy(hydr)oxides surfaces and/or clay minerals, and also precipitated as Ca minerals. Thus, there has been an enhancement in the understanding of the dynamics of applied P and/or released P from submerged paddy soils. A high concentration of amorphous Fe and Al concentrations (6 to 16-fold higher on average, compared to soils tested in New Zealand) were recorded in paddy soils of Sri Lanka (Table 6.1), supporting the observed significant P sorption in the soils and low dissolved P in soils. It was also found that there was a downward movement of P from soils with surface applied P fertilisers and transformation of those P to the moderately labile P pool in subsurface soils, which is likely accessible to rice plants over the longer term. Tapping P from the labile pool may be one reason for not seeing a yield drop when P fertiliser was omitted for several seasons in previous studies (Sirisena et al., 2013).

In the New Zealand glasshouse and field studies, both Recent and Pallic soils released P to porewater upon short-term (hours to 3 days) submergence. The non-significant difference in DRP release from the 2 and 10 cm depths indicated the importance of subsoils in terms of P loss from submerged soils. This finding is aligned with previous research on Melanic Orthic Gley soils which highlighted the capacity for DRP release from subsoil (Smith et al., 2021). This present study has found that the Recent soil diffused DRP to floodwater, increasing the floodwater DRP concentration significantly ($p<0.05$), while the Pallic soils did not change floodwater DRP with time. Under field conditions, the Recent and Pallic soils reported elevated floodwater DRP concentrations which were 35 and 43-fold higher than the targeted DRP concentration (0.01 mg/L) for the Manawatū River. Although other factors such as P contribution from the upstream catchment, rainfall volume and path length affect the amount of dissolved P transported to freshwater bodies, the proximity of the two CSA sites to the Manawatū River (especially Recent soil CSA) together with the elevated DRP concentrations, indicated risk of P contamination to the freshwater bodies. Under field conditions, following intermittent rainfall, reductive dissolution of Fe and Mn P minerals and oxy(hydr)oxides contributed to P release in the Recent and Pallic soils. Compared to the glasshouse experiment, the absence of significant correlations with parameters such as Eh, p*e*+pH and porewater cations under field conditions imply the complexity/contribution of uncontrolled factors such as field hydrology and landscape position on P release under natural conditions and highlight the importance of controlled experiments (eg: glasshouse experiment) to develop a mechanistic understanding of the P release from soils. The glasshouse experiment further highlighted the potential use of Allophanic soil as a P sorbing material in CSAs.

6.5 Implications and future directions

The incubation study conducted for paddy soils in Sri Lanka is the first study to develop a mechanistic understanding of the dynamics of applied P fertilisers in submerged paddy soils. Building upon this study as a baseline for understanding the inconsistent yield response of rice to added P fertilisers in Sri Lanka, future research can investigate rice plants and rhizosphere soils to uncover the impact of the unique micro-environment of the rice plant rhizosphere. Future studies should focus on analysing dissolved P both in overlying water and porewater in rice plant systems to get a full picture of the transformation of P in applied fertilisers. This will help to elucidate the mechanisms behind P release from soils during submergence to identify strategies for maintaining consistent rice yields even without fertiliser application in alternative seasons. The use of advanced techniques such as X-ray absorption near-edge structure spectroscopy (XANES) would validate the gathered results and improve the current understanding of the changes of P species under submergence. Further, this research could be expanded to develop more effective P management strategies for paddy soils, such as developing strategies to tap P in the moderately labile P pools, and thereby develop efficient P fertiliser recommendations/reducing P fertiliser input without affecting rice yield and introducing slow-release P fertilisers for rice cultivation. Furthermore, future studies could explore replacing the Olsen P test, which extracts P under high pH (8.5) conditions compared to lower field pH common under submergence, using an alternative test such as the Resin P test.

Together with the glasshouse study, the field study conducted in New Zealand revealed the potential of short-term submerged CSA soils to release DRP to porewater and floodwater. The CSAs serve as significant nutrient hotspots, inherently connected to the hydrological networks of waterways. In addition, the findings in the present study reveal that CSAs themselves act as sources of P, possibly releasing DRP into overlying water along the P transport pathway to waterways, which is alarming. The results indicate that the Pallic soil released P into porewater, and to a certain extent, it also resorbed P from porewater. This suggests that, considering the locations of CSAs along P transport pathways, some soils may eventually saturate their P sorption sites, especially those with medium P sorption capacities, potentially leading to P release over time. The method developed in this study can be applied at a farm-scale to identify CSAs with potential risk of P release upon short-term submergence specially for soils with less than 30% anion sorption capacity. Since the CSAs occupy a relatively small fraction of the farm area (~20% of the farm area), once identified as potential risk sites, targeted mitigation measures can be applied to CSAs in a more cost-effective way. In line with previous research, the present study also suggests Allophanic soils are less likely to release dissolved P under submergence, owing to the presence of P sorbing Al. Furthermore, the method developed in this study can be applied to assess DRP release from soils in similar temporary water logging situations such as in detainment bunds and constructed wetlands. The field study implied the importance of considering other factors such as hydrology, landscape position and proximity to freshwater bodies in assessing potential risk of CSAs in terms of P release upon short-term intermittent rainfall experienced specially during the winter season. This study has developed a robust method which can be used in future research to measure P release associated with redox changes across a wider range of CSAs during rainfall events. A future study, with replicated CSAs within the same soil type and across several seasons would generate more insights on P transformation in soils within CSAs. Future studies should also focus on exploring dissolved P release of soils with intermediate anion storage capacity (30-60%). As previously mentioned, using advanced techniques such as XANES would be helpful to validate the changes in P species in CSA soils under short-term submergence in future studies.

According to the current findings, porewater nutrient concentrations of P, Ca, Fe and Mg were elevated during short-term submergence of CSAs, suggesting fertilisation of CSA sites or potentially saturated sites within farms could be precision managed to avoid/reduce nutrient losses. However, application of N fertilisers in these CSA areas could be beneficial in terms of reducing dissolved P losses during rainfall events, but this requires further research at a field-scale. Further, particularly in the Recent soil, since a loss of organic fraction was demonstrated along with dissolved P loss, it could affect the retention of cations such as Ca and Mg and thereby affect other related soil properties such as pH and cation exchange capacity, with time. However, this matter should be further investigated using replicated field study sites.

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Appendix I

Supplementary Materials-Chapter 3

Phosphorus release and transformations in contrasting tropical paddy soils under fertiliser application

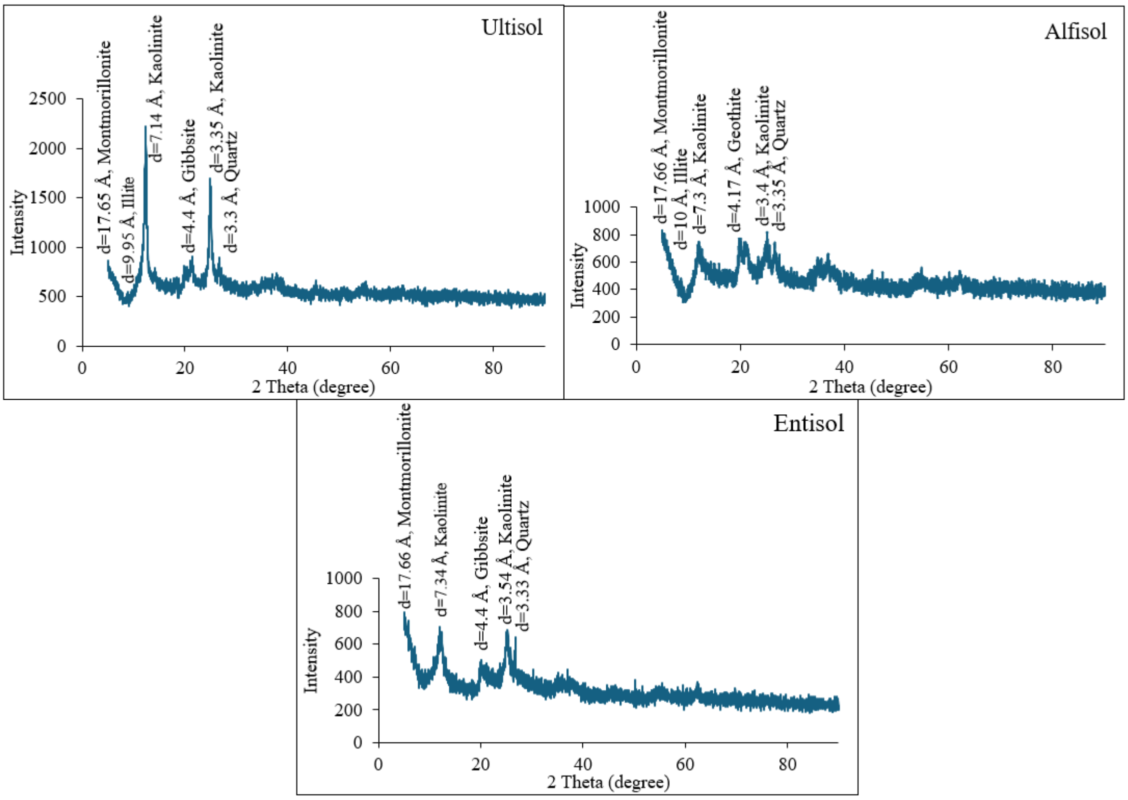

Fig. 3.S1 X-ray diffraction patterns of the clay fraction of Ultisol, Alfisol and Entisol soils

Table 3.S1 Statistical analysis results for porewater pH of three soils with treatments and days after submergence

Effect	DF	F Value	Pr > F
Soil	2	122.48	<.0001
N Trt	1	1.43	0.2397
Soil * N Trt	2	1.87	0.1686
P Trt	2	0.09	0.9154
Soil * P Trt	4	0.35	0.8440
N Trt * P Trt	2	3.82	0.0313
Soil * N Trt * P Trt	4	3.30	0.0210
DAS	12	753.13	<.0001
Soil * DAS	24	28.12	<.0001
N Trt * DAS	12	2.61	0.0065
Soil * N Trt * DAS	24	1.35	0.1577
P Trt * DAS	24	3.15	<.0001
Soil * P Trt * DAS	48	2.00	0.0009
N Trt * P Trt * DAS	24	2.59	0.0005
Soil * N Trt * P Trt * DAS	48	2.31	<.0001

The main effects and interaction between factors; Soil, N fertiliser treatments (N Trt), P fertiliser treatments (P Trt), DAS, Soil * N Trt, Soil * P Trt, Soil * DAS, Soil * N Trt * P Trt, Soil * N Trt * DAS, N Trt * P Trt, N Trt * DAS, P Trt * DAS, N Trt * P Trt * DAS, Soil * N Trt * P Trt * DAS

Table 3.S2 Statistical analysis results for porewater DRP of three soils with treatments and days after submergence

Effect	DF	F Value	Pr > F
Soil	2	2.06	0.1422
N Trt	1	1.66	0.2053
P Trt	2	12.59	<.0001
DAS	12	37.49	<.0001
Soil * N Trt	2	0.07	0.9365
Soil * P Trt	4	1.44	0.2412
Soil * DAS	24	1.83	0.0102
Soil * N Trt * P Trt	4	0.22	0.9241
Soil * N Trt * DAS	24	0.18	1
N Trt * P Trt	2	3.08	0.0582
N Trt * DAS	12	1.2	0.2792
P Trt * DAS	24	11.75	<.0001
N Trt * P Trt * DAS	24	2.65	<.0001
Soil * N Trt * P Trt * DAS	96	1.24	0.0781

The main effects and interaction between factors; Soil, N fertiliser treatments (N Trt), P fertiliser treatments (P Trt), Days after submergence (DAS)

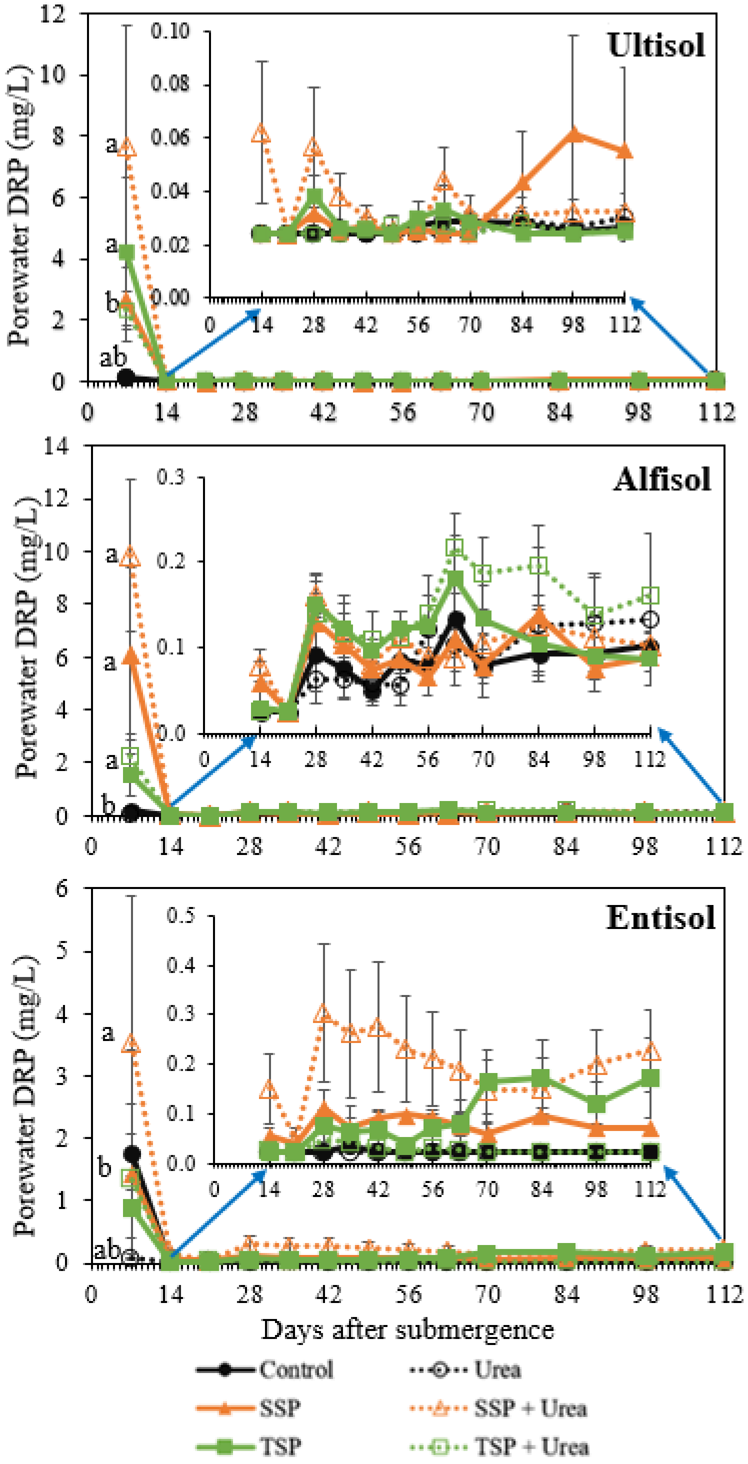

Fig. 3.S2 Variation of dissolved reactive phosphorus in porewater during submergence of the three soils with all the treatments. Mean values of the three replicates of each P fertiliser treatment ± standard error of means are shown in the graphs, SSP: Single superphosphate, TSP: Triple superphosphate

Table 3.S3 Correlations among porewater DRP, Fe, Mn, Ca, Mg, pH, and Eh

Correlations							
	DRP	Fe	Mn	Ca	Mg	pH	Eh
DRP	1	-.078	.071	.452**	.101	-.023	.350**
Fe	-.078	1	.519**	-.311**	-.491**	.557**	-.176**
Mn	.071	.519**	1	.325**	.512**	.912**	-.245**
Ca	.452**	-.311**	.325**	1	.451**	-.439**	.509**
Mg	.101	-.491**	.512**	.451**	1	-.573**	.603**
pH	-.023	.557**	.912**	-.439**	-.573**	1	.301**
Eh	.350**	-.176**	-.245**	.509**	.603**	.301**	1

**. Correlation is significant at the 0.01 level

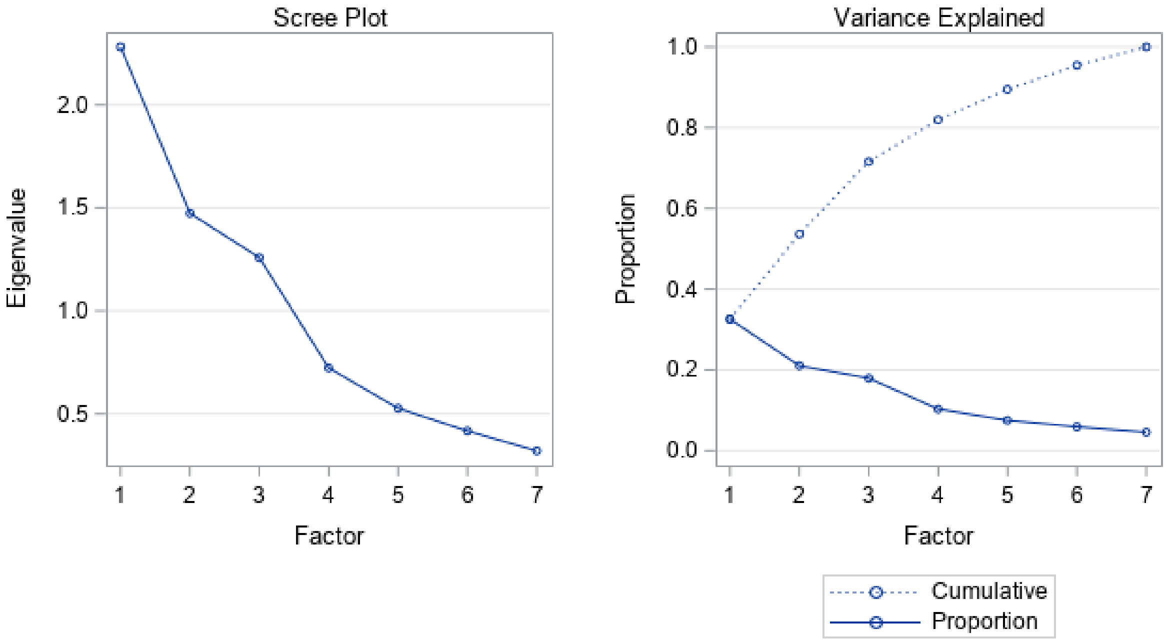

Fig. 3.S3 The scree plot and proportion of variance explained by the principal components

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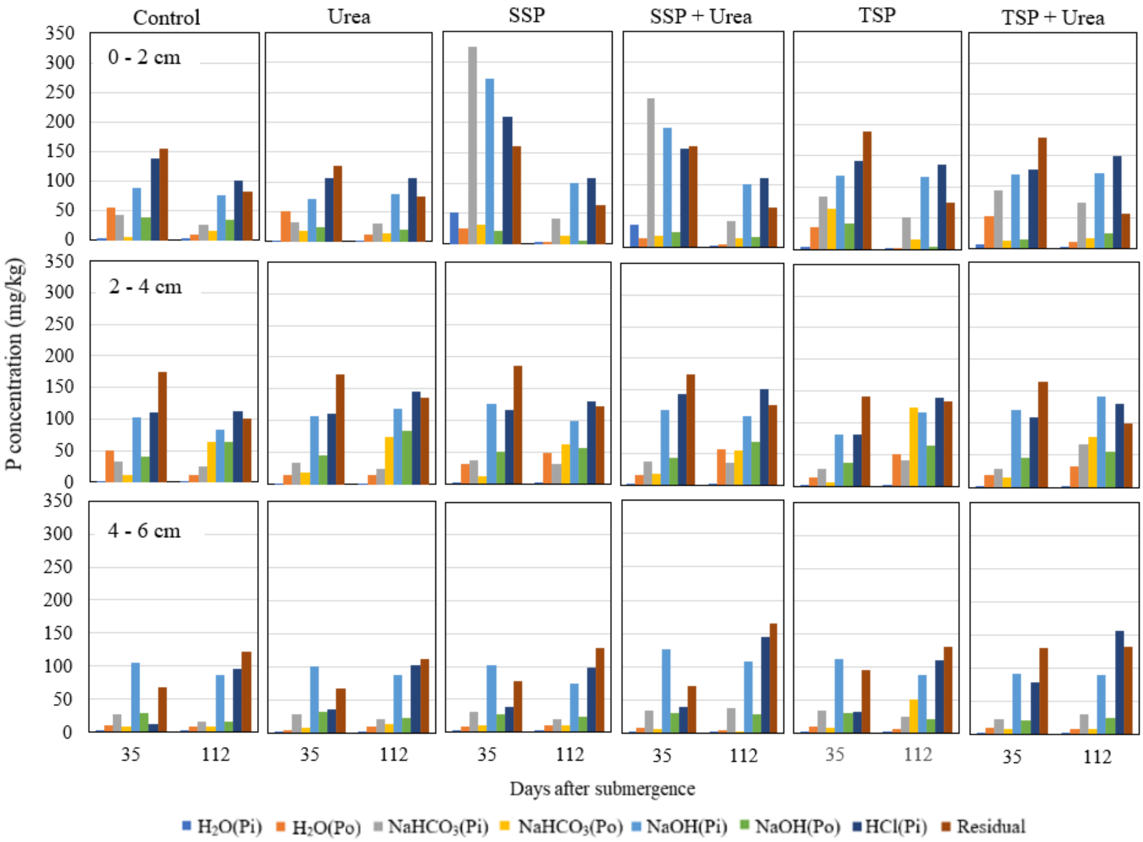

Fig. 3.S4 Changes in different P fractions at depths 0 - 2, 2 - 4 and 4 - 6 cm at 35 and 112 days after submergence due to different fertiliser treatments of Ultisol soils. Pi; inorganic phosphorus, Po; organic phosphorus, H_2O; distilled water extractable P, $NaHCO_3$; 0.5 M sodium bicarbonate extractable P, NaOH; 0.1 M sodium hydroxide extractable P, HCl; 1.0 M hydrochloric acid extractable P, residual; residual P

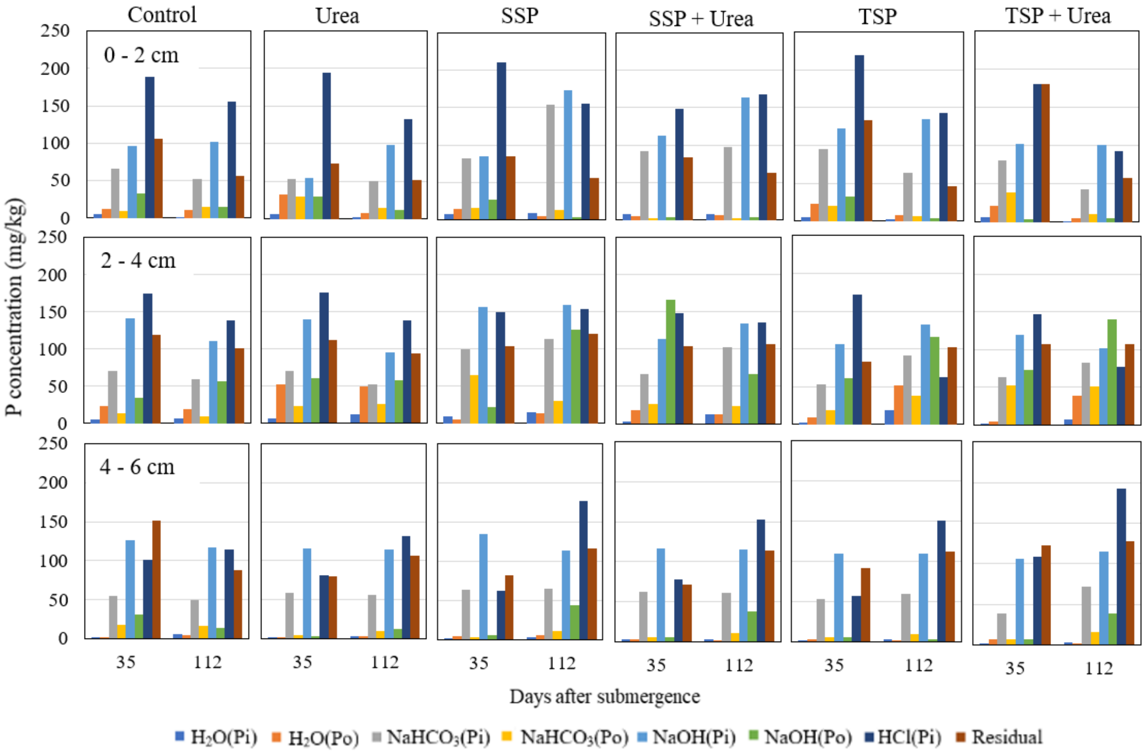

Fig. 3.S5 Changes in different P fractions at depths 0-2, 2-4 and 4-6 cm at 35 and 112 days after submergence due to different fertiliser treatments of Alfisol soils. Pi; inorganic phosphorus, Po; organic phosphorus, H_2O; distilled water extractable P, $NaHCO_3$; 0.5 M sodium bicarbonate extractable P, NaOH; 0.1 M sodium hydroxide extractable P, HCl; 1.0 M hydrochloric acid extractable P, residual; residual P

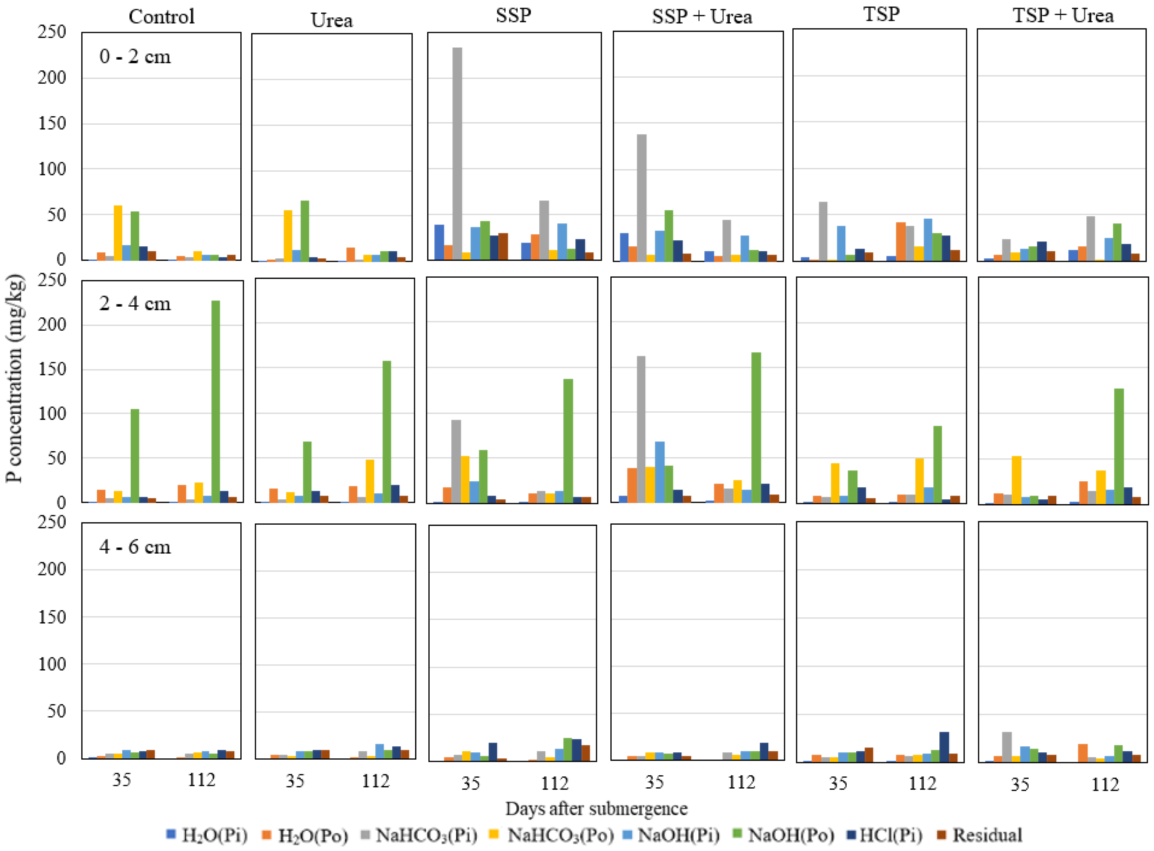

Fig. 3.S6 Changes in different P fractions at depths 0-2, 2-4 and 4-6 cm at 35 and 112 days after submergence due to different fertiliser treatments of Enltisol soils. Pi; inorganic phosphorus, Po; organic phosphorus, H_2O; distilled water extractable P, $NaHCO_3$; 0.5 M sodium bicarbonate extractable P, NaOH; 0.1 M sodium hydroxide extractable P, HCl; 1.0 M hydrochloric acid extractable P, residual; residual P

Appendix II

Supplementary Materials-Chapter 4

Phosphorus release under short-term submergence of pasture soils in critical source areas

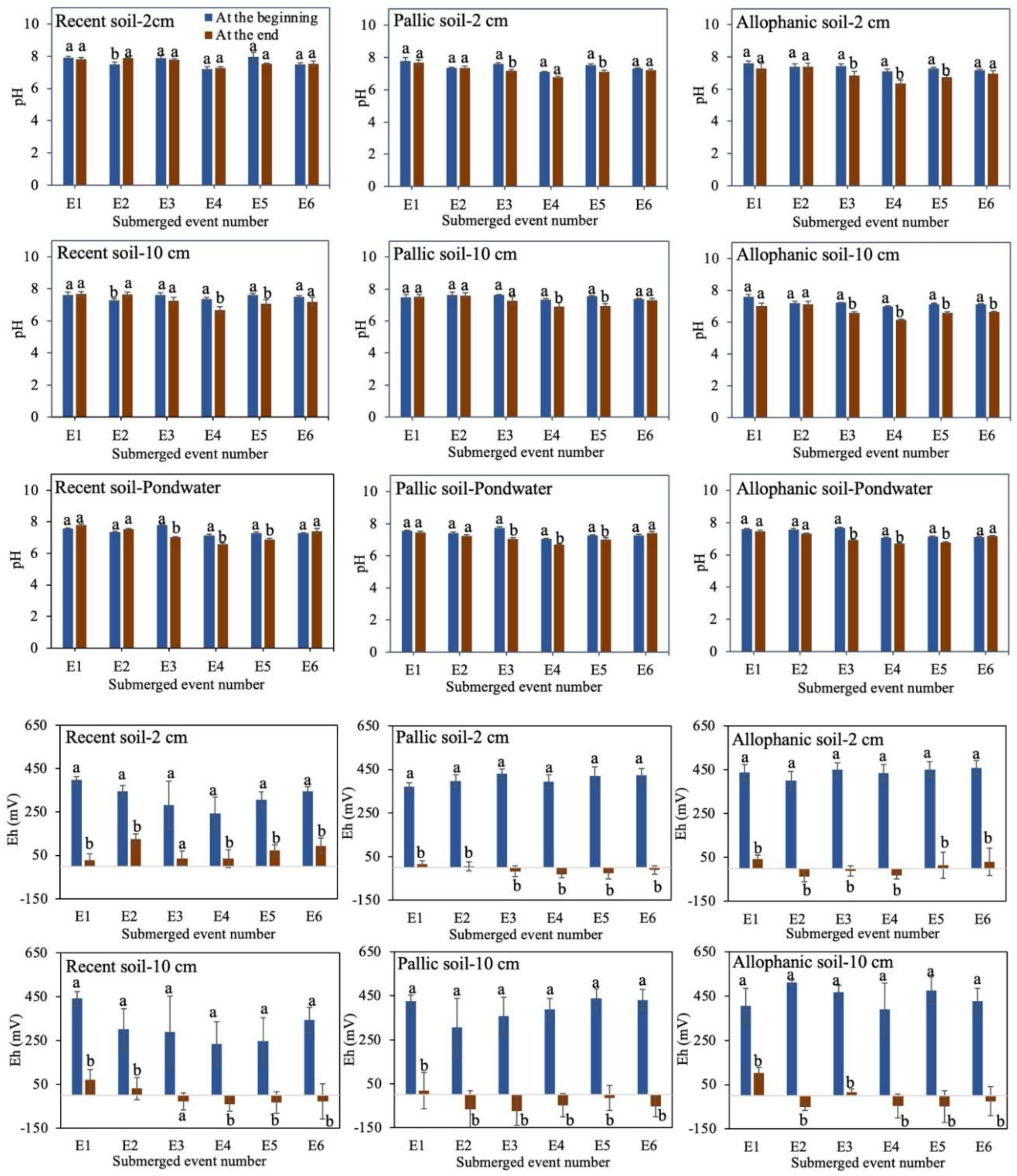

Fig. 4.S1 Variations of porewater pH at 2 cm and 10 cm depths and pondwater pH of the Recent soil, Pallic soil, Allophanic soil at the beginning and at the end of six submergence events. The error bars represent the standard errors of the means. Variations of soil redox potential at 2 cm and 10 cm depths of the Recent soil, Pallic soil, Allophanic soil at the beginning and at the end of six submergence events.

Table 4.S1 Pearson Correlation (r) analysis of the DRP concentration at two depths with pondwater

Soil		2 cm	10 cm
Recent soil	Beginning	0.575**	0.491**
	End	0.539**	0.700**
Pallic soil	Beginning	0.813**	0.771**
	End	0.546**	0.663**
Allophanic soil	Beginning	0.608**	0.346
	End	0.191	0.305

** Correlation is significant at the 0.01 level

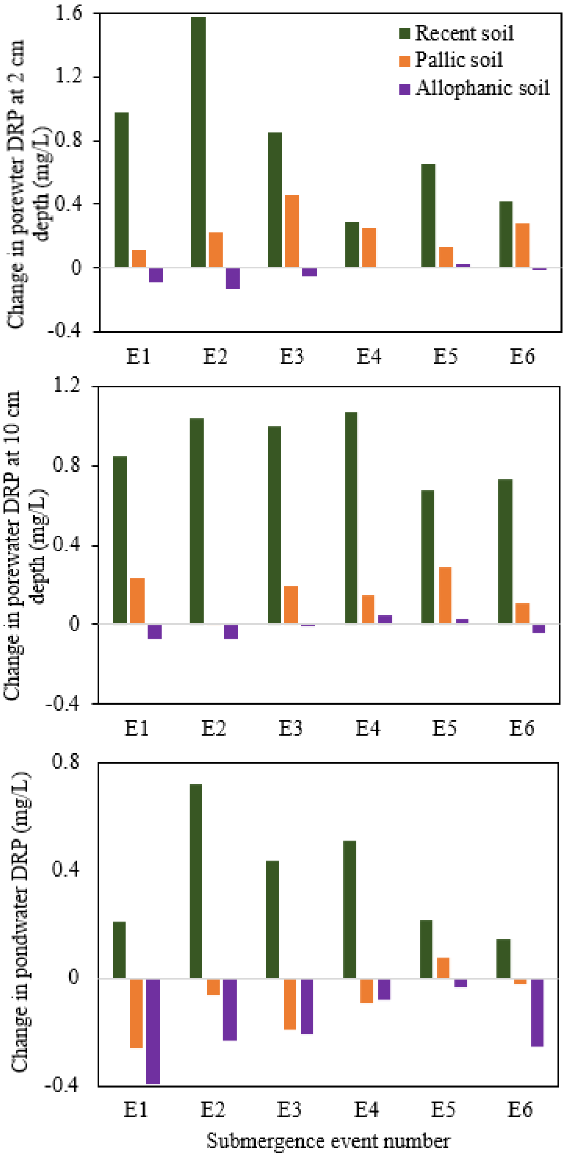

Fig. 4.S2 Change in dissolved reactive phosphorus concentrations of porewater between the beginning and at the end of six submergence events at 2 and 10 cm soil depths and pondwater of the Recent soil, Pallic soil, Allophanic soil.

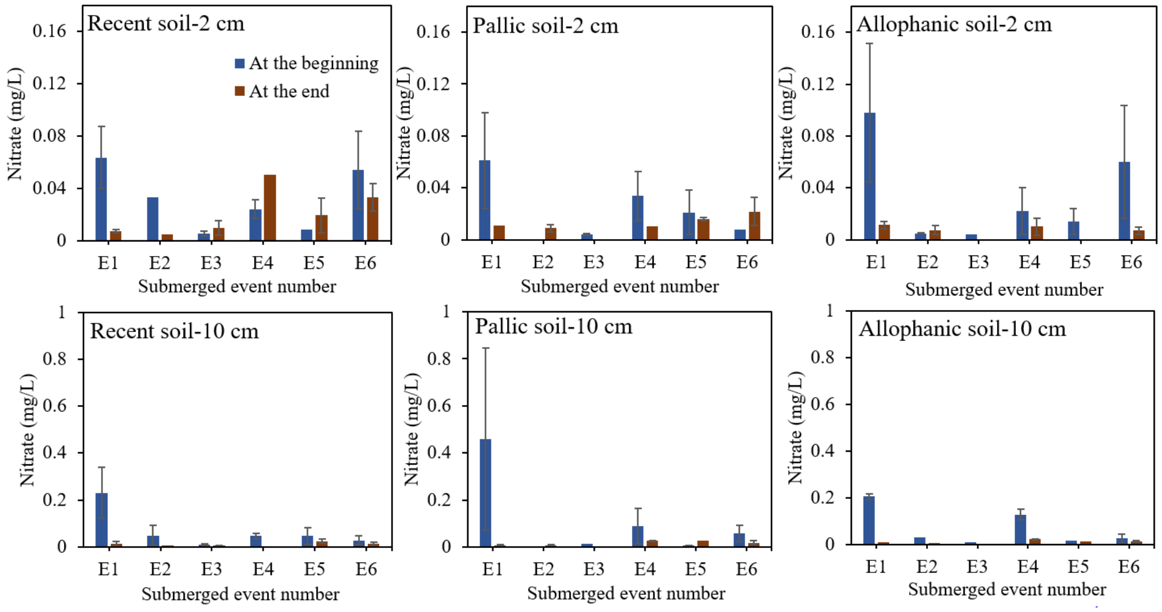

Fig. 4.S3 Porewater nitrate concentrations of 2 and 10 cm depths of the six submergence events of the Recent, Pallic and Allophanic soils.

Table 4.S2 Loading numbers (rotated components) for the principal component for the data set (DRP, DOC, Eh, pH, pe+pH, and porewater Fe, Al, Mn, Ca and Mg) of the three soils (significant loadings in bold)

	Recent soil		Pallic soil			Allophanic soil		
Variable	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3
pH	.051	**.717**	**-.569**	-.138	**.582**	-.319	.030	**.764**
Eh	**-.698**	**.539**	**-.934**	-.016	-.168	**-.699**	-.102	**.545**
DRP	**.711**	-.080	.372	.119	**.785**	.153	-.056	**.765**
DOC	**.655**	-.222	**.541**	**.510**	.180	**.533**	**.618**	.131
Ca	**.925**	.048	**.907**	.193	.085	**.928**	.145	-.165
Fe	.153	**-.720**	.358	**.715**	-.135	.271	**.841**	-.167
Mn	**.629**	-.207	**.772**	.054	-.178	**.572**	-.288	.042
Mg	**.848**	.096	**.922**	.154	.116	**.885**	.240	-.052
Al	.098	**-.727**	-.223	**.887**	.103	-.211	**.850**	.000
pe+pH	**-.677**	**.598**	**-.950**	-.027	-.111	**-.691**	-.093	**.591**

Varimax rotation

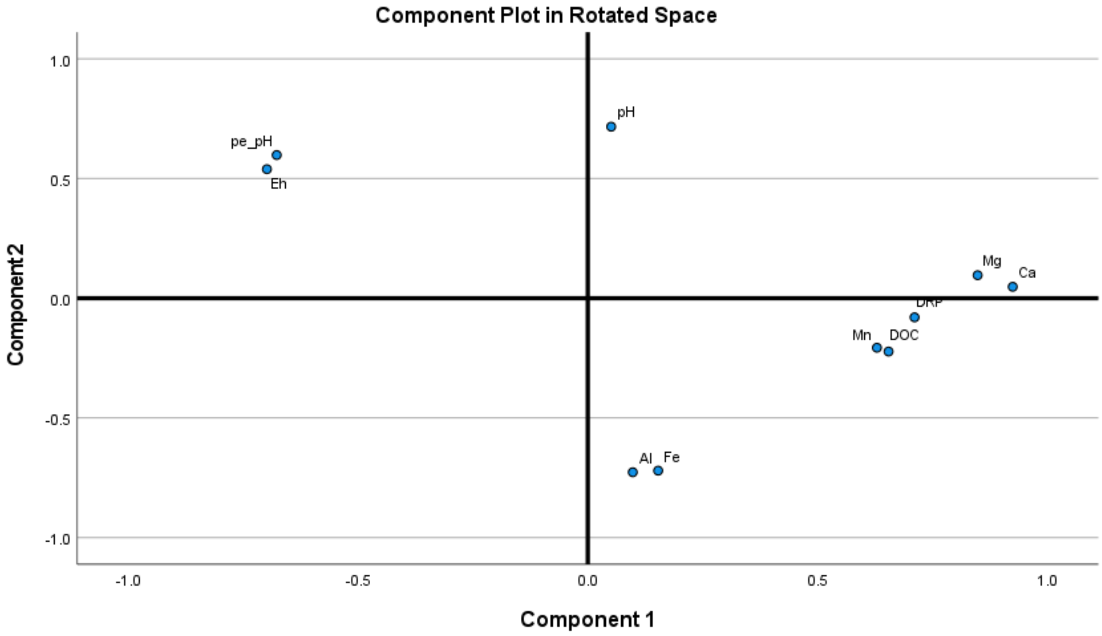

Fig. 4.S4 Principal components of the Recent soil in rotated space

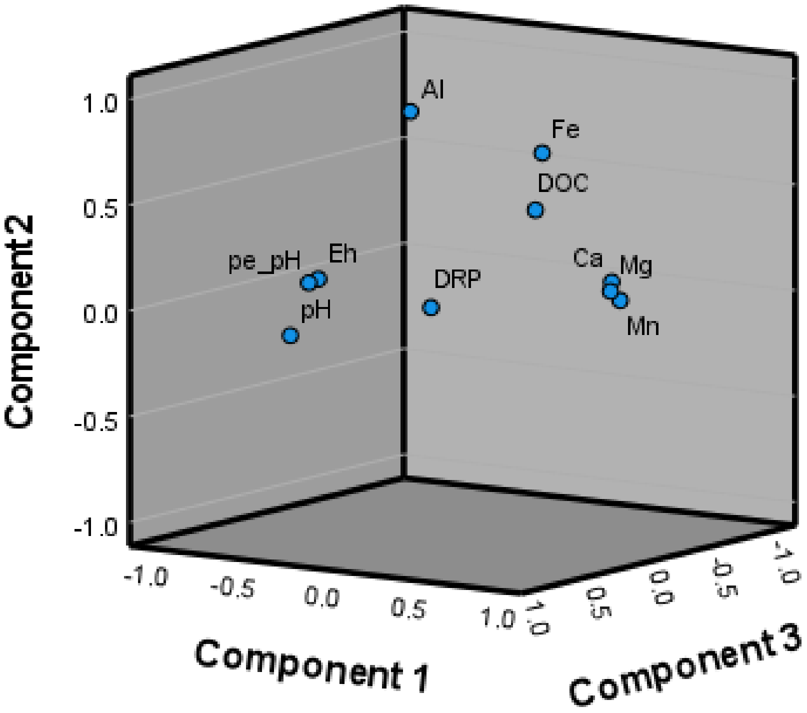

Fig. 4.S5 Principal components of the Pallic soil in rotated space

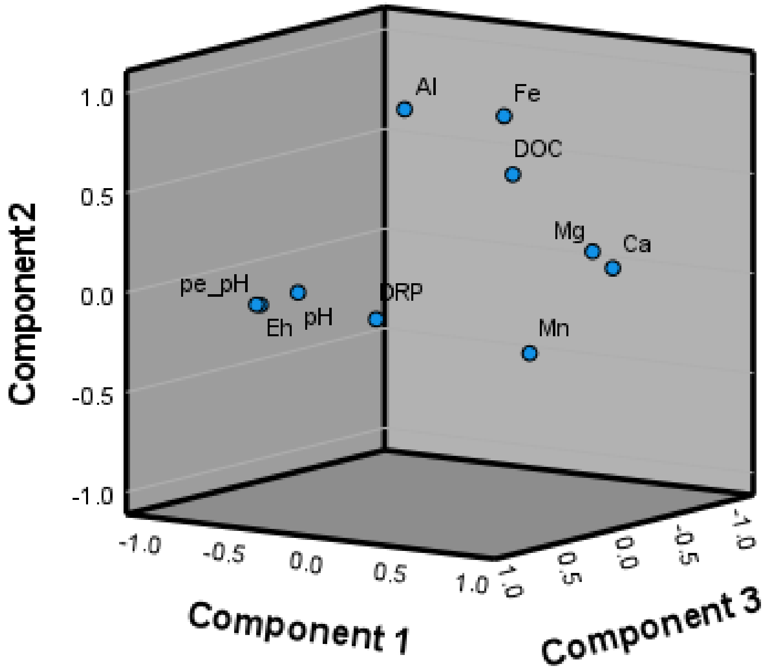

Fig. 4.S6 Principal components of the Allophanic soil in rotated space

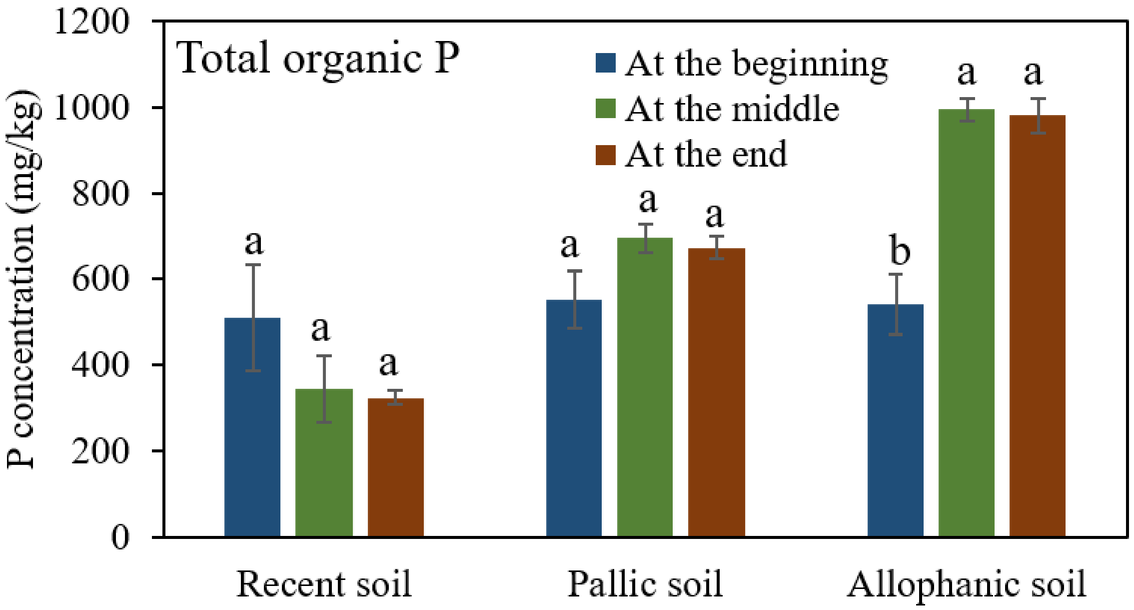

Fig. 4.S7 Total organic P fractions (sum of water extractable, sodium bicarbonate and sodium hydroxide extractable organic P) of 0-2 cm depth of the Recent, Pallic and Allophanic soils during the experimental period. The error bars represent the standard errors of the means (n=3).

Table 4.S3 Saturation indices of P minerals from MINTEQ for Recent soil during submergence (X indicates negative saturation indices)

	Event 1		Event 2		Event 3		Event 4		Event 5		Event 6	
	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end
Ca phosphates												
$Ca_3(PO_4)_2$ (β)	X	0.04	X	0.18	X	X	X	X	X	X	X	X
FCO_3-Apatite	16.12	19.54	11.93	19.63	11.88	19.45	10.56	13.63	16.10	15.67	12.03	15.16
Hydroxyapatite	5.72	7.22	2.76	7.47	5.46	6.63	1.73	3.33	5.31	4.83	2.78	4.31
Fe/Mn phosphates												
Vivianite (Fe^{II})	X	X	X	X	X	X	X	X	X	2.78	X	2.09
$MnHPO_4$ (Mn^{II})	2.14	2.69	1.81	2.88	2.46	2.69	2.13	2.59	2.40	2.76	1.90	2.51
Fe/Mn carbonates												
Siderite (Fe^{II})	X	X	X	X	X	X	X	X	X	0.48	X	0.65
Rhodochrosite (Mn^{II})	0.64	1.01	0.58	1.12	1.09	1.49	0.29	0.92	1.24	0.82	0.40	1.02
$MnCO_3$ (am)	0.14	0.51	0.08	0.62	0.59	0.99	X	0.42	0.74	0.32	X	0.52
Fe/Al oxy(hydr)oxides												
$Fe(OH)_{2.7}Cl_{0.3}$	3.52	3.62	2.80	4.73	3.61	3.80	2.62	2.96	3.59	5.73	2.37	6.01
Ferrihydrite (Fe^{III})	0.61	0.66	X	1.82	0.67	0.84	X	X	0.68	2.66	X	2.93
Ferrihydrite (aged)	1.12	1.17	0.28	2.33	1.18	1.35	0.01	0.35	1.19	3.17	X	3.43
Goethite (Fe^{III})	3.32	3.37	2.48	4.53	3.38	3.55	2.21	2.55	3.39	5.37	2.03	5.64
Hematite (Fe^{III})	9.05	9.15	7.36	11.45	9.15	9.49	6.82	7.50	9.17	13.14	6.46	13.69
Hercynite (Fe^{II})	X	3.34	X	1.50	X	3.51	X	2.27	X	5.58	X	5.55
Lepidocrocite (Fe^{III})	2.44	2.49	1.60	3.65	2.50	2.67	1.33	1.67	2.51	4.49	1.15	4.76
Maghemite (Fe^{III})	1.24	1.34	X	3.65	1.35	1.69	X	X	1.37	5.34	X	5.88
Magnesioferrite (Fe^{III})	2.80	2.97	0.21	5.29	2.82	3.19	X	0.10	3.06	6.16	X	6.64
Magnetite (Fe^{III}, Fe^{II})	6.22	12.94	5.18	14.67	10.58	13.36	6.40	10.91	8.13	18.47	3.86	18.90
$Al(OH)_3$	0.80	0.52	0.34	X	X	0.57	0.13	0.18	X	0.87	X	0.92
Boehmite	0.51	0.23	0.06	X	X	0.28	X	X	X	0.58	X	0.63
Diaspore	2.22	1.94	1.76	1.30	1.29	1.99	1.55	1.60	1.25	2.29	X	2.33
Gibbsite	1.35	1.07	0.89	0.44	0.42	1.12	X	X	X	X	X	1.47

Table 4.S4 Saturation indices of P minerals from MINTEQ for Pallic soil during submergence (X indicates negative saturation indices)

	Event 1		Event 2		Event 3		Event 4		Event 5		Event 6	
	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end
Ca phosphates												
$Ca_3(PO_4)_2$ (β)	X	X	X	X	X	X	X	X	X	X	X	X
FCO_3-Apatite	13.97	11.79	10.19	13.18	6.29	12.72	6.95	8.92	10.53	10.56	9.41	12.70
Hydroxyapatite	4.93	5.65	2.39	3.96	2.77	3.28	0.34	0.71	2.58	2.00	1.81	3.24
Fe/Mn phosphates												
Vivianite (Fe^{II})	X	X	X	X	X	X	X	X	X	0.17	X	2.32
$MnHPO_4$ (Mn^{II})	2.34	2.77	2.12	2.78	1.85	2.65	1.83	2.37	1.97	2.45	1.98	2.47
Fe/Mn carbonates												
Siderite (Fe^{II})	X	X	X	X	X	X	X	X	X	X	X	0.77
Rhodochrosite (Mn^{II})	0.45	1.39	0.20	0.87	0.62	0.92	0.02	0.55	0.45	0.82	0.19	0.91
$MnCO_3$ (am)	X	0.89	X	0.37	0.12	0.42	X	0.05	X	0.32	X	0.41
Fe/Al oxy(hydr)oxides												
$Fe(OH)_{2.7}Cl_{0.3}$	3.22	3.37	1.55	3.11	2.91	1.77	2.54	0.88	2.79	2.72	2.29	3.80
Ferrihydrite (Fe^{III})	0.33	0.43	X	0.10	X	X	X	X	X	X	X	0.67
Ferrihydrite (aged)	0.84	0.94	X	0.61	0.47	X	X	X	0.31	0.09	X	1.18
Goethite (Fe^{III})	3.04	3.14	1.23	2.81	2.67	1.37	2.11	0.35	2.51	2.29	1.93	3.38
Hematite (Fe^{III})	8.48	8.68	4.85	8.02	7.74	5.14	6.63	3.11	7.42	6.98	6.25	9.15
Hercynite (Fe^{II})	X	2.76	X	X	X	1.06	X	X	X	3.34	X	5.08
Lepidocrocite (Fe^{III})	2.16	2.26	0.35	1.93	1.79	0.49	1.23	X	1.63	1.41	1.05	2.50
Maghemite (Fe^{III})	0.67	0.88	X	0.21	X	X	X	X	X	X	X	1.35
Magnesioferrite (Fe^{III})	1.85	2.12	X	0.79	0.74	X	X	X	0.29	X	X	1.69
Magnetite (Fe^{III}, Fe^{II})	6.17	12.59	0.71	12.05	4.22	8.34	3.69	5.89	4.01	11.30	2.41	14.20
$Al(OH)_3$	0.92	0.17	X	X	0.62	X	X	X	0.35	0.26	0.35	0.77
Boehmite	0.63	X	X	X	0.33	X	X	X	0.06	X	0.06	0.48
Diaspore	2.34	1.59	0.85	X	2.04	1.09	1.27	0.57	1.77	1.67	1.77	2.18
Gibbsite	1.47	0.72	X	X	1.17	0.22	0.40	X	0.90	0.81	0.90	1.32

Table 4.S5 Saturation indices of P minerals from MINTEQ for Allophanic soil during submergence (X indicates negative saturation indices)

	Event 1		Event 2		Event 3		Event 4		Event 5		Event 6	
	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end	At the beginning	At the end
Ca phosphates												
$Ca_3(PO_4)_2$ (β)	X	X	X	X	X	X	X	X	X	X	X	X
FCO_3-Apatite	8.94	9.20	7.00	7.05	4.80	3.56	1.19	X	2.34	2.29	2.82	4.33
Hydroxyapatite	1.97	1.76	0.96	0.60	X	X	X	X	X	X	X	X
Fe/Mn phosphates												
Vivianite (Fe^{II})	X	X	X	X	X	X	X	X	X	X	X	X
$MnHPO_4$ (Mn^{II})	2.34	2.77	1.69	1.80	1.85	2.65	1.08	0.61	0.96	0.95	1.98	2.47
Fe/Mn carbonates												
Siderite (Fe^{II})	X	X	X	X	X	X	X	X	X	X	X	0.20
Rhodochrosite (Mn^{II})	0.45	1.39	0.07	1.04	0.62	0.92	0.01	X	0.21	X	0.19	0.91
$MnCO_3$ (am)	X	0.30	X	0.54	X	0.29	X	X	X	X	X	X
Fe/Al oxy(hydr)oxides												
$Fe(OH)_2.7Cl_{0.3}$	2.99	3.02	2.46	X	2.51	1.77	2.49	X	3.43	2.54	2.55	3.66
Ferrihydrite (Fe^{III})	0.07	X	X	X	X	X	X	X	0.34	X	X	0.43
Ferrihydrite (aged)	0.58	0.49	X	X	0.03	X	X	X	0.85	X	X	0.94
Goethite (Fe^{III})	2.78	2.69	2.15	X	2.23	1.27	2.08	X	3.05	1.97	2.14	3.14
Hematite (Fe^{III})	7.96	7.78	6.70	X	6.85	4.93	6.56	0.88	8.51	6.33	6.68	8.68
Hercynite (Fe^{II})	X	2.99	X	4.26	X	1.07	X	X	X	2.93	X	4.81
Lepidocrocite (Fe^{III})	1.90	1.81	1.27	X	1.35	0.39	1.20	X	2.17	1.09	1.26	2.26
Maghemite (Fe^{III})	0.15	X	X	X	X	X	X	X	0.70	X	X	0.88
Magnesioferrite (Fe^{III})	0.85	0.47	X	X	X	X	X	X	0.75	X	X	0.64
Magnetite (Fe^{III}, Fe^{II})	4.44	11.14	3.35	X	2.72	8.24	2.89	3.01	5.38	10.03	2.57	13.05
$Al(OH)_3$	0.81	0.56	0.81	0.55	0.66	X	0.37	X	1.24	0.37	0.88	0.97
Boehmite	0.52	0.27	0.52	0.26	0.37	X	0.08	X	0.95	0.08	0.59	0.68
Diaspore	2.22	1.98	2.23	1.97	2.08	1.05	1.79	X	2.66	1.79	2.30	2.38
Gibbsite	1.36	1.11	1.36	1.10	1.21	0.18	0.92	X	1.79	0.92	1.43	1.52

Table 4.S6 Ammonium oxalate extractable Fe, Al and Mn concentrations in the Recent, Pallic and Allophanic soils at the end of the experiment

Oxalate extractable ions (mg/kg)	Recent soil	Pallic soil	Allophanic soil
Fe	3535	5260	7575
Al	870	1455	8095
Mn	100	660	635

Appendix III

Supplementary Materials-Chapter 5

Redox-induced phosphorus release from critical source areas following rainfall events in New Zealand

Table 5.S1 Summary of selected rainfall characteristics and air temperature of the five rainfall events; Data from the Palmerston North Ews NIWA weather station 21963 (S 40^o 22' 52", E 175^o 36' 32")

Rainfall event	Previous 24hr rainfall amount (mm)	Previous 24hr dry period (hr)	Previous four-day rainfall amount (mm)	Previous four-day dry period (hr)	Average air temperature of the day of sampling (^{o}C)
E1	33.5	6	82	36	13
E2	16.1	15	52.1	51	12
E3	7.1	18	7.5	89	13
E4	15.8	6	29	48	17
E5	34.8	15	49.6	64	12

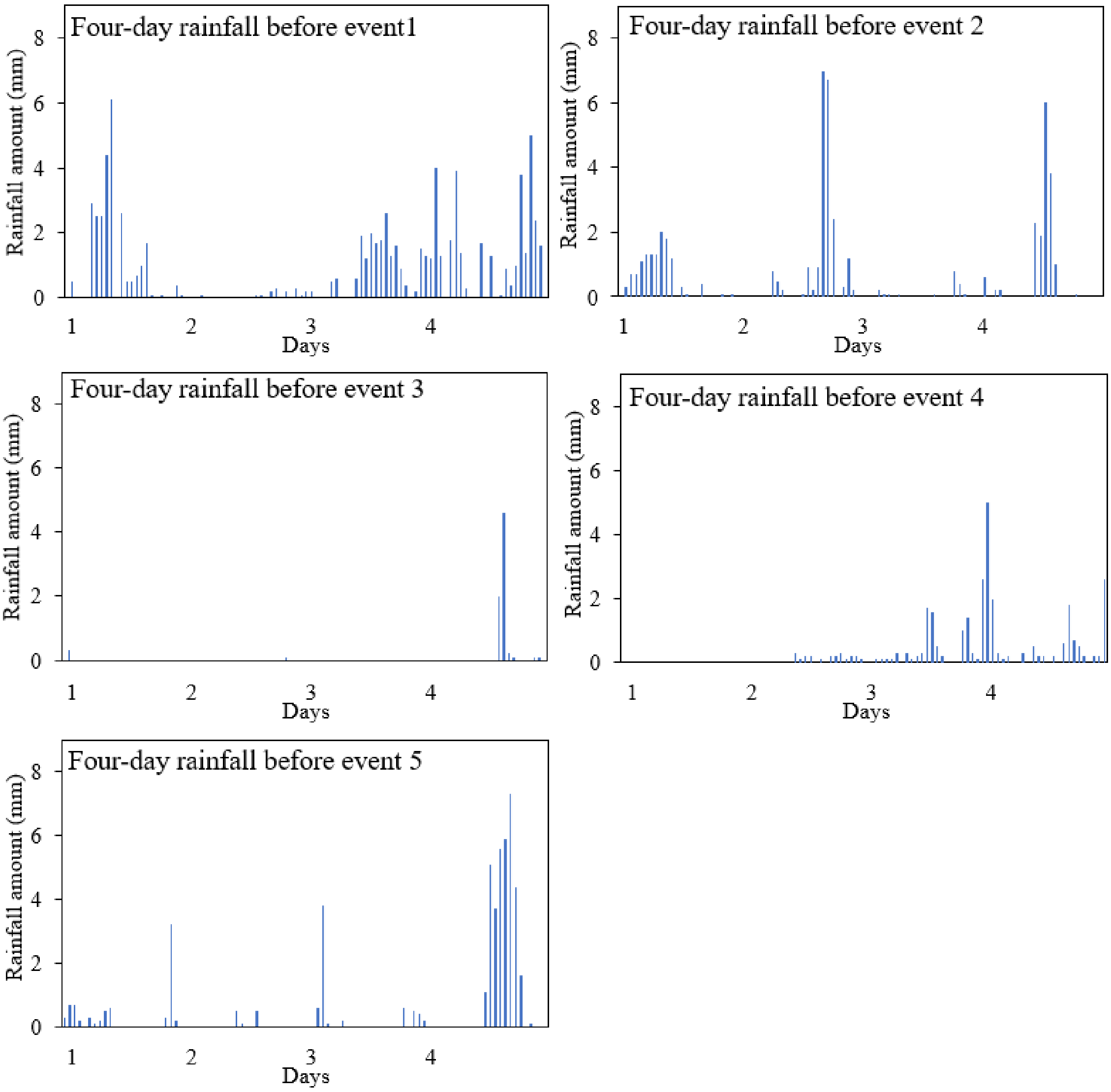

Fig. 5.S1 Hourly four-day rainfall amounts before porewater and floodwater sample collection of each event.

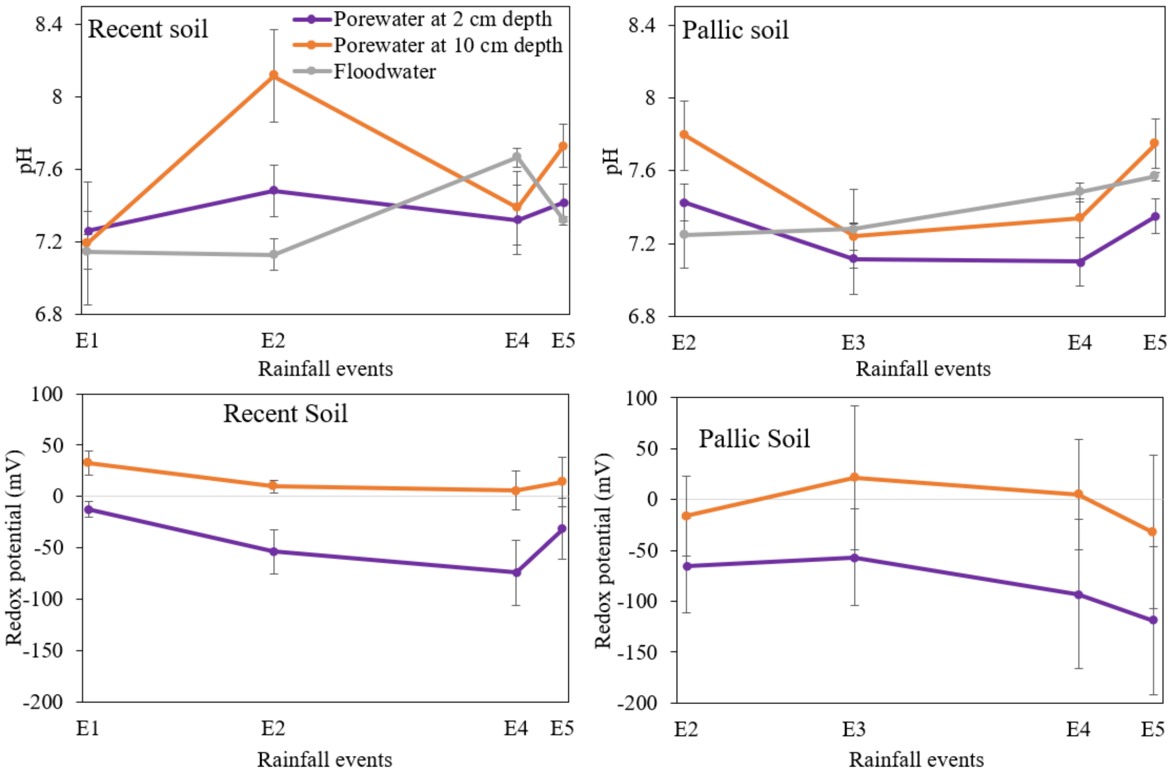

Fig. 5.S2 Variations of porewater pH at 2 cm and 10 cm depths and floodwater pH of the Recent soil and Pallic soils soil over five rainfall events and variations of soil redox potential at 2 cm and 10 cm depths of the Recent and Pallic soils over five rainfall events. The error bars represent the standard errors of the means. The rainfall events (Y axis) are spaced based on the days between the events.

Table 5.S2 Pearson correlations (r) of porewater DRP of the two depths of the Recent and Pallic soils with pH, Eh, *pe*+pH, DOC and selected porewater cations

	pH	Eh	*pe*+pH	DOC	Ca	Mg	Mn	Fe
Recent soil	.244	-.332	-.247	-.028	-.212	.087	-.075	-.135
Pallic soil	-.357*	.103	.051	.408**	-.103	.311	-.103	-.110

**$p<0.01$, *$p<0.05$

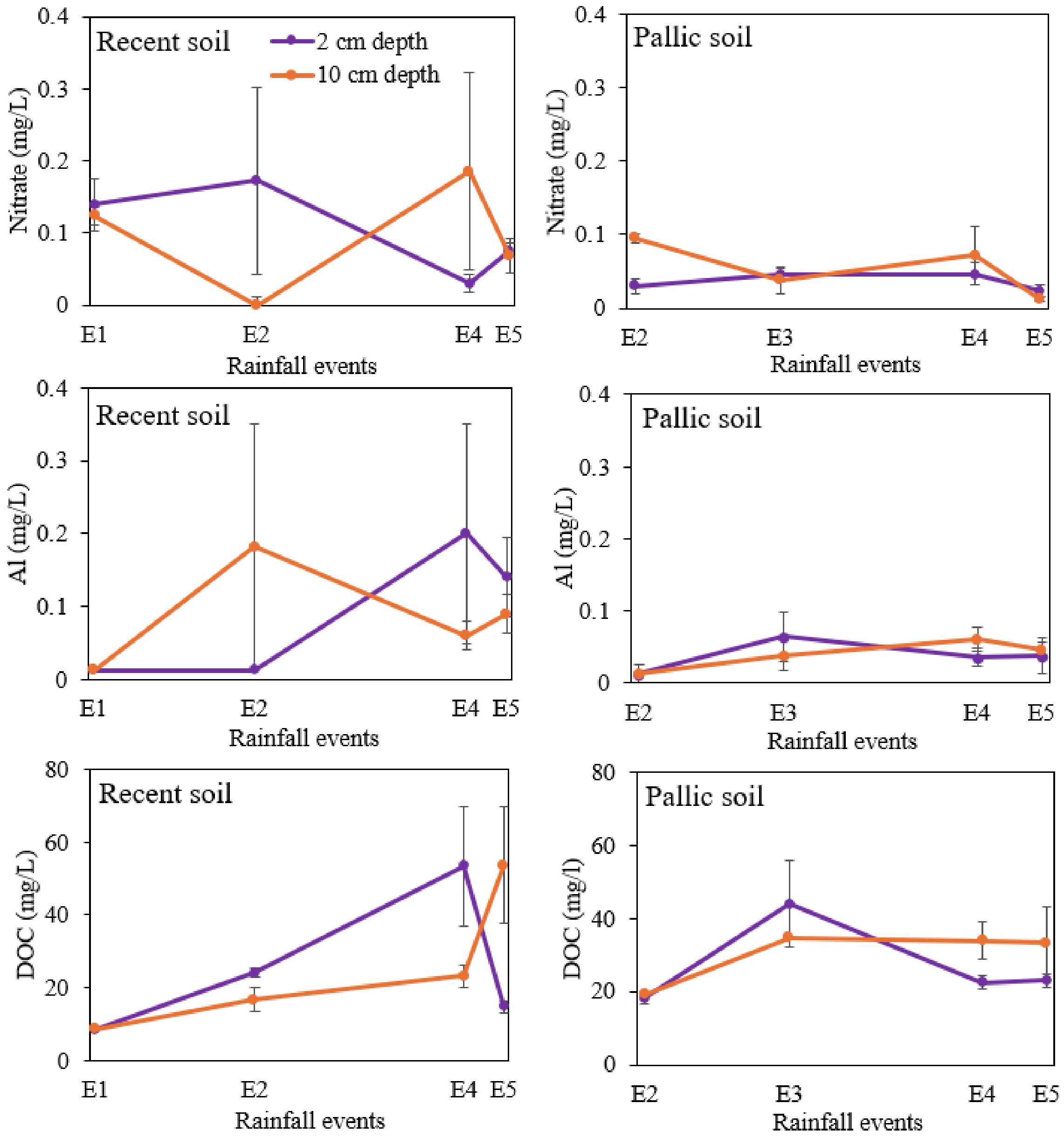

Fig. 5.S3 Variations of porewater nitrate, Al and dissolved organic carbon at 2 cm and 10 cm depths of the Recent soil and Pallic soils over the five rainfall events. The error bars represent the standard errors of the means. The rainfall events (Y axis) are spaced based on the days between the events.

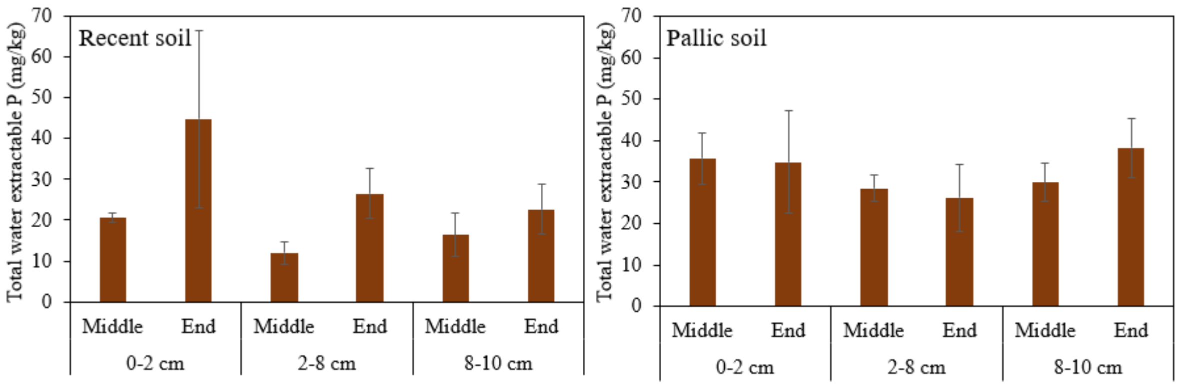

Fig. 5.S4 Total water extractable P (sum of organic and inorganic P) of 0-2, 2-8, 8-10 cm depths of the Recent and Pallic soils measured at the middle and at the end of the experimental period. The error bars represent the standard errors of the means (n=3).

Table 5.S3 Ammonium oxalate extractable Fe, Al and Mn concentrations in the Recent, and Pallic soils at the end of the experiment

Oxalate extractable ions (mg/kg)	Recent soil	Pallic soil
Fe	3356	5208
Al	747	1260
Mn	90	325

Appendix IV

DRC-16 Forms

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Palihakkara, J., Burkitt, L., Jeyakumar, P., Attanayake, C.P., 2024. Exploring phosphorus dynamics in submerged soils and its implications on the inconsistent rice yield response to added inorganic phosphorus fertilisers in paddy soils in Sri Lanka. J Soil Sci Plant Nutr 24, 1-20. https://doi.org/10.1007/s42729-023-01553-4

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Date:	24-Dec-2024
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Palihakkara, J., Burkitt, L., Jeyakumar, P., and Attanayake, C. P. (2025). Redox-induced phosphorus release from critical source areas following rainfall events in New Zealand. Journal of Environmental Management (Accepted)

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Date:	24-Dec-2024
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This form should appear at the end of each thesis chapter/section/appendix submitted as a manuscript/ publication or collected as an appendix at the end of the thesis.

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