REDOX-INDUCED PHOSPHORUS RELEASE IN CRITICAL SOURCE AREAS UNDER SHORT-TERM SUBMERGENCE IN WINTER

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Abstract

Critical source areas (CSA) contribute significant nutrient loss from pastoral lands in New Zealand. The potential contribution of phosphorus (P) from these areas due to short-term, but repeated submergence of soils during winter seasons, is not well studied. A field study was conducted to explore P dynamics under short-term submergence of two dairy farm soils (Recent Soil and Pallic Soil) at Massey University, in ephemeral flow pathways which act as CSA during wet weather. Ten sampling stations were installed in each field enabling the sampling of porewater from 2 and 10 cm depths below the surface. Porewater and floodwater samples were collected within 24 hours after five rainfall events from July to August 2022. Soil texture, Olsen P, Mehlich extractable P, and anion storage capacity (ASC) of the initial soils (0- 10 cm depth) were measured. Redox potentials (Eh) of the two soil depths were measured in situ. Dissolved reactive phosphorus (DRP), pH, dissolved organic carbon, selected cations, and alkalinity of the collected water samples were measured. Sand and clay percentages for the Recent Soil were 39 and 18%, respectively, and 14 and 32% for Pallic Soil, respectively. Olsen P (69 and 66 mg P/L) and Mehlich 3 extractable P concentrations were similar (147 and 133 mg P/L, for Recent and Pallic, respectively) between the two soils. The Pallic Soil showed higher ASC (29%) than the Recent Soil (19%). The pH of water samples was in the neutral range in both soils. The average DRP concentration in porewater (2 cm) varied from 0.65 to 1.03 mg/L in the Recent Soil, and the range was from 0.26 to 2.31 mg/L in the Pallic Soil during the study period. The average floodwater DRP concentration varied from 0.13 to 0.87 (Recent Soil) and 0.19 to 0.54 mg/L (Pallic Soil). The average Eh of both depths for the two soils showed less than 33 mV, indicating that both soils were reduced enough to release P associated with Fe and Mn oxy(hydr)oxides, enhancing the risk of P loss to water. The study continues with P fractionation modelling to explore the mechanisms and relationships behind P release upon submergence in the CSA.

Keywords: Critical source areas, dissolved reactive phosphorus, Pallic Soil, Recent Soil, redox potential

Introduction

Critical source areas accumulate runoff from adjacent slopes and flats and deliver to nearby water ways. They generally represent about 20% of the farmland area but contribute to about 80% of P loss from the farm (McDowell and Sinivasan, 2009). Livestock manure and elevated soil P fertility act as major sources of P in CSA and there is a possibility of soil acting as a P source itself when it is submerged.

Soils release P when they are submerged, mainly due to reductive dissolution of iron and manganese phosphates and dissolution of calcium and magnesium phosphates (Jayarathne et al, 2016; Amarawansha et al, 2015), which are under the direct influence of Eh and pH variations in soil. But this release is due to a collaborative process of different inherent soil characteristics such as clay mineralogy, P sorption capacity and soil organic matter. For example, in highly weathered tropical soils, the released P upon submergence can be resorbed to the surfaces of sparingly available Fe/Al oxy(hydr)oxide which perhaps results in zero net release of P. On the other hand, in alkaline soils with more active clay in the temperate zones, a steady increase of P over the submergence period has been reported (Amarawansha et al, 2015).

The concept of CSA had been studied around the world since mid-1990 (Sharpley et al, 2011). However, no previous studies appear to examine the ability of CSA to act as a source of P during winter in pasture soils in New Zealand, as per our knowledge. The mechanism and the relationship between P release and soil characteristics are also rarely studied in relation to CSA. Therefore, a field study was conducted to explore P dynamics under short-term submergence on two dairy farm soils (Recent Soil and Pallic Soil) at Massey University, in ephemeral flow pathways which act as CSA during wet weather.

Materials and Methods

Study sites

Two CSA sites were selected at Dairy Farm 1 and Dairy Farm 4 at Massey University, Palmerston North, New Zealand (Figure 1). The soil types were Recent Soil and Pallic Soil in Dairy Farm 1 and 4, respectively. Ten sampling stations were installed in each farm in an area of 6×2 m^2. Each sampling station had two porewater samplers at two depths (2 cm and 10 cm below the ground level) and two platinum half-cell electrodes at the same two depths.

Figure 1: The study sites at dairy farms located at Massey University, Palmerston North, New Zealand A: Dairy Farm 1 (Recent Soil), B: Dairy Farm 4 (Pallic Soil)

Sample collection

Representative bulk soil samples (0-10 cm depth) were collected from both fields for initial soil characterisation. Porewater was collected within 24 hours after five rainfall events during July to August 2022. The floodwater drainage pattern of the two sites were different. Water accumulated with time following a rainfall event at Dairy farm 1 and it drained off quickly following a rainfall event at Dairy farm 4. Therefore, a sufficient amount of porewater was collected only in four events out of five at each site. Floodwater was collected close to the soil surface using a syringe. Redox potential was measured using a Ag/AgCl reference electrode and a voltmeter in-situ. 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 Nernst equation (Lindsay, 1979).

Sample analysis

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) within 12 hours of collection. The pH of porewater samples was measured using a glass pH electrode. Cation concentrations (Ca, Mg, K, Na, Fe, Al, and Mn) of porewater were measured using MP- AES. Dissolved organic carbon concentrations were measured using a TC/TN analyser. Alkalinity of the porewater samples was measured by titrating against 0.1 N H_2SO_4 in the presence of methyl orange indicator. All the data will be used as input data for the thermodynamic modelling software to predict P dynamics.

Results and Discussion

Initial soil characteristics

Selected initial soil characteristics of both soils are given in Table 1. The initial soil pH of the two soils were slightly acidic to neutral. The silt percentages of the soils were > 40%. The Olsen P

concentrations of the two soils were similar, but high (>60 mg/L). The ASC of both soils was < 30% indicating low P retention, but the Recent Soil had the lower ASC at 19%.

Table 1: Selected initial characteristics of soils

	Recent Soil	Pallic Soil
pH	6.5	5.8
Sand %	39	14
Silt %	43	54
Clay %	18	32
Olsen P (mg/L)	69	66
Anion storage capacity %	19	29
CEC (me/100g)	12	22
Total organic carbon (g/100g)	2	5
Mehlich 3 extractable cations		
Ca (mg/L)	1233	1735
Mg (mg/L)	170	254
Fe (mg/L)	681	545
Mn (mg/L)	46	75

Variation of Eh, pH and pe

The average Eh of the Recent Soil following the four rainfall events was -43 ($\pm$13) mV and 16 ($\pm$6) mV at 2 cm and 10 cm depths, respectively. In the Pallic Soil, the average Eh was -84 ($\pm$14) mV and -5 ($\pm$12) mV at 2 cm and 10 cm depths, respectively. The Eh of the 10 cm depth was higher than that of the 2 cm depth, in both soils. This may be due to a fine silt layer on the runoff pathway obstructing water infiltration below ground level. This could create a comparatively oxic layer towards the subsoil layers compared to the topsoil. A theory which was visibly observed in fresh soil profiles taken from both study sites.

Soil Eh reduces gradually after submergence. The sequential reduction of Mn^{4+} to Mn^{2+} and Fe^{3+} to Fe^{2+} occur in between 280-220 mV and 180-150 mV, respectively (Sahrawat, 2004). In this experiement, the highest average Eh of single rainfall events of the two soils was <33 mV which is lower than the above values.
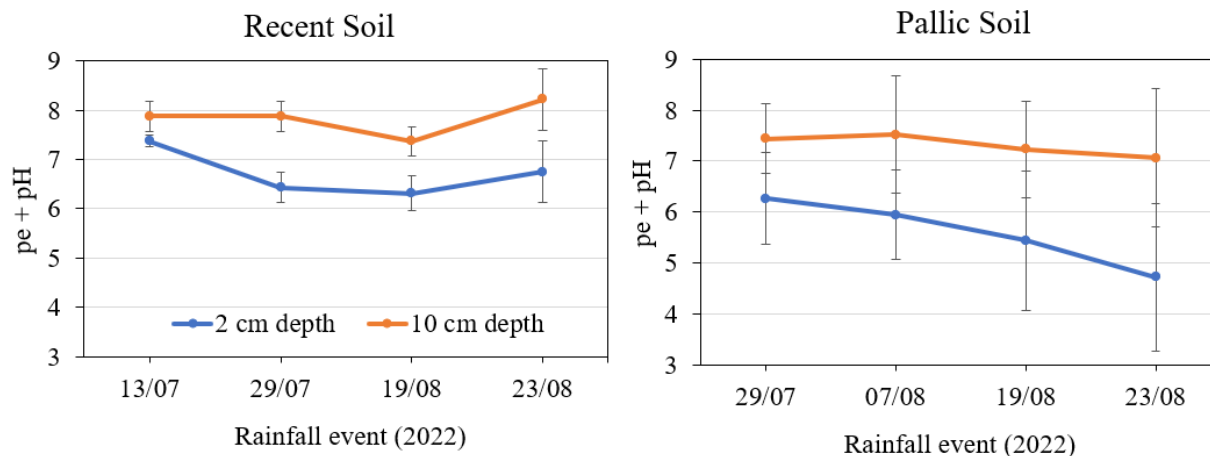
Figure 2: Variation of pe + pH at two study sites following rainfall events between July and August 2022. Mean values ± standard error of means are shown in the graphs.

The pH of the porewater samples from the Recent Soil ranged from 7.3 to 7.5 at 2 cm depth and 7.2 to 8.1 at the 10 cm depth. In the Pallic Soil, it varied from 7.1 to 7.4 at 2 cm depth and 7.2 to 7.8 at the 10 cm depth. The initial soil pH of both soils had increased with submergence. The reason may be the consumption of H$^+$ ions for the reduction of Fe and Mn oxides during submergence (Fageria et al., 2011; Ponnamperuma, 1972).

Figure 2 shows the variation of pe + pH of the two soils during the rainfall events. The parameter pe + pH is a single term expression for defining the redox status of aqueous systems (Lindsay, 1979). Further, many redox induced mineral transformations in soils occur at fixed pe + pH values. The pe + pH is > 14 for oxic soils, between 9 and 14 for suboxic soils, and < 9 for anoxic soils (Essington, 2004). The pe + pH value varied between 9 and 6 in the Recent Soil and between 9 and 3 in the Pallic Soil. Therefore, the redox status was anoxic in both soils during the observed rainfall events.

Variation of porewater and floodwater DRP

The variation of porewater and floodwater DRP of the two sites during July to August rainfall events is shown in Figure 3. The average porewater DRP concentration varied from 0.65 (±0.13) to 1.03 (±0.37) mg/L and from 0.32 (±0.13) to 0.98 (±0.71) mg/L at 2 cm and 10 cm depths respectively in the Recent Soil. The porewater DRP concentration ranged from 0.26 (±0.04) to 2.31 (±0.92) mg/L and from 0.27 (±0.05) to 1.02 (±0.26) mg/L at 2 cm and 10 cm depths respectively in the Pallic Soil. The average floodwater DRP concentration varied from 0.13 (±0.01) to 0.87 (±0.14) and 0.19 (±0.02) to 0.54 (±0.04) mg/L in the Recent and Pallic Soils, respectively.
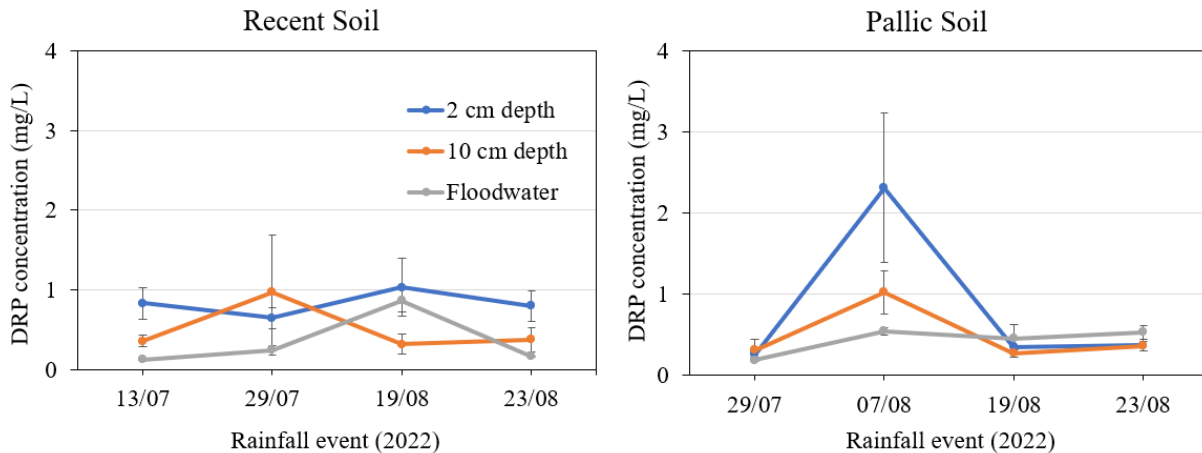
Figure 3: Variation of porewater and floodwater DRP at two study sites following rainfall events between July and August 2022. Mean values ± standard error of means are shown in the graphs

The average porewater DRP concentration from the four rainfall events at the 2 cm depth was 1.63 times and 1.67 times higher than that of the 10 cm depth in Recent and Pallic Soils respectively. The average porewater DRP concentration was higher in the 2 cm than the 10 cm depths in both soils. This observation is in agreement with the more anoxic condition in soils at 2 cm depth compared to the soils at 10 cm depth suggesting that the reductive dissolution reactions contribute to P release from soils in CSA. The nature of the inherent clay mineralogy (eg: presence of Fe and Mn oxy(hydr)oxides) of the two layers in the two soils would also contribute the DRP differences in the two depths. The average porewater DRP concentration measured from the four rainfall events at the 2 cm depth was 2.35 times and 1.92 times higher than the floodwater DRP concentration from the Recent and Pallic Soil surface, respectively. Although the floodwater DRP may contain P from other sources such as fertiliser or animal manure deposits on the runoff pathway, it can be assumed based on the literature, that the two soils studied may also be contributing to the DRP elevation in floodwater, considering the DRP gradient measured between the soil and the floodwater close to the soil surface. The floodwater DRP was lower compared the porewater DRP regardless of the P addition to floodwater from P sources such as fertiliser and animal manure. Therefore, the reductive dissolution may contribute to significant P loss from the system than the P losses from other P sources through runoff.

Conclusions

Redox potential of both the Recent and Pallic Soils was reduced enough to release P attached to Fe and Mn oxy(hydr)oxides during the observed rainfall events. More P release was observed in the surface layer which was more reduced compared to the subsurface layer. Loss of P through reductive dissolution seems more significant in CSA than the P loss from source P (i.e. manure and P fertilisers) through runoff. The floodwater DRP was more than 10 times higher than the New Zealand's lowland river DRP target concentration of 0.011 mg/L. This indicates a potential risk of freshwater contamination. However, further investigation the P fractionation and modelling of P minerals will be completed to explain the P dynamics in these soils and to explore the relationship between soil characteristics and P release upon submergence in these soils.

Acknowledgement

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