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Research article

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

Janani Palihakkara [a,b,*], Lucy Burkitt [a], Paramsothy Jeyakumar [a], Chammi P. Attanayake [c]

[a] Environmental Sciences Group, School of Agriculture and Environment, Massey University, Palmerston North, 4442, New Zealand
[b] Department of Soil Science, Faculty of Agriculture, University of Peradeniya, Peradeniya, 20400, Sri Lanka
[c] Institute for Sustainability, Energy and Environment, University of Illinois Urbana-Champaign, Urbana, IL, 61801, USA

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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^{-1} and 0.26–2.31 mg L^{-1}, 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^{-1}) for the Manawatū River. The study highlights the substantial risk of P loss from CSAs to surface water, driven primarily by the reductive dissolution of Fe and Mn oxy(hydr)oxides. The findings underscore the importance of targeted management strategies to mitigate dissolved P runoff, particularly in high-risk CSAs frequent submerged during rainfall events. This study developed an effective method for monitoring soil porewater P and redox conditions, offering valuable insights and practical tools for resource managers seeking to reduce P contamination.

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, being hydrologically sensitive areas, often saturate/submerge following rainfall events due to the accumulation of water as a result of topography. 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 surface water flow (Smith et al., 2021).

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* Corresponding author. Environmental Sciences Group, School of Agriculture and Environment, Massey University, Palmerston North, 4442, New Zealand
E-mail address: j.palihakkara@massey.ac.nz (J. Palihakkara).

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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 an 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, 2017; King 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.

2. Materials and methods

2.1. Experimental sites

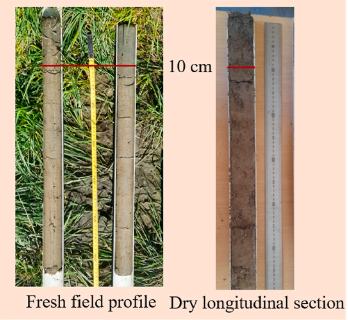
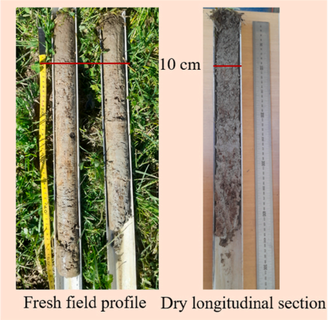
Critical source areas (Fig. 1) were identified on two Massey University farms located in the Manawatū-Whanganui region of New Zealand, namely Dairy 1 (S 40° 22′ 27″, E 175° 37′ 05″), and Dairy 4 (S 40° 23′ 39″, E 175° 36’ 55’’). According to the *New Zealand Soil Classification*, the soil types were a Recent and Pallic soil, respectively (Hewitt et al., 2021). A brief comparison of the two sites is given in Table 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 subsurface drainage water collected by the tile drainage system was discharged to the Hopkins River downstream from the sampling location.

2.2. Experimental setup

Ten sampling stations were installed within each CSA in an area of 6 × 2 m^2. Out of the ten stations, five were installed along the centre line with 1 m spacing between each station. The other five stations were installed in two parallel offset lines, positioned 0.5 m from the centre line. 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

Fig. 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).

Table 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

the P from P fertiliser additions, dung and litter returns via sorption and therefore disproportionally contributes to P runoff via desorption (Vadas et al., 2007a, 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. 1.

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 p.m., 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 this paper. 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 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 *pe* 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 40° 22′ 52″, E 175° 36’ 32”) located adjacent to Dairy 1 farm and ~1400 m from Dairy 4 farm. Representative soil samples from 0 to 2, 2–8 and 8–10 cm 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 °C 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.

2.4. Initial soil characterisation

After air drying and sieving through a 2 mm sieve, soil samples were analysed for soil texture by hydrometer method (1986, Standards Association of New Zealand), soil pH in 1:2 (v/v) soil:water slurry followed by potentiometric determination, anion storage capacity (Saunders, 1965) and cation exchange capacity (Blackmore et al., 1987). Available P was determined by Olsen method (Olsen and Sommers, 1982) followed by molybdenum blue colorimetry (Murphy and Riley, 1962) and Mehlich-3 method (Mehlich, 1984) followed by Inductively coupled plasma optical emission spectroscopy (ICP-OES). Phosphorus fractionation was undertaken by a modified Hedley procedure (Hedley et al., 1982) as explained in section 2.6. Mehlich-3 extractable Ca, Mg, Fe, Mn, Al and Zn concentrations were determined by ICP-OES. Total organic carbon (TOC) was determined by thermal conductivity detector (Elementar Analyser) by catalytic combustion (900 °C, O_2) and separation (Nelson and Sommers, 1996). The oxalate extractable cations (Fe, Al and Mn) were determined by acid ammonium oxalate method (McKeague and Day, 1966) followed by Microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4200) and this was repeated the soil samples collected at the end of the experiment.

2.5. Porewater and floodwater sample analysis

After filtering the porewater and floodwater samples through 0.45 μm cellulose membrane filters, they were analysed for DRP by molybdate blue colour method (Murphy and Riley, 1962) using ultraviolet–visible spectrophotometer (JENWAY 7315) and pH using a glass pH electrode (ORION STAR A214) within 12 h of sampling. Porewater samples were analysed for cations (Ca, Mg, K, Na, Fe, Al, and Mn) using

MP-AES (Agilent 4200) and for anions (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}) using ion chromatography (Dionex™ Aquion™). Alkalinity of the porewater samples was measured by titrating against 0.1 N H_2SO_4 in the presence of methyl orange indicator. Dissolved organic carbon (DOC) of porewater were measured using a carbon/nitrogen analyser (Shimadzu TOC-LCSH).

2.6. Phosphorus fractionation study

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 porewater samplers (2 cm and 10 cm depth). The samples were subjected to sequential P fractionation using a modified Hedley procedure (Hedley et al., 1982). The first few steps of the extraction which involved transferring soil, the supernatant of distilled water extract and adding 0.5 M $NaHCO_3$, were conducted while purging nitrogen gas. Acidified potassium persulfate oxidation was used for the digestion and the residue was analysed for total P (TP). The difference between TP and inorganic P (Pi) was estimated to be organic P (Po) (Tiessen and Moir, 1993). Aqua regia digestion was used to determine the P in the soil residue left after sequential extraction (Chen and Ma, 2001).

2.7. Phosphorus speciation study by thermodynamic modelling

Visual MINTEQ 3.1 (Gustafsson, 2013) thermodynamic modelling software was used to predict the solid P species based on the composition of porewater samples across the rainfall events. Soil Eh, pH, porewater DRP, DOC, alkalinity, concentrations of cations (Ca, Mg, Na, K, Mn, Al and Fe), and anions (Cl^-, F^-, NO_3^-, NO_2^- and SO_4^{2-}) were used as input parameters. The Stockholm Humic Model (SHM) was used as the state-of-the-art model to simulate the complexation to natural organic matter while assuming 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.

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, $pe + pH$, DOC, porewater Fe, Mn, Ca, Mg and Al concentrations. Regression analyses were performed to explore the relationships between rainfall characteristics (previous 24 h precipitation, previous 24 h 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.

3. Results

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 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 2). The Olsen P concentration of both the Recent (69 mg L^{-1}) and Pallic (66 mg L^{-1}) soils were high. Anion storage capacity (ASC) 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.

Table 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
Anion storage capacity %	19	29
Olsen P (mg L^{-1})	69	66
Mehlich-3 P (mg L^{-1})	147	133
Total organic carbon (g $100g^{-1}$)	2.0	4.7
Textural class	Loam	Silty clay loam
Clay%	18	32
Sand%	39	14
CEC ($cmol_{(+)}$ kg^{-1})	12	22
Oxalate extractable cations (mg kg^{-1})		
Fe	3642	4645
Al	833	1312
Mn	88	231
P fractions (mg kg^{-1})		
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
Mehlich-3 extractable cations (mg L^{-1})		
Fe	681	545
Mn	46	75
Ca	1233	1735
Mg	170	254
Al	568	800

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.

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 h interval. However, out of 36 rainfall events, only 5 were selected for sampling based on their timing of the rainfall event (morning hours) and their ability to create temporary flooding conditions in the CSA sites. The rainfall event characteristics were analysed to examine the rainfall amount in the previous 24 h before sample collection, the number of dry hour within 24 h before sample collection, the previous four-day rainfall amount and the dry hour within four days before sample collection (Supplementary Table S1). The highest rainfall intensity recorded during this experimental period was 7.3 mm/h at the last day of sample collection (Supplementary Fig. S1). Average air temperatures on the sample collection days were 13, 12, 13, 17 and 12 °C for events 1, 2, 3, 4 and 5, respectively (Supplementary Table S1).

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 (Supplementary Fig. 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. 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. 2). The average Eh recorded for any depths of any of the rainfall events of the two soils were below 33 mV (Supplementary Fig. S2). The Eh of the 10 cm depth of both soils showed high Eh values (more oxidised) compared to the 2 cm depth (Supplementary Fig. 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 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 ($p < 0.05$).

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 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^{-1} and it varied from 0.32 to 0.98 mg L^{-1} at the 10 cm depth of the Recent soil across four rainfall events (Fig. 3). In the Pallic soil, the porewater DRP concentrations varied from 0.26 to 2.31 mg L^{-1} at the 2 cm depth and 0.27–1.02 mg L^{-1} at the 10 cm depth.

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). The floodwater DRP concentrations during the experimental period varied from 0.13 to 0.87 mg L^{-1} and 0.19–0.54 mg L^{-1} in the Recent and Pallic soils, respectively. The DRP concentration measured from neither depth of the two soils were significantly correlated with floodwater DRP (data is 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 h and four-day rainfall amounts (Fig. 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 h 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 h and four-day dry periods (Fig. 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.

3.5. Variations in porewater cation 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 1.9–3.9-fold higher compared to that of the 2 cm depth (Fig. 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). 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.

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 (Supplementary Table 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, $p < 0.001$).

3.6. Changes in P fractions

The total water extractable P fraction (H_2O-P) of the Pallic soil (21.2 mg kg^{-1}) was slightly higher than the Recent soil (16.8 mg kg^{-1}) 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 (Supplementary Fig. S4). The H_2O-P fraction of the Pallic soil remained the same at the 0–2 and

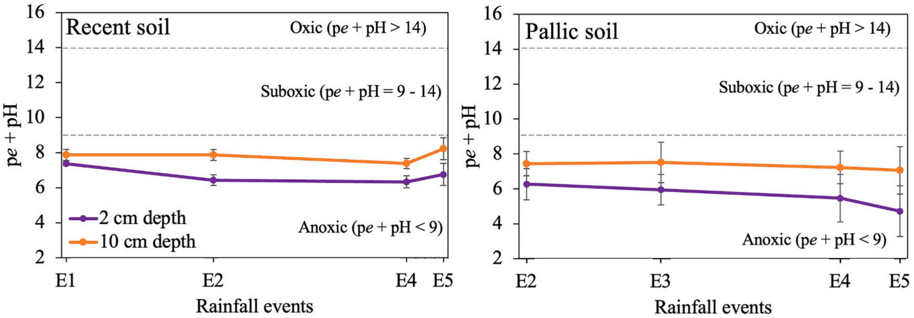


Fig. 2. Overall redox status of the soil solution during each event as p*e* + pH varied in the 2 and 10 cm depths of the two soils following rainfall events. Redox zones are indicated by dashed lines. The error bars represent the standard errors of the means. The rainfall events (X axis) are spaced based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

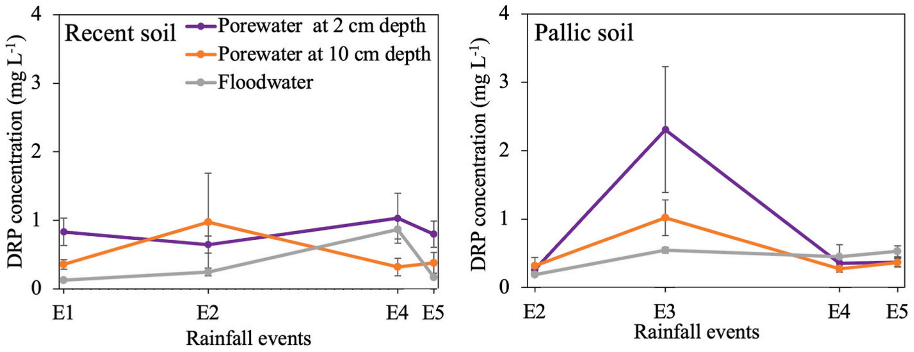


Fig. 3. Variations in dissolved reactive phosphorus in porewater at the 2 and 10 cm depths and in floodwater measured from a critical source area on a Recent and Pallic soil following five rainfall events. The error bars represent the standard errors of the means. The rainfall events (X axis) are spaced based on the number of days between the events.

2–8 cm depths and increased by 0.3-fold at the 8–10 cm depth towards the end of the experiment (Supplementary Fig. 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 to 368 mg kg^{-1} at the beginning of the experiment (Table 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. 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. 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. 6).

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. 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, 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. 6).

3.7. *Changes in P species during rainfall events - thermodynamic modelling*

Two depths 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 (Tables 3 and 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 3). The Pallic soil was supersaturated with Fe(III) oxy(hydr)oxides such as ferrihydrite, maghemite and magnesioferrite only at the 10 cm depth (Table 4).

4. Discussion

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 h and four-day rainfall amounts (Fig. 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 h 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 also aided the draining of runoff in this site (Table 1). The significant positive regression relationships between the porewater DRP measured on the Pallic soil in the previous 24 h and four-day dry period (Fig. 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).

4.2. *Effect of overall redox status on DRP release*

Although previous laboratory incubation studies with soil monoliths on pH, Eh, *pe* + 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 (Supplementary Table S2). A glasshouse study, 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 *pe* + pH (Unpublished: under review). 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 increase in pH in both soils upon submergence is likely due to the reduction of Fe and Mn oxides, which consumes H^+ ions (Fageria et al., 2011). This is supported by Eh values below 33 mV and the *pe* + pH values below 8.2, indicating that Mn and Fe reduction had already

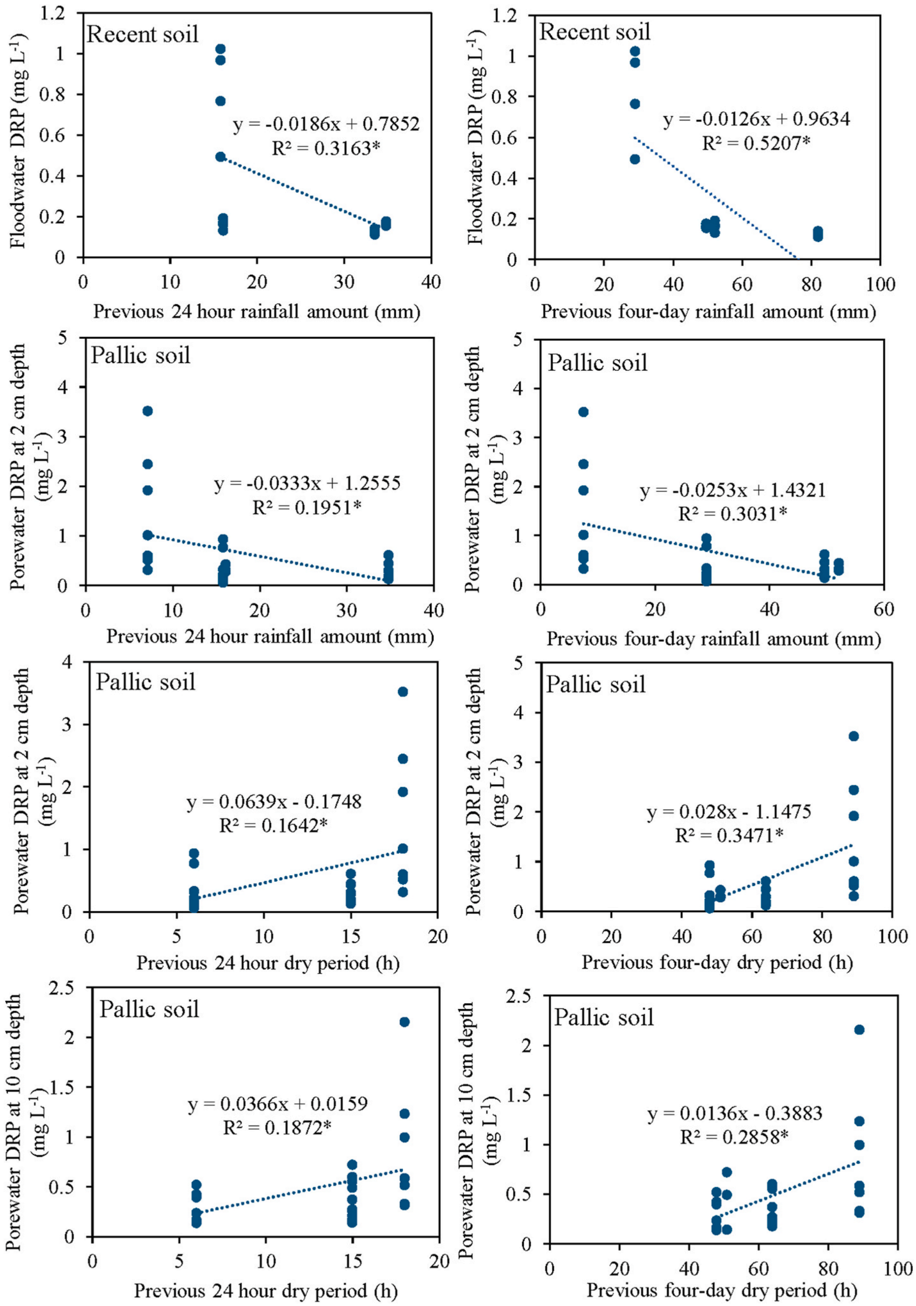


Fig. 4. Regression relationships between rainfall characteristics and porewater DRP at the 2 and 10 cm depths and floodwater DRP from the Recent and Pallic soils. * Indicates statistically significant regression ($p < 0.05$) relationships. Statistically non-significant regression relationships are not shown.

commenced in these 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). 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, 2004) from rainfall under field condition.

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 1.5–1.9-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., 2020). 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 (Unpublished: under review). 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 (eg: dilution effect and

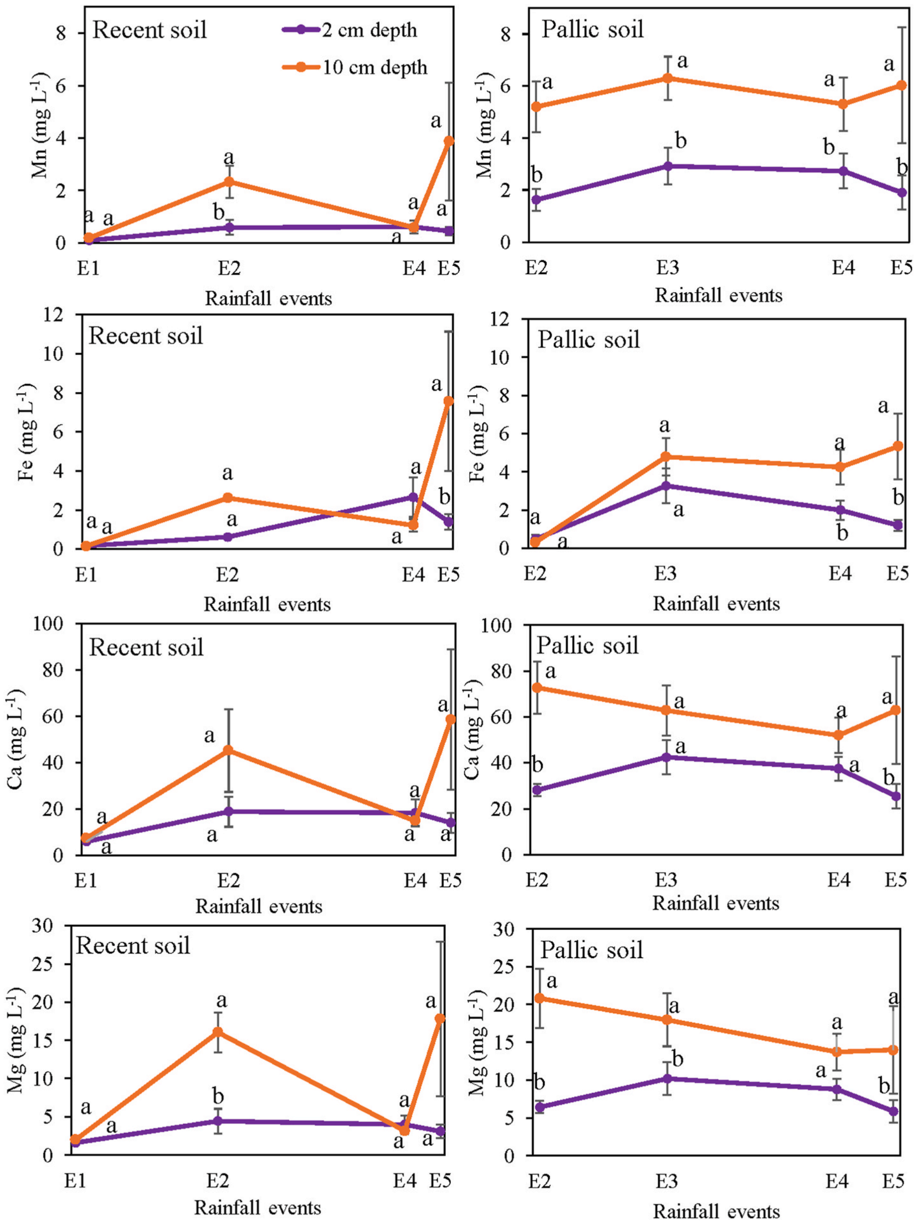


Fig. 5. Porewater concentrations of selected cations (Mn, Fe, Ca, and Mg) measured at the 2 cm and 10 cm depths following five rainfall events on the Recent and Pallic soils. The error bars represent the standard errors of the means. Different scales are used for different cation concentrations (Y axis). Significant ($p < 0.05$) differences indicate comparison between depths only.

contribution from other P sources). 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^{-1}) 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 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

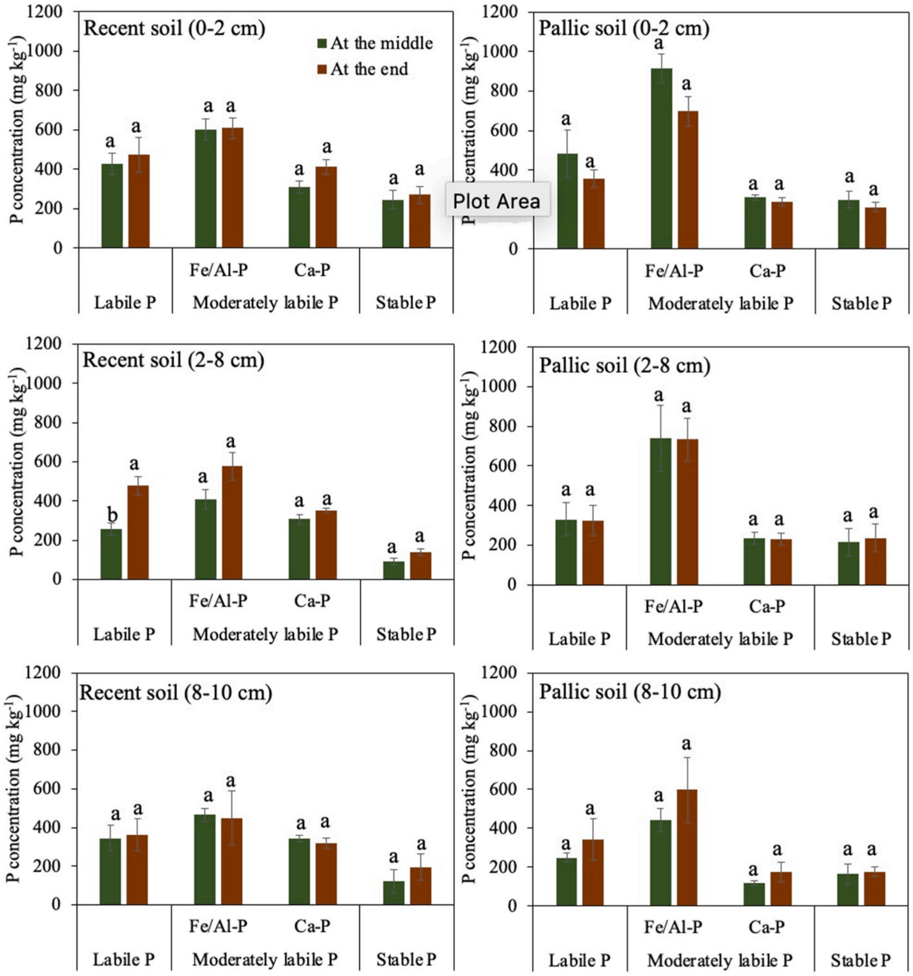


Fig. 6. Labile, moderately labile (NaOH extractable P: Fe/Al-P, and HCl extractable P: Ca-P) and stable P fractions of 0–2, 2–8 and 8–10 cm depths of the Recent and Pallic soils at the middle and at the end of the experimental period. The error bars represent the standard errors of the means (n = 3).

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, 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 2), further implying a higher risk of P loss from this soil.

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. This was supported by severe reduced status in soils, with low Eh values (<33 mV) and elevated porewater Mn and Fe concentrations (Fig. 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(III) 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 3 and 4), suggested that the reductive dissolution of Fe(III) and Mn(IV)/Mn(III) 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., 2021; 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(III)-P and Mn(IV)/Mn(III)-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).

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). 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.

Table 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 (FeIII)	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 (FeIII)	1.45	1.90	1.93	5.50	1.93	3.28	2.50	4.93
Hematite (FeIII)	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 (FeIII)	1.01	1.46	1.53	5.11	1.34	2.69	2.11	4.53
$Fe_3(OH)_8$ (FeIII, FeII)	X	X	X	4.32	X	X	X	2.88
Maghemite (FeIII)	X	X	X	6.57	X	1.75	0.57	5.42
Magnesioferrite (FeIII)	X	X	X	6.69	X	0.63	X	4.86
Magnetite (FeIII, 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 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								
$Fe(OH)_{2.7}Cl_{0.3}$	2.23	3.79	2.44	4.34	1.71	4.35	1.41	4.68
Ferrihydrite (FeIII)	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 (FeIII)	1.54	3.03	1.58	3.46	1.03	3.66	0.69	4.04
Hematite (FeIII)	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 (FeIII)	1.14	2.63	1.15	3.02	0.44	3.07	0.29	3.64
$Fe_3(OH)_8$ (FeIII, FeII)	X	X	X	X	X	X	X	1.00
Maghemite (FeIII)	X	1.62	X	2.40	X	2.50	X	3.63
Magnesioferrite (FeIII)	X	1.20	X	1.00	X	1.88	X	2.97
Magnetite (FeIII, 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. 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 findings of this study underscore the importance of targeted management strategies to mitigate dissolved P runoff from CSAs which undergo frequent submergence during rainfall events. The method established in this study can be used as a practical tool for resource managers aiming to reduce P contamination and manage eutrophication risks 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 redox-induced P release from CSAs during short-term submergence; therefore, as future research, the effect of seasonal variations in soil nitrate abundance on P release should be investigated to develop targeted P management strategies.

CRediT authorship contribution statement

Janani Palihakkara: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Lucy Burkitt:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Paramsothy Jeyakumar:** Writing – review & editing, Visualization, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Chammi P. Attanayake:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Janani Palihakkara, Lucy Burkitt & Paramsothy Jeyakumar reports financial support, article publishing charges, and travel were provided by Kathleen Spragg Research Award, New Zealand. Janani Palihakkara reports financial support was provided by AHEAD Scholarship, Sri Lanka. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.124006.

Data availability

Data will be made available on request.

References

Amarawansha, E.A.G.S., Kumaragamage, D., Flaten, D., Zvomuya, F., Tenuta, M., 2015. Phosphorus mobilization from manure-amended and unamended alkaline soils to overlying water during simulated flooding. J. Environ. Qual. 44, 1252–1262. https://doi.org/10.2134/jeq2014.10.0457.

Attanayake, C.P., Dharmakeerthi, R.S., Kumaragamage, D., Indraratne, S.P., Goltz, D., 2022. Flooding-induced inorganic phosphorus transformations in two soils, with and without gypsum amendment. J. Environ. Qual. 51, 90–100. https://doi.org/10.1002/jeq2.20319.

Barlow-Busch, L., Baulch, H.M., Taylor, W.D., 2006. Phosphate uptake by seston and epilithon in the Grand River, southern Ontario. Aquat. Sci. 68, 181–192. https://doi.org/10.1007/s00027-006-0806-9.

Blackmore, L.L., Searle, P.L., Daly, B.K., 1987. New Zealand Soil Bureau Scientific Report, vol. 80. New Zealand.

Buda, A.R., Kleinman, P.J.A., Srinivasan, M.S., Bryant, R.B., Feyereisen, G.W., 2009. Effects of hydrology and field management on phosphorus transport in surface runoff. J. Environ. Qual. 38, 2273–2284. https://doi.org/10.2134/jeq2008.0501.

Che, X., Di, H.J., Cameron, K.C., Dodd, R., 2022. Treating farm dairy effluent with polyferric sulphate dramatically reduces phosphorus and E. coli leaching through subsurface drains—a physical drainage model study. Soil Use Manag. 38, 1493–1504. https://doi.org/10.1111/sum.12809.

Chen, M., Ma, L.Q., 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. Soil Sci. Soc. Am. J. 65, 491–499. https://doi.org/10.2136/sssaj2001.652491x.

Crush, J.R., Easton, H.S., Waller, J.E., 2006. Genetic variation in perennial ryegrass for root profile characteristics. In: Mercer, C.F. (Ed.), Breeding for Success: Diversity in Action. Proceedings of the 13th Australasian Plant Breeding Conference, New Zealand 18-21 April 2006, pp. 1073–1077.

Dahlke, H.E., Easton, Z.M., Lyon, S.W., Todd Walter, M., Destouni, G., Steenhuis, T.S., 2012. Dissecting the variable source area concept - subsurface flow pathways and water mixing processes in a hillslope. J. Hydrol. (Amst) 420, 125–141. https://doi.org/10.1016/j.jhydrol.2011.11.052.

Doody, D.G., Archbold, M., Foy, R.H., Flynn, R., 2012. Approaches to the implementation of the Water Framework Directive: targeting mitigation measures at critical source areas of diffuse phosphorus in Irish catchments. J. Environ. Manag. 93 (1), 225–234. https://doi.org/10.1016/j.jenvman.2011.09.002.

Doody, D., Moles, R., Tunney, H., Kurz, I., Bourke, D., Daly, K., O'Regan, B., 2006. Impact of flow path length and flow rate on phosphorus loss in simulated overland flow from a humic gleysol grassland soil. Sci. Total Environ. 372 (1), 247–255. https://doi.org/10.1016/j.scitotenv.2006.08.029.

Fageria, N.K., Carvalho, G.D., Santos, A.B., Ferreira, E.P.B., Knupp, A.M., 2011. Chemistry of lowland rice soils and nutrient availability. Commun. Soil Sci. Plant Anal. 42, 1913–1933. https://doi.org/10.1080/00103624.2011.591467.

Gustafsson, J.P., 2013. Visual MINTEQ, version 3.1. https://vminteq.com/download/.

Hart, M.R., Quin, B.F., Nguyen, M.L., 2004. Phosphorus runoff from agricultural land and direct fertilizer effects: a review. J. Environ. Qual. 33, 1954–1972. https://doi.org/10.2134/jeq2004.1954.

Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sci. Soc. Am. J. 46, 970–976. https://doi.org/10.2136/sssaj1982.03615995004600050017x.

Hewitt, A.E., Balks, M.R., Lowe, D.J., 2021. The soils of Aotearoa New Zealand. World Soils Book Series. Springer Nature Switzerland. https://doi.org/10.1007/978-3-030-64763-6.

Hudson, J.J., Taylor, W.D., Schindler, D.W., 2000. Phosphate concentrations in lakes. Nature 406, 54–56. https://doi.org/10.1038/35017531.

Kleinman, P.J.A., Srinivasan, M.S., Dell, C.J., Schmidt, J.P., Sharpley, A.N., Bryant, R.B., 2006. Role of rainfall intensity and hydrology in nutrient transport via surface runoff. J. Environ. Qual. 35, 1248–1259. https://doi.org/10.2134/jeq2006.0015.

King, K.W., Williams, M.R., Johnson, L.T., Smith, D.R., LaBarge, G.A., Fausey, N.R., 2017. Phosphorus availability in Western Lake Erie Basin drainage waters: legacy evidence across spatial scales. J. Environ. Qual. 46 (2), 466–469. https://doi.org/10.2134/jeq2016.11.0434.

King, K.W., Williams, M.R., Macrae, M.L., Fausey, N.R., Frankenberger, J., Smith, D.R., Kleinman, P.J.A., Brown, L.C., 2015. Phosphorus transport in agricultural subsurface drainage: a review. J. Environ. Qual. 44, 467–485. https://doi.org/10.2134/jeq2014.04.0163.

Kröger, R., Lizotte, R.E., Douglas Shields, F., Usborne, E., 2012. Inundation influences on bioavailability of phosphorus in managed wetland sediments in agricultural landscapes. J. Environ. Qual. 41, 604–614. https://doi.org/10.2134/jeq2011.0251.

Kumaragamage, D., Concepcion, A., Gregory, C., Goltz, D., Indraratne, S., Amarawansha, G., 2020. Temperature and freezing effects on phosphorus release from soils to overlying floodwater under flooded-anaerobic conditions. J. Environ. Qual. 49, 700–711. https://doi.org/10.1002/jeq2.20062.

Lindsay, W., 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York.

Lou, H., Yang, S., Zhao, C., Shi, L., Wu, L., Wang, Y., Wang, Z., 2016. Detecting and analyzing soil phosphorus loss associated with critical source areas using a remote sensing approach. Sci. Total Environ. 573, 397–408. https://doi.org/10.1016/j.scitotenv.2016.08.048.

Maranguit, D., Guillaume, T., Kuzyakov, Y., 2017. Effects of flooding on phosphorus and iron mobilization in highly weathered soils under different land-use types: short-term effects and mechanisms. Catena 158, 161–170. https://doi.org/10.1016/j.catena.2017.06.023.

Marschner, P., 2021. Processes in submerged soils – linking redox potential, soil organic matter turnover and plants to nutrient cycling. Plant Soil 464, 1–12. https://doi.org/10.1007/s11104-021-05040-6.

McDowell, R., Sinaj, S., Sharpley, A., Frossard, E., 2001. The use of isotopic exchange kinetics to assess phosphorus availability in overland flow and subsurface drainage waters. Soil Sci. 166 (6), 365–373.

McDowell, R.W., Biggs, B.J.F., Sharpley, A.N., Nguyen, L., 2004. Connecting phosphorus loss from agricultural landscapes to surface water quality. Chem. Ecol. 20 (1), 1–40. https://doi.org/10.1080/02757540310001626092.

McDowell, R.W., Nash, D.M., Robertson, F., 2007. Sources of phosphorus lost from a grazed pasture soil receiving simulated rainfall. J. Environ. Qual. 36, 1281–1288. https://doi.org/10.2134/jeq2006.0347.

McDowell, R.W., Sharpley, A.N., 2002. Effect of plot scale and an upslope phosphorus source on phosphorus loss in overland flow. Soil Use Manag. 18, 112–119. https://doi.org/10.1111/j.1475-2743.2002.tb00228.x.

McDowell, R.W., Srinivasan, M.S., 2009. Identifying critical source areas for water quality: 2. Validating the approach for phosphorus and sediment losses in grazed headwater catchments. J. Hydrol. (Amst) 379, 68–80. https://doi.org/10.1016/j.jhydrol.2009.09.045.

McKeague, J.A., Day, J.H., 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46 (1), 13–22. https://doi.org/10.4141/cjss66-003.

Mehlich, A., 1984. Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15, 1409–1416. https://doi.org/10.1080/00103628409367568.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–39. https://doi.org/10.1057/9781137461131.

Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (Eds.), Methods of Soil Analysis, Part 3 Chemical Methods. American Society of Agronomy, Soil Science Society of America, Madison, pp. 961–1010. https://doi.org/10.2136/sssabookser5.3.c34.

Olsen, S.R., Sommers, L.E., 1982. Phosphorus. In: Page, A.L. (Ed.), Methods of Soil Analysis Part 2 Chemical and Microbiological Properties. American Society of Agronomy, Madison, pp. 403–430. Soil Science Society of America.

One Plan, 2024. Horizons regional council. New Zealand. https://www.horizons.govt.nz/CMSPages/GetFile.aspx?guid=ad4efdf3-9447-45a3-93ca-951136c7f3b3.

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.

Pionke, H.B., Gburek, W.J., Sharpley, A.N., 2000. Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. Ecol. Eng. 14 (4), 325–335. https://doi.org/10.1016/S0925-8574(99)00059-2.

Ponnamperuma, F.N., 1972. The chemistry of submerged soils. Adv. Agron. 24, 29–96. https://doi.org/10.1016/S0065-2113(08)60633-1.

Pradhan, S.N., Ghosh, A.K., Seema, Ram, S., Pal, Y., Pradhan, C., 2021. Changes in degree of phosphorus saturation and risk of P loss upon twelve years of manuring and reduced tillage. Geoderma 404. https://doi.org/10.1016/j.geoderma.2021.115277.

Ross, C.A., Moslenko, L.L., Biagi, K.M., Oswald, C.J., Wellen, C.C., Thomas, J.L., Raby, M., Sorichetti, R.J., 2022. Total and dissolved phosphorus losses from agricultural headwater streams during extreme runoff events. Sci. Total Environ. 848. https://doi.org/10.1016/j.scitotenv.2022.157736.

Saunders, W.M.H., 1965. Phosphate retention by New Zealand soils and its relationship to free sesquioxides, organic matter, and other soil properties. New Zeal. J. Agric. Res. 8 (1), 30–57. https://doi.org/10.1080/00288233.1965.10420021.

Scalenghe, R., Edwards, A.C., Barberis, E., Ajmone-Marsan, F., 2012. Are agricultural soils under a continental temperate climate susceptible toepisodic reducing conditions and increased leaching of phosphorus? J. Environ. Manag. 97, 141–147. https://doi.org/10.1016/j.jenvman.2011.11.015.

Sharpley, A.N., Kleinman, P.J.A., Flaten, D.N., Buda, A.R., 2011. Critical source area management of agricultural phosphorus: experiences, challenges and opportunities. Water Sci. Technol. 64, 945–952. https://doi.org/10.2166/wst.2011.712.

Sharpley, A.N., Kleinman, P.J.A., McDowell, R.W., Gitau, M., Bryant, R.B., 2002. Modeling phosphorus transport in agricultural watersheds: processes and possibilities. J. Soil Water Conserv. 57, 425–439.

Shigaki, F., Sharpley, A., Prochnow, L.I., 2007. Rainfall intensity and phosphorus source effects on phosphorus transport in surface runoff from soil trays. Sci. Total Environ. 373, 334–343. https://doi.org/10.1016/j.scitotenv.2006.10.048.

Shore, M., Jordan, P., Mellander, P.E., Kelly-Quinn, M., Wall, D.P., Murphy, P.N.C., Melland, A.R., 2014. Evaluating the critical source area concept of phosphorus loss from soils to water-bodies in agricultural catchments. Sci. Total Environ. 490, 405–415. https://doi.org/10.1016/j.scitotenv.2014.04.122.

Smith, C., Monaghan, R., Mcdowell, R., Carrick, S., 2016. Nitrogen and phosphorus leaching losses from pasture, winter forage crop and native bush sites in the West Matukituki Valley Report prepared for Otago Regional Council. https://www.orc.govt.nz/media/2177/agresearch-report-nitrogen-and-phosphorus-leaching-losses-from-pasture-winter-forage-in-the-west-matukituki-valley.pdf.

Smith, G.J., McDowell, R.W., Condron, L.M., Daly, K., Ó hUallacháin, D., Fenton, O., 2021. Reductive dissolution of phosphorus associated with iron-oxides during saturation in agricultural soil profiles. J. Environ. Qual. 50, 1207–1219. https://doi.org/10.1002/jeq2.20256.

Standards Association of New Zealand (NZS 4402: 1986) Soil Testing Methods. Determination of the Particle Size Distribution Subsidiary Method for Fine Soils (Hydrometer Method).

Tarboton, D.G., 2003. Rainfall-runoff Processes. A Workbook to Accompany the Rainfall-Runoff Processes Web Module. Utah State University. In: https://hydrology.usu.edu/rrp/pdfs/RainfallRunoffProcesses.pdf.

Thomas, I.A., Jordan, P., Mellander, P.E., Fenton, O., Shine, O., Ó hUallacháin, D., Creamer, R., McDonald, N.T., Dunlop, P., Murphy, P.N.C., 2016. Improving the identification of hydrologically sensitive areas using LiDAR DEMs for the delineation and mitigation of critical source areas of diffuse pollution. Sci. Total Environ. 556, 276–290. https://doi.org/10.1016/j.scitotenv.2016.02.183.

Thomas, I.A., Jordan, P., Shine, O., Fenton, O., Mellander, P.E., Dunlop, P., Murphy, P.N.C., 2017. Defining optimal DEM resolutions and point densities for modelling hydrologically sensitive areas in agricultural catchments dominated by microtopography. Int. J. Appl. Earth Obs. Geoinf. 54, 38–52. https://doi.org/10.1016/j.jag.2016.08.012.

Tiessen, H., Moir, J.O., 1993. Characterization of available P by sequential extraction. In: Carter, M.R. (Ed.), Soil Sampling and Methods of Analysis. Lewis Publishers, Boca Raton, pp. 75–86.

Vadas, P.A., Gburek, W.J., Sharpley, A.N., Kleinman, P.J.A., Moore Jr., P.A., Cabrera, M.L., Harmel, R.D., 2007a. A model for phosphorus transformation and runoff loss for surface-applied manures. J. Environ. Qual. 36, 324–332. https://doi.org/10.2134/jeq2006.0213.

Vadas, P.A., Harmel, R.D., Kleinman, P.J.A., 2007b. Transformations of soil and manure phosphorus after surface application of manure to field plots. Nutr. Cycl. Agroecosyst. 77, 83–99. https://doi.org/10.1007/s10705-006-9047-5.

Vitharana, U.W.A., Kumaragamage, D., Balasooriya, B.L.W.K., Indraratne, S.P., Goltz, D., 2021. Phosphorus mobilization in unamended and magnesium sulfate-amended soil monoliths under simulated snowmelt flooding. Environ. Pollut. 287. https://doi.org/10.1016/j.envpol.2021.117619.

Weerasekara, C., Kumaragamage, D., Akinremi, W., Indraratne, S., Goltz, D., 2021. Phosphorus mobilization from intact soil monoliths flooded under simulated summer versus spring snowmelt with intermittent freeze–thaw conditions. J. Environ. Qual. 50, 215–227. https://doi.org/10.1002/jeq2.20182.

Zhang, Y., Huang, L., Zhang, Z., Wei, L., Sun, C., Chen, D., Wu, W., 2016. Phosphorus fractions and phosphorus adsorption characteristics of soils from the water-level fluctuating zone of Nansi Lake, China. Pol. J. Environ. Stud. 25, 865–872. https://doi.org/10.15244/pjoes/61007.