

## **REDOX-INDUCED PHOSPHORUS RELEASE IN DIFFERENT SOILS UNDER SHORT-TERM SUBMERGENCE**

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### **Abstract**

Reductive dissolution of phosphorus (P) associated with iron and manganese oxy(hydr)oxides, dissolution of phosphates upon submergence of soil, and consequent release of P to soil porewater depends on inherent soil characteristics. The released P is subsequently mobilised to ponded water accelerating P accumulation in receiving water bodies. The extent of P release under short-term, frequent submergence is not well-studied in New Zealand soils. This lack of research is particularly experienced in critical source areas (CSAs) which act as pathways for contaminant transport to water ways. A glasshouse study was conducted to explore P dynamics under short-term submergence of three contrasting dairy and sheep/beef farm soils (Recent soil, Pallic soil and Allophanic soil). Five undisturbed soil blocks (20×20×15 cm) were sampled and placed in plastic containers from each site. Porewater samplers and half-cell platinum electrodes were installed in each container at 2 and 10 cm depths below the surface. Soil texture, pH, total organic carbon, Olsen P, cation exchange capacity, and anion storage capacity of the initial soils (0-10 cm depth) were measured. Porewater and pondwater samples were collected immediately after submergence and again three days later, across six repeated submergence events. Redox potentials (Eh) of the two soil depths were measured in-situ. Dissolved reactive phosphorus (DRP), pH, dissolved organic carbon, cations, anions, and alkalinity of the water samples were measured. Soil Olsen P concentrations were 69, 66 and 32 mg P/L, and anion storage capacities were 19, 29, 56% for Recent, Pallic and Allophanic soils, respectively. The average DRP concentration in porewater at the 2 cm depth increased by 154% in Recent soil and 55% in Pallic soil upon submergence. However, the average DRP concentration at the same depth decreased by 40% in the Allophanic soil. The average pondwater DRP concentration increased by 62% in the Recent soil while it decreased by 18 and 63% in the Pallic and Allophanic soils, respectively. The average Eh across soil types and depths was <66 mV upon submergence, suggesting the potential for P release associated with iron and manganese oxy(hydr)oxides. The study continues with P fractionation and modelling to explore the mechanisms of P release and/or sorption upon short-term submergence of these soils.

**Keywords:** Allophanic, dissolved reactive phosphorus, Pallic, Recent, Redox potential

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## **Introduction**

Phosphorus loss from agricultural lands is a major contributor to freshwater contamination (Dharmakeerthi et al. 2019; Smith et al. 2021). The P loss in the form of dissolved P is significant for eutrophication as its readily available for undesirable aquatic growth (Boyd, 2020). Critical source areas located in agricultural lands act as a transport pathway for surface water flow during heavy rainfall, due to their topography. During rainfall events, soil properties of CSAs including soil pH and Eh change due to the anaerobic condition created by frequent submergence. Upon submergence, depending on soil characteristics, soils can release P to porewater by reductive dissolution of iron (Fe) and manganese (Mn) oxy(hydr)oxides, or dissolution of different other phosphates minerals such as calcium, magnesium, iron and manganese phosphates (Fageria et al. 2011). By definition, CSAs contain a transport pathway and contaminant source, but changes in soil chemistry under submergence can enhance further release of dissolved P to porewater which can subsequently end up in nearby freshwater bodies.

The ability of different soils to release P to porewater upon short-term and frequent submergence has not been studied in agricultural landscapes such as CSAs in New Zealand. Therefore, a glasshouse study was conducted to explore P dynamics under short-term submergence of three contrasting soils namely Recent, Pallic and Allophanic soils.

## **Materials and Methods**

Soils were collected from CSAs from Massey University research farms; two dairy farms, Dairy 1 and Dairy 4 and from a sheep/beef farm at Tuapaka. Five undisturbed soil blocks (20×20×15 cm) were sampled and placed in plastic containers from each site. Porewater samplers and half-cell platinum electrodes were installed in each container at 2 and 10 cm depths below the surface. Soil texture, pH, total organic carbon, Olsen P, cation exchange capacity, and anion storage capacity of the initial soils (0-10 cm depth) were measured. Porewater and pondwater samples were collected immediately after submergence (within one hour) and again three days later, across six repeated submergence events. Redox potentials of the two soil depths were measured in situ. Dissolved reactive P, pH, dissolved organic carbon, cations, anions, and alkalinity of the water samples were measured. Statistical analysis was performed using SAS 9.4 software.

## **Results and Discussion**

### ***Initial soil characteristics***

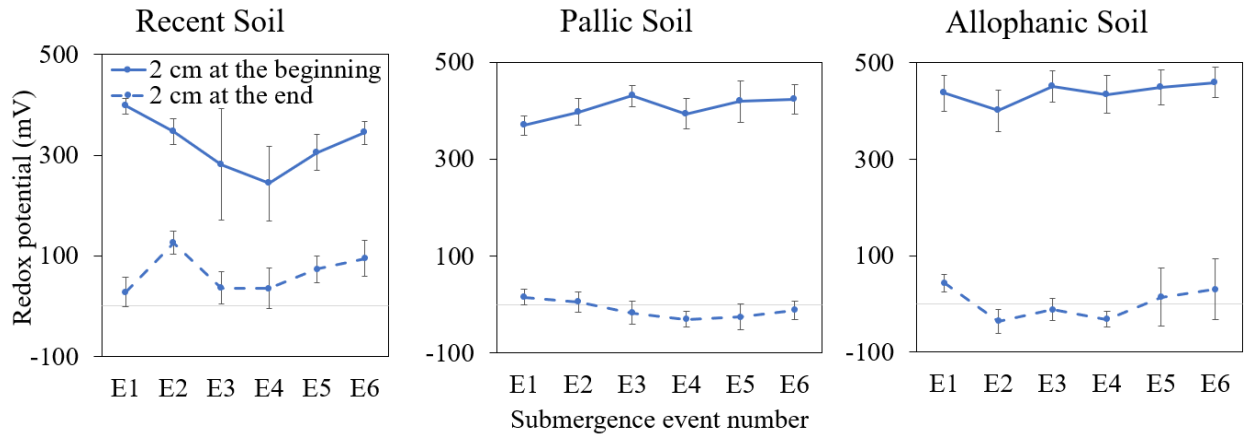
The initial pH of the three soils varied from 5.8 (Pallic soil) to 6.5 (Recent soil) indicating moderately to slightly acidic pH. Both Recent (69 mg/L) and Pallic (66 mg/L) soils had high Olsen P concentrations while the Allophanic soil (32 mg/L) had comparatively low Olsen P concentration. Anion storage capacity was lowest in the Recent soil (19%), moderate in the Pallic soil (29%), and high in the Allophanic soil (56%).

### ***Variation of pH and Eh***

The average pH of porewater at both soil depths and pondwater pH of the six ponding events of the three soils varied in a neutral pH range ranging from 6.7 to 7.7 during submergence. The Eh of any of the three soils did not show significant ( $p>0.05$ ) difference between the two soil depths. Therefore, the Eh values of only 2 cm depth are shown in Figure 1. The Eh of 2 cm depth decreased

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significantly ( $p < 0.0001$ ) with submergence in the three soils (Figure 1). As an average of the six ponding events, the reduced Eh values of the 2 cm depth were 66 mV in Recent soil, -11 mV in Pallic soil and 1 mV in Allophanic soil. According to literature, in neutral soils ( $\text{pH} = 7$ ) in the presence of equal concentrations of oxidant and reductant, Mn(IV) ions reduce to Mn(II) ions at the redox range of 200 to 100 mV and Fe(III) ions reduce to Fe(II) ions at the redox range of 0 to -100 mV (Marschner 2021). Therefore, the Eh reduction of the three soils suggests the potential reduction of Mn and/or Fe oxy(hydr)oxides.

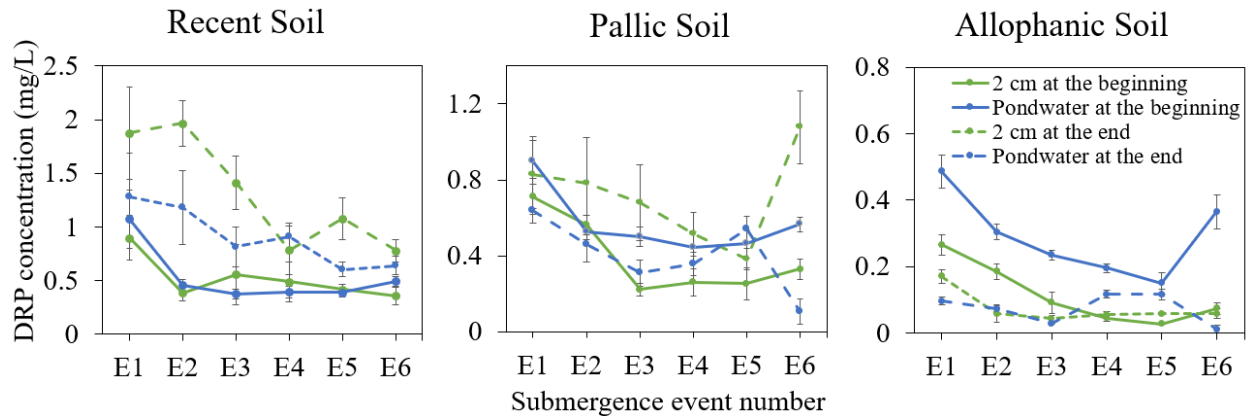


**Figure 1:** Variation of pH and Eh at the 2 cm depth with each ponding event in Recent, Pallic and Allophanic soils. The error bars represent the standard errors of the means.

#### ***Variation of porewater and floodwater DRP***

The P release upon submergence was significantly ( $p < 0.0001$ ) different among the three soils (Figure 2). The average DRP concentration in porewater at the 2 cm depth increased by 154% in the Recent soil and 55% in the Pallic soil upon submergence. However, the average DRP concentration at the same depth decreased by 40% in the Allophanic soil. The average pondwater DRP concentration increased by 62% in the Recent soil while it decreased by 18% and 63% in the Pallic and the Allophanic soils, respectively.

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**Figure 2:** Variations of dissolved reactive phosphorus (DRP) of porewater at 2 cm depth and pondwater of Recent, Pallic, and Allophanic soils with each ponding event. The error bars represent the standard errors of the means. Different scales are used for the DRP concentration (Y axis) of the three soils. The green colour lines represent porewater and the blue colour lines represent pondwater DRP.

The Recent soils released P to porewater and subsequently released P to overlaying pondwater (Figure 2). The Pallic soils released P upon submergence, but it did not increase pondwater P concentration. The Allophanic soils did not release P to porewater and decreased pondwater DRP significantly ( $p < 0.0001$ ) with submergence. These results suggest a probable resorption of the released P, particularly in the Pallic and the Allophanic soils.

## Conclusions

Redox conditions in the three soils reduced enough to release P associated with Mn or/and Fe oxy(hydr)oxides and phosphates. However, the three contrasting soils showed different P release patterns upon short-term and frequent submergence. The Recent soil which had the lowest anion storage capacity showed the highest P release upon submergence, while the Allophanic soil which had the highest anion storage capacity showed no P release to porewater or to pondwater during this period, probably due to resorption of the released P. This study continues with P fractionation and modelling to explore the mechanisms of P release and/or sorption upon short-term submergence of these soils.

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