

# Degree of Phosphorus Saturation as a Predictor of Redox-Induced Phosphorus Release from Flooded Soils to Floodwater

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## Abstract

Phosphorus (P) loss from soils is often enhanced under flooded, anaerobic conditions, increasing the risk of freshwater eutrophication. We aimed to develop a predictive tool to identify soils with greater P release potential under summer-flooded conditions, which would help in developing strategies to mitigate P losses. One in situ mesocosm study was conducted in field plots with three treatments: cattle manure amended, monoammonium phosphate amended, and unamended. Two ex situ field mesocosm studies were conducted, each having 12 surface soils from agricultural fields. Prior to flooding, soils were analyzed for various soil test P (STP, intensity) and P sorption measures (capacity), and degree of P saturation (DPS) indices were calculated using different intensity and capacity combinations. Mesocosms were flooded and redox potential, pore water, and floodwater dissolved reactive P (DRP) concentrations were determined periodically up to 42 (in situ) and 56 d (ex situ) after the onset of flooding. Floodwater DRP increased significantly in most soils with flooding time, and the maximum DRP ( $DRP_{max}$ ) was considered as the flooding-induced P release risk. Relationships between floodwater  $DRP_{max}$  and STP or DPS indices were established separately for low-P (Olsen  $P \leq 30$  mg kg<sup>-1</sup>) and high-P (>30 mg kg<sup>-1</sup>) soils. Several STP indices effectively predicted the P release risk from high-P soils, but not from low-P soils. However, DPS calculated using Olsen P (intensity) and P sorption capacity or P saturation index (capacity) performed better in predicting summer flooding-induced P release across all soil categories, with a higher predictive power.

## Core Ideas

- Floodwater P concentration increased with flooding time in most soils.
- High P release risk with flooding was shown even in soils with low soil test P.
- Soil test P was not a good predictor of flooding-induced risk of P release from soils.
- Several degree of P saturation indices were better predictors than soil test P.
- Identifying soils with high P release risk can help in efforts to mitigate P losses.

PHOSPHORUS (P) is a major nonpoint source water pollutant (Carpenter et al., 1998), and its presence, even at low concentrations, can impair water quality of freshwater bodies through stimulating algal growth (Daniel et al., 1998; Schindler et al., 2012, 2016). Phosphorus loss from agricultural soils is a major source of P to waterways that are regulated by various biogeochemical and hydrological processes (Heathwaite and Dils, 2000; McDowell et al., 2001). In the northern Great Plains of North America, most lands are poorly drained due to relatively flat landscapes and low-permeable soils (Bedard-Haughn, 2009; Corriveau et al., 2013), frequently leading to flooding during spring snowmelt and summer precipitation events (Heathwaite and Dils, 2000; Villarini, 2016). Prolonged flooding makes the soils anaerobic (Young and Ross, 2001; Amarawansa et al., 2015), a condition that can release substantial amounts of P from soils to pore water (Ajmone-Marsan et al., 2006; Scalenghe et al., 2014) and subsequently diffuse to floodwater (Amarawansa et al., 2015; Jayarathne et al., 2016). Thus, the concentration of dissolved reactive P (DRP), the predominant form of P loss from agricultural field in the region (Little et al., 2007; Cade-Menun et al., 2013), as well as the most bioavailable form of P (Daloğlu et al., 2012), will increase in the overlying floodwater, which may get transported out of the field and contribute toward P enrichment of water bodies.

Research investigating flooding-induced P release from soils revealed that the magnitude of P released from flooded soils varies with soil properties and time of flooding (Shenker et al., 2005; Amarawansa et al., 2015; Jayarathne et al., 2016). It has been also reported that P release is greater under warmer temperatures ( $+20 \pm 2^\circ\text{C}$ ) than colder temperatures ( $+4 \pm 1^\circ\text{C}$ ), suggesting greater P release from soils under summer flooding than spring snowmelt flooding (Dharmakeerthi et al., 2019). In alkaline and calcareous soils typical of the northern Great Plains, the change in DRP concentrations in floodwater ranged widely, from a slight decrease to >15-fold increase with time of flooding under laboratory conditions (Amarawansa et al., 2015; Jayarathne et al., 2016). Huge variations in P release in soils with flooding make it extremely

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**Abbreviations:** DAF, days after flooding; DPS, degree of phosphorus saturation; DRP, dissolved reactive phosphorus;  $DRP_{max}$ , maximum dissolved reactive phosphorus concentration in floodwater; Eh, redox potential;  $M3P_{MBP}$ , Mehlich-3 extractable molybdate reactive phosphorus;  $M3P_{TP}$ , Mehlich-3 extractable total phosphorus; PSI, phosphorus saturation index; STP, soil test phosphorus.

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challenging to make decisions regarding drainage management to minimize P losses to floodwater. Therefore, identifying soils that have a greater potential for P release, prior to impending flooding event, would help in developing drainage management strategies to reduce P loadings to waterways.

The degree of P saturation (DPS), defined as the ratio of extractable P or labile P to the sorption capacity of soil (Sharpley, 1995; Zhou and Li, 2001) has been effective in predicting potential P release from flooded, anaerobic soils in the laboratory under controlled environments (Sallade and Sims, 1997; Amarawansa et al., 2016). However, to our knowledge, the reliability of using DPS to predict the flooding-induced P release from diverse soils under field-flooded conditions has not been documented. We hypothesized that DPS measured prior to flooding could effectively predict the potential flooding-induced P release from soils under field conditions. To test this hypothesis, we conducted field mesocosm studies under summer flooding with the following objectives: to investigate (i) the effect of flooding on DRP concentrations in pore water and floodwater, (ii) whether pre-flooded soil test P (STP) and DPS (calculated using different equations) indices can be used to predict the flooding-induced P release, and (iii) whether pre-flooding fertilization treatments have any impact on the DRP concentrations in pore water and floodwater (evaluated in the in situ experiment).

## Materials and Methods

### Field Mesocosm Experiments

We conducted three separate mesocosm experiments with packed soils under field conditions. Two ex situ mesocosm studies were conducted at the “Point” Field Research Laboratory located on the University of Manitoba’s Fort Garry Campus in Winnipeg, MB, Canada. An in situ mesocosm experiment was conducted in an experimental field at the Glenlea Research Station in the Red River Valley of southern Manitoba, Canada (49°38′25″ N, 97°8′28″ W, 238 m asl).

Twenty-four (12 in 2013, and 12 in 2014) surface soils (0- to 15-cm depth) were collected from agricultural fields in different locations of Manitoba, which included flood-prone areas of the Interlake Region and the Red River basin for the two ex situ mesocosm studies (Supplemental Table S1). Fields selected had no recent history (in the past 6 mo) of livestock manure or synthetic P fertilizer applications. A subsample of each soil was air dried, sieved (2 mm), and analyzed for initial properties. Plastic tubs (46-cm i.d., 40-cm height) packed to a depth of 15 cm with 12 field-moist soils were used as mesocosms for each study. Soils were packed to have a bulk density of 1.2 g cm<sup>-3</sup> for coarse-textured soils and 1.0 g cm<sup>-3</sup> for fine-textured soils by calculating the fresh soil weight to be packed using the total volume of the tub for 15-cm depth and the moisture factor. Packed soil mesocosms were then buried in the field to a depth of 15 cm. For each ex situ mesocosm study, 12 soils were replicated four times and arranged in a randomized complete block design.

A field site for the in situ mesocosm study was established with three fertility treatments (unamended, solid cattle manure amended, or monoammonium phosphate amended), with four replicated plots arranged in a randomized complete block design. Manure and fertilizer were applied at a rate of 100 kg of total P ha<sup>-1</sup>. All plots were 2 × 2 m and were roto-tilled twice to thoroughly incorporate the manure and fertilizer into the

soil. One month after treatment application, mesocosms (1 × 1 m) were constructed at the center of each plot by excavating the upper 15 cm of soil, installing a watertight liner, then replacing the excavated soil back inside the liner. Each mesocosm had a wooden frame enclosure to hold the vinyl liner high enough to allow water ponding to a depth of 15 cm above the soil surface.

In both in situ and ex situ mesocosm experiments, a Rhizon flex pore water sampler with a 2.5-mm o.d. and 0.15- $\mu$ m pore size (Rhizosphere Research Products) was permanently installed at 10 cm below the soil surface to extract pore water. A redox potential probe (Paleo Terra) with a platinum sensor was also installed at 10-cm depth in each mesocosm to measure the soil redox potential (Eh). Mesocosms were ponded to a depth of 15 cm above the surface (Fig. 1) using reverse osmosis water with low concentrations of P (<0.005 mg L<sup>-1</sup>), and each mesocosm was protected from rainwater with a plastic cover fastened at an angle to allow free exchange of air. The soils were kept under simulated summer flooded conditions for a period of 42 d (in situ experiment) or 56 d (ex situ experiment). Pore water and floodwater from mesocosms were collected immediately after inundation and twice a week for in situ experiment or once a week for ex situ experiments, over the flooding period. Pore water samples were extracted using syringes attached to the end of the Rhizon flex pore water samplers. Overlying floodwater samples were taken using a syringe from the center of the mesocosms and immediately filtered through 0.45- $\mu$ m membrane filters. Floodwater and pore water samples were analyzed for dissolved reactive P (DRP) within 8 h using the molybdate blue color method (Murphy and Riley, 1962). Soil Eh was measured using permanently installed Pt electrodes coupled with a temporarily installed silver–silver chloride reference electrode and a portable millivolt meter on each day of the sampling. Redox readings were adjusted to that of a standard hydrogen electrode.

### Analysis of Pre-Flooded Soil Samples

Subsamples of each soil used for the ex situ mesocosm studies and soil samples taken from unamended, manured, and fertilized plots from the in situ mesocosm study prior to flooding were air dried, sieved (2 mm), and analyzed for texture (Pipette method; Gee and Bauder, 1986), organic matter content (loss-on-ignition; Dean, 1974), pH (1:2 soil/water suspension), electrical conductivity (1:2 soil/water), Olsen P (Olsen et al., 1954), and Mehlich-3 extractable P, calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), and aluminum (Al) (Mehlich, 1984). Molybdate reactive P in Olsen (Olsen P) and Mehlich-3 extracts (M3P<sub>MRP</sub>) was determined by the molybdate blue color method (Murphy and Riley, 1962), and absorbance was measured at 882 nm using an Ultraspec 2100 Pro ultraviolet–visible spectrophotometer. Mehlich-3 extractable total P (M3P<sub>TP</sub>), Ca, Mg, Fe, Mn, and Al were determined using inductively coupled plasma atomic emission spectroscopy (iCAP 6500, Thermo Scientific).

A single-point P adsorption study was conducted to identify the P sorption ability of each soil by equilibrating a soil sample with a solution containing 150 mg P L<sup>-1</sup>, as previously described (Amarawansa et al., 2016). The amount of P sorbed ( $P_{150}$ ) was determined by the difference between the amount of P added to the soil and the equilibrium P solution concentration. Phosphorus sorption index (PSI) was calculated by dividing the amount of P sorbed (mg P kg<sup>-1</sup> soil) by the logarithm of the P concentration in the equilibrium solution (Bache and Williams, 1971; Börling et al., 2001).

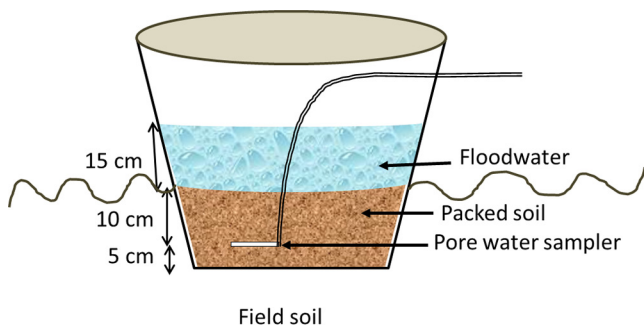


Fig. 1. A schematic drawing of the experimental setup for ex situ and in situ mesocosm studies.

## Calculation of Degree of Phosphorus Saturation

The DPS is calculated as the ratio between the intensity factor (soil extractable P) to the capacity factor (P sorption capacity) expressed as a percentage (Sallade and Sims, 1997; Ige et al., 2005; Xue et al., 2014). For this study, we calculated DPS using 15 different equations (Eq. [1]–[15]). In a previous study under laboratory conditions, DPS indices calculated from Eq. [1] to [6] were used as variables to develop a model to predict P release from flooded, alkaline soils (Amarawansa et al., 2016). In addition to these six DPS measures, we calculated DPS using Eq. [7] to [9], previously proposed for neutral to alkaline soils in Manitoba (Ige et al., 2005). In all these equations (Eq. [1]–[9]),  $P_{150}$  or Mehlich-3 extractable Ca + Mg [ $M3(Ca+Mg)$ ] were taken as the measure of the P sorption capacity. Since PSI is known to be a good parameter to predict P release into surface waters (Sallade and Sims, 1997; Hughes et al., 2000), we used six more equations (Eq. [10]–[15]) where  $P_{150}$  was replaced by PSI from Eq. [1] to [3] and Eq. [7] to [9].

$$DPS_1 = \frac{\text{Olsen P}}{2P_{150} + \text{Olsen P}} \times 100 \quad [1]$$

$$DPS_2 = \frac{M3P_{MRP}}{2P_{150} + M3P_{MRP}} \times 100 \quad [2]$$

$$DPS_3 = \frac{M3P_{TP}}{2P_{150} + M3P_{TP}} \times 100 \quad [3]$$

$$DPS_4 = \frac{\text{Olsen P}}{\alpha[M3(Ca + Mg)] + \text{Olsen P}} \times 100 \quad [4]$$

$$DPS_5 = \frac{M3P_{MRP}}{\alpha[M3(Ca + Mg)] + M3P_{MRP}} \times 100 \quad [5]$$

$$DPS_6 = \frac{M3P_{TP}}{\alpha[M3(Ca + Mg)] + M3P_{TP}} \times 100 \quad [6]$$

$$DPS_7 = \frac{\text{Olsen P}}{P_{150}} \times 100 \quad [7]$$

$$DPS_8 = \frac{M3P_{MRP}}{P_{150}} \times 100 \quad [8]$$

$$DPS_9 = \frac{M3P_{TP}}{P_{150}} \times 100 \quad [9]$$

$$DPS_{10} = \frac{\text{Olsen P}}{2PSI + \text{Olsen P}} \times 100 \quad [10]$$

$$DPS_{11} = \frac{M3P_{MRP}}{2PSI + M3P_{MRP}} \times 100 \quad [11]$$

$$DPS_{12} = \frac{M3P_{TP}}{2PSI + M3P_{TP}} \times 100 \quad [12]$$

$$DPS_{13} = \frac{\text{Olsen P}}{PSI} \times 100 \quad [13]$$

$$DPS_{14} = \frac{M3P_{MRP}}{PSI} \times 100 \quad [14]$$

$$DPS_{15} = \frac{M3P_{TP}}{PSI} \times 100 \quad [15]$$

In the above equations,  $\alpha$  is the slope of the regression line of  $2P_{150}$  against Mehlich-3 extractable (Ca + Mg) through the origin. We used  $\alpha = 0.1$  as used previously for Manitoba soils (Akinremi et al., 2007; Amarawansa et al., 2016).

## Statistical Analysis

Analysis of variance was performed separately for each of the three mesocosm studies for Eh, and both DRP in pore water and floodwater using the MIXED procedure of SAS version 9.3 (SAS Institute, 2008). Normality was evaluated using Shapiro–Wilk’s test from PROC UNIVARIATE, and variables with  $W \leq 0.9$  were natural-log transformed prior to statistical analysis. For the ex situ mesocosm studies, soil was analyzed as the fixed variable and days after flooding (DAF) as the repeated measures factor. For the in situ mesocosm study, treatment was the fixed variable and DAF was the repeated measures factor. Mean comparisons for all studies were performed using the LSMeans statement in SAS with the diff option and the Tukey–Kramer adjustment for multiple comparisons. Linear regression analysis was performed to establish quantitative relationships between maximum DRP concentration ( $DRP_{max}$ ) in floodwater during the flooding period and various STP and DPS indices using the IBM SPSS version 19 software (IBM Corporation, 2010). For all statistical analyses, the threshold for determining significance was  $P < 0.05$ .

## Results and Discussion

### Soil Properties and Phosphorus Status

The soils used for the three mesocosm studies were highly variable in their physical and chemical properties (Supplemental Table S1). The available P concentrations and P sorption capacities also varied widely, resulting in a wide range of calculated values of different DPS indices (Supplemental Table S2). Application of fertilizer and manure in the in situ mesocosm study significantly ( $P < 0.05$ ) increased the STP concentrations prior to flooding, with greater increases in the fertilized treatment than in the manured treatment, irrespective of the STP method used.

Similar results have been previously reported for various STP comparing manured and fertilized soils (Kumaragamage et al., 2011). The greater increase in STP with the application of synthetic fertilizer compared with solid cattle manure was likely due to the larger proportion of total P in water-soluble forms in synthetic fertilizer than in solid cattle manure, whereas solid cattle manure has a larger proportion of P in nonlabile and recalcitrant forms (Kumaragamage et al., 2012). Application of fertilizer or manure slightly, but significantly, decreased the P sorption capacity measured as  $P_{150}$  and PSI (Supplemental Table S1).

The DPS values ranged from 0.6 to 130.1% with the lowest DPS values for  $DPS_1$  calculated using Olsen P and  $P_{150}$  (Eq. [1]), whereas the  $DPS_{15}$ , calculated using  $M3P_{TP}$  and the PSI (Eq. [15]), gave the greatest DPS values in general. Soils with low Olsen or Mehlich-3 extractable P generally had lower DPS values and vice versa, with a few exceptions (Supplemental Table S2). As expected, the application of synthetic P fertilizer or livestock manure increased the DPS values in the in situ mesocosm study, with greater increases in the fertilized than in the manured treatment.

### Redox Potential Changes with Flooding

At 0 DAF, the Eh values of soils ranged between +240 and +492 mV and decreased with DAF in all soils used for the three mesocosm studies. Different trends in Eh changes with flooding are illustrated in Fig. 2a and 2b for soils from ex situ mesocosm

Studies 1 and 2, respectively. By the 56th DAF, all except for five soils were reduced to less than +100 mV, the approximate threshold Eh value at which  $Fe^{3+}$  is reduced to  $Fe^{2+}$  (Gotoh and Patrick, 1974). In both ex situ mesocosm studies, we observed a significant soil  $\times$  DAF interaction for Eh changes ( $P < 0.05$ ). Both the rate and the degree of Eh reduction varied among soils (Fig. 2a and 2b), which is to be expected since the redox reactions are microbially mediated and thus depend on soil properties influencing the microbial activity and the nature and content of electron acceptors in soils (Ponnamperuma, 1972). In all soils, Eh at 56 DAF was significantly ( $P < 0.05$ ) less than the initial Eh at 0 DAF.

For the in situ mesocosm study, the main effect of DAF was significant for Eh, but the treatment effect and treatment  $\times$  DAF interaction were not significant. In all treatments, Eh at the end of 42 DAF was significantly lower than at 0 DAF with values near 0 mV (Fig. 2c).

### Pore Water and Floodwater Dissolved Reactive Phosphorus Concentration Changes with Time of Flooding

Pore water DRP concentrations of flooded soils increased with time of flooding in both ex situ mesocosm studies (Fig. 3) with the range of increase of 1.3-fold (Scanterbury 1) to 9.7-fold (Arborg) compared with the concentration on 0 DAF. The soil  $\times$  DAF interaction effect on pore water DRP concentration was

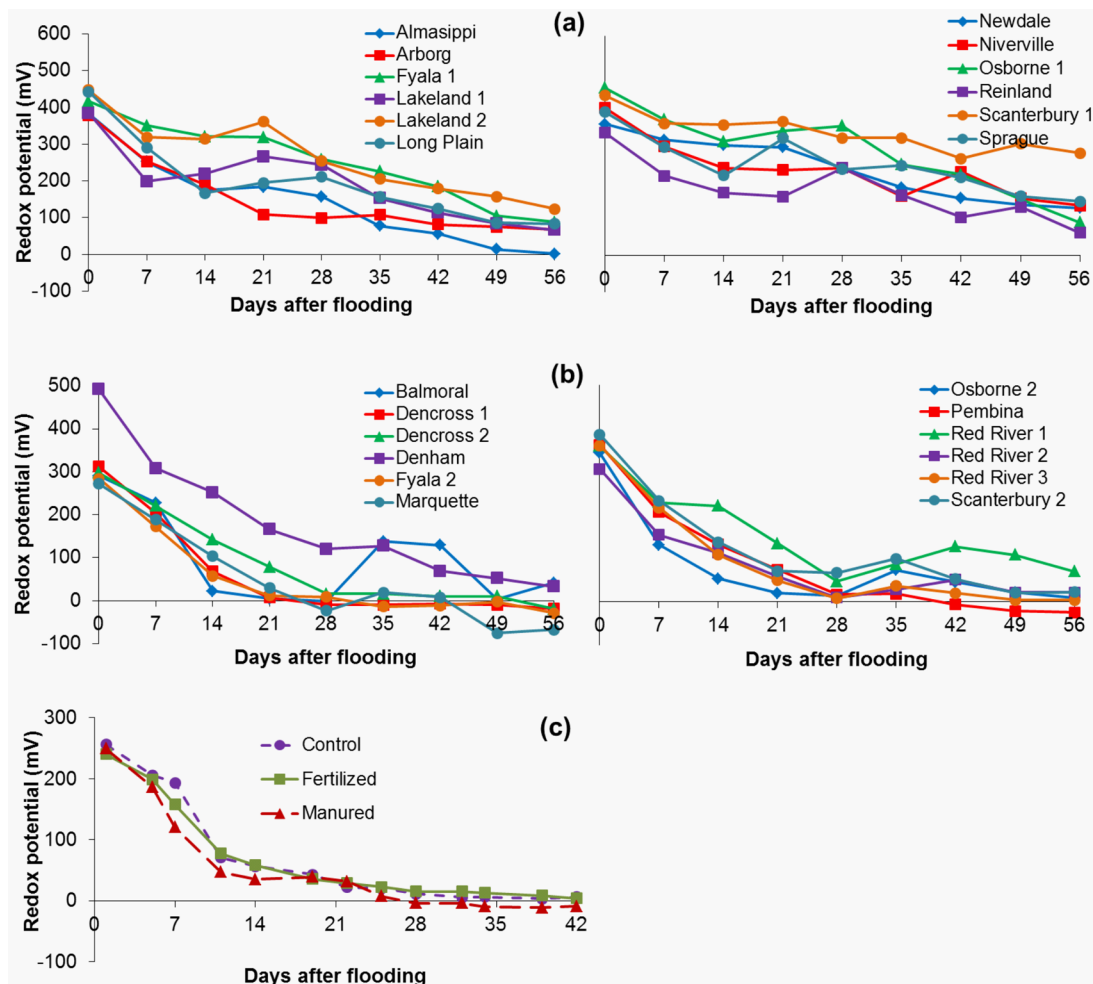


Fig. 2. Changes in soil redox potential (Eh) with time of flooding in (a) 12 soils in ex situ mesocosm Study 1, (b) 12 soils in the ex situ mesocosm Study 2, and (c) fertilized, manured, and unamended control treatments in the in situ mesocosm study (Scanterbury 3).

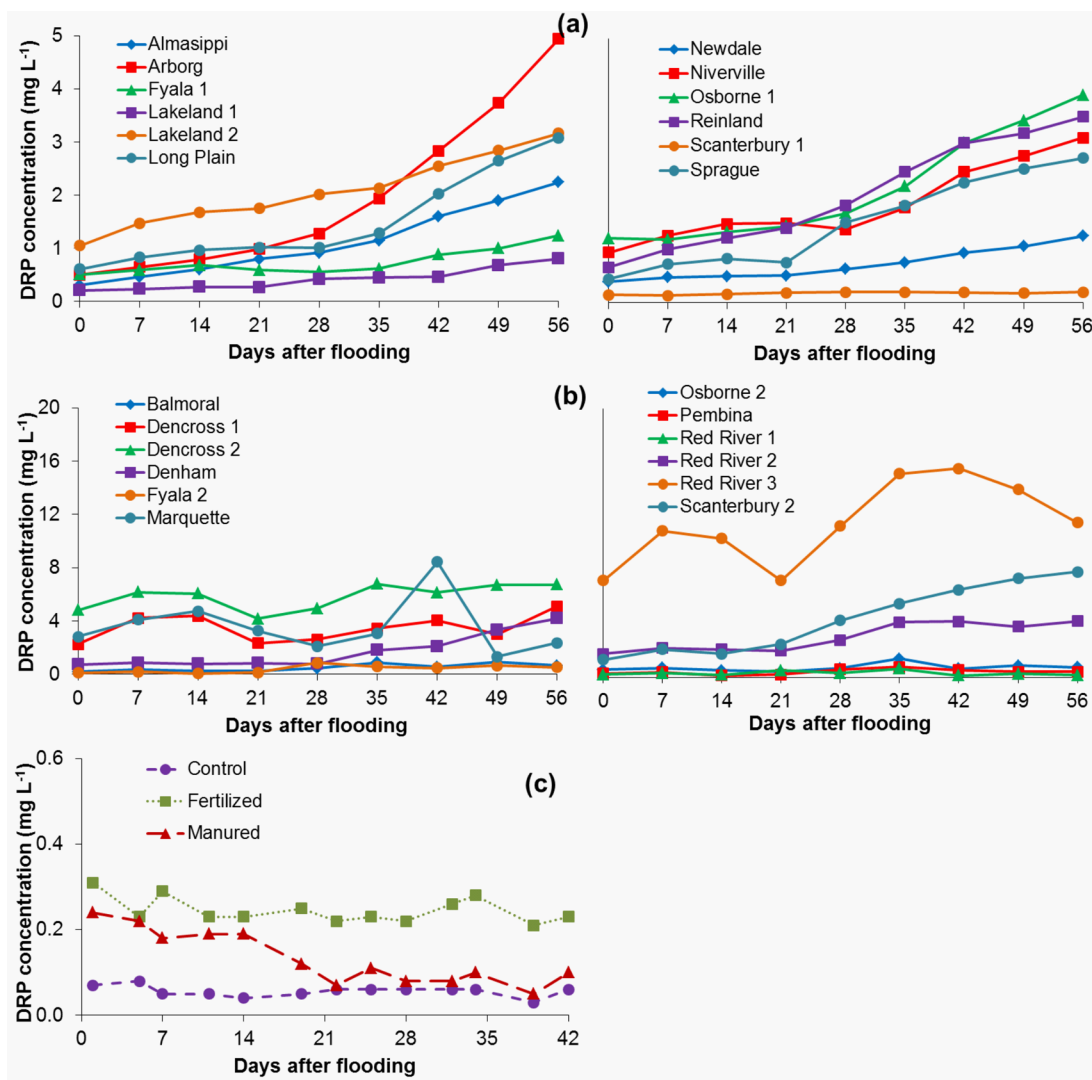


Fig. 3. The mean dissolved reactive P (DRP) concentrations in pore water in (a) 12 soils in ex situ mesocosm Study 1, (b) 12 soils in the ex situ mesocosm Study 2, and (c) fertilized, manured, and unamended control treatments in the in situ mesocosm study (Scanterbury 3).

highly significant ( $P < 0.0001$ ) in both studies. Pore water DRP concentrations significantly increased with DAF in 10 out of 12 soils in each of the ex situ mesocosm studies (Supplemental Table S3). The soils that did not show a significant increase with DAF were Scanterbury 1 and Fyala 1 in the first study and Dencross 1 and Red River 2 in the second study.

In the in situ mesocosm study (Scanterbury 3), the mean DRP concentrations in pore water in unamended, fertilized, and manured soils slightly decreased or remained relatively stable over the flooded period (Fig. 3c). In this soil, an enhanced release of P was not observed with flooding; this contrasted with most soils used for ex situ mesocosm studies, with the exception of Scanterbury 1, Fyala 1, Dencross 1, and Red River 2, all of which are clay soils with somewhat similar properties to Scanterbury 3. Low P release in these soils is probably because of the high clay content, low Olsen P, and high amount of Mehlich-3 extractable Ca, Mg, and Fe, all of which lead to low calculated DPS values, which may result in less P release because of greater P sorption. Although the treatment effect was significant ( $P < 0.05$ ), the DAF and the treatment  $\times$  DAF interaction were not significant. For pooled data over days of flooding, mean pore water DRP concentrations in fertilized plots were significantly greater

than in unamended and manure-amended plots (Supplemental Table S5). The lack of significant differences, despite much larger numerical values in the manured treatments than in the unamended control, was probably caused by the large variability in pore water DRP concentrations due to spatial variability within these larger, field-worked mesocosms.

The DRP concentrations in pore water, in general, were greater than in floodwater for most DAF, thus promoting upward diffusion of P. However, the increase in DRP concentration in pore water did not always result in a corresponding increase in DRP concentration in surface floodwater. Changes in floodwater DRP concentration in response to flooding varied widely among soils from slightly decreasing concentrations (e.g., Almasippi) to a 9.3-fold increase (Reinland), compared with concentration at 0 DAF (Fig. 4). In both ex situ mesocosm studies, we observed a significant ( $P < 0.0001$ ) soil  $\times$  time interaction for floodwater DRP concentrations. In most soils, floodwater DRP concentrations increased with DAF; however, the magnitude of increase was less than that for pore water and statistically significant ( $P < 0.05$ ) in only three soils in Study 1, and seven soils in Study 2 (Supplemental Table S4). Previous studies also showed greater increases in pore water than floodwater DRP concentrations

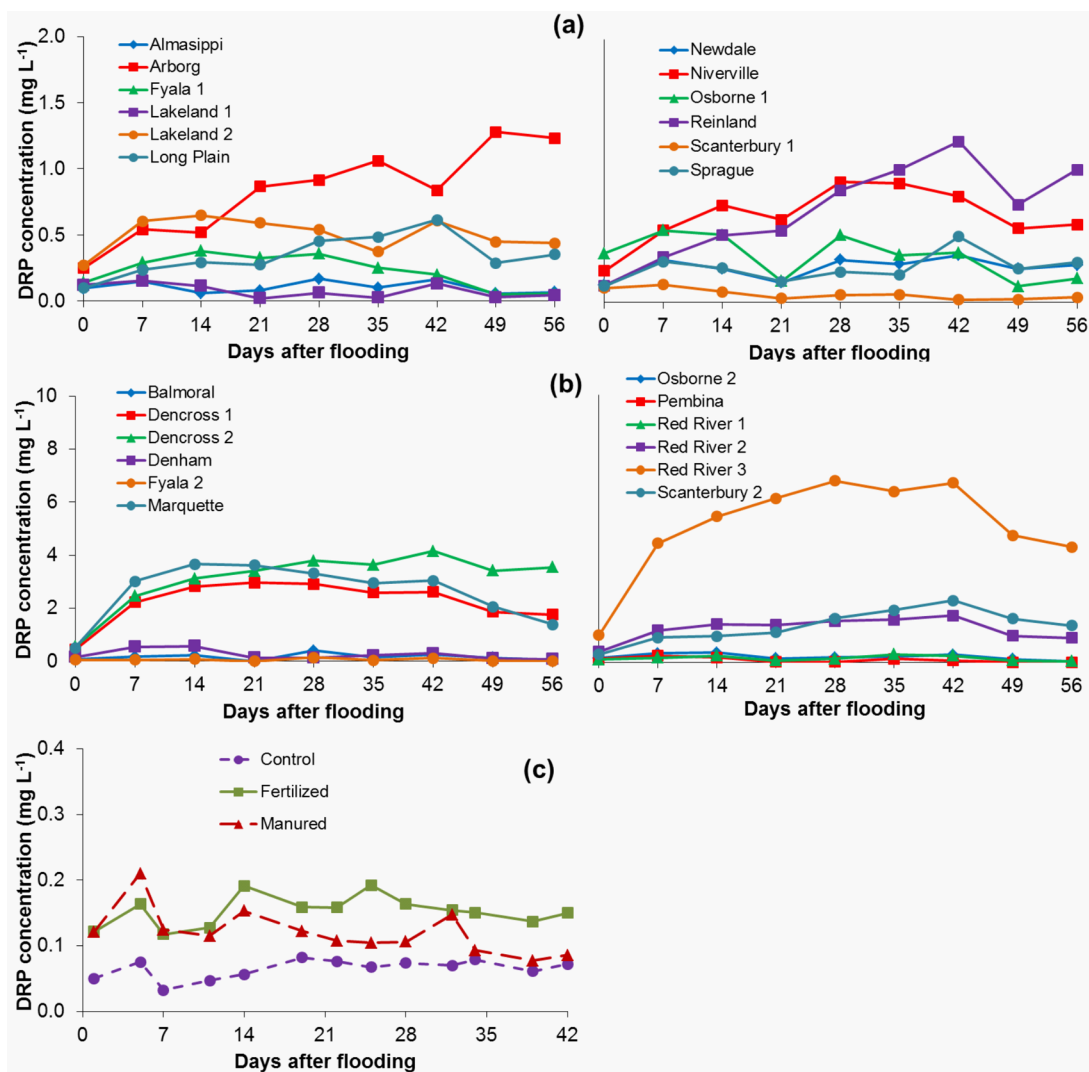


Fig. 4. The mean dissolved reactive P (DRP) concentrations in surface floodwater in (a) 12 soils in ex situ mesocosm Study 1, (b) 12 soils in the ex situ mesocosm Study 2, and (c) fertilized, manured, and unamended control treatments in the in situ mesocosm study (Scanterbury 3).

with flooding under laboratory conditions (Young and Ross, 2001; Amarawansa et al., 2015). A few soils showed relatively stable DRP concentrations in floodwater with DAF, whereas floodwater DRP concentrations in two soils decreased significantly with DAF (Fig. 4, Supplemental Table S4). The decrease in floodwater DRP is likely due to resorption and/or reprecipitation of P at the oxidized soil layer, immediately below the ponded surface water, as previously reported (Shober and Sims, 2009; Jayarathne et al., 2016; Hua et al., 2017).

In the in situ mesocosm study, surface floodwater DRP concentrations were more or less stable and did not increase significantly with DAF regardless of the treatment (Fig. 4c). However, a significant treatment effect was observed (Supplemental Table S5). The mean DRP concentrations in surface floodwater were numerically greater in the fertilized and manured plots than in unamended (control) plots, as expected; however, the difference was significant only between fertilized and unamended treatments (Supplemental Table S5).

The variation in floodwater DRP concentration with time of flooding differed widely in the three mesocosm studies using diverse soils. In the majority of soils, we observed an initial increase in DRP concentration, followed by more or less stable

or slightly declining DRP concentrations with DAF, whereas a few soils showed somewhat stable or slightly declining DRP concentration throughout the flooding period (Fig. 4). Similar variations in DRP concentrations of floodwater have been previously observed with soils of contrasting properties under laboratory conditions with simulated summer flooding (Amarawansa et al., 2015; Jayarathne et al., 2016). The increase in floodwater DRP concentrations with time of flooding can be attributed to the enhanced P release to pore water with reductive dissolution, and subsequent diffusion of released P from pore water to floodwater through the soil–water interface. The DRP concentrations in pore water, in general, were greater than in floodwater for most DAF, thus promoting upward diffusion of P. However, the increase in DRP concentration in pore water did not always result in a corresponding increase in DRP concentration in surface floodwater. It is likely that precipitation and adsorption reactions at the interface between the soil and overlying floodwater removed the released P from dissolved phase to solid phase, as previously reported (Shober and Sims, 2009; Jayarathne et al., 2016; Hua et al., 2017).

Our data under field conditions confirm the results of previous laboratory studies that found flooding can mobilize

soil P and increases P availability (Amarawansa et al., 2015; Jayarathne et al., 2016; Maranguit et al., 2017). Although this effect was observed in the majority of soils, a few soils did not show this trend. Generally, in soils that showed an increase in DRP concentration in pore water and floodwater, the release of increasing quantities of P started after 21 to 28 d of flooding, which often corresponded with a decrease in Eh below +200 mV, the approximate critical Eh at which  $Mn^{4+}$  is reduced to  $Mn^{2+}$  (Patrick and Jugsujinda, 1992). Although  $Fe^{3+}$  reduction usually takes place at lower Eh values around +150 mV, there is some overlap in oxidation and reduction of the Mn and Fe systems (Patrick and Jugsujinda, 1992). The contribution of  $Mn^{4+}$  reduction in enhancing P release under anaerobic conditions has been previously documented in paddy soils (Shahandeh et al., 2003). Application of livestock manure or synthetic fertilizer in the in situ mesocosm study increased the DRP concentrations in both pore water and floodwater but did not change the soil's overall response to flooding in releasing P to pore and floodwater.

### Predicting Phosphorus Release to Floodwater Using Pre-Flooded Soil Phosphorus Measures

The DRP concentrations in both pore water and floodwater changed with flooding time; therefore, we used the maximum DRP concentration ( $DRP_{max}$ ) over the flooding period as the measure of the soil's ability to release P under flooded, anaerobic conditions. Simple linear regression analysis for floodwater  $DRP_{max}$  and STP or DPS indices was conducted separately for soils with low Olsen P (Olsen  $P \leq 30$  mg  $kg^{-1}$ ,  $n = 15$ ), high Olsen P (Olsen  $P > 30$  mg  $kg^{-1}$ ,  $n = 12$ ), and all soils ( $n = 27$ ). Olsen P of 30 mg  $kg^{-1}$  was used as the threshold to differentiate between high and low P soils based on the findings of Wang et al. (2015). They observed that soils with Olsen  $P < 30$  mg  $kg^{-1}$  would have an equilibrium P concentration at zero P sorption ( $EPC_0$ ) of  $<0.1$  mg  $L^{-1}$ . Their findings suggest that soils with Olsen  $P > 30$  mg  $P$   $kg^{-1}$  may cause significant runoff DRP loss.

Olsen P,  $M3P_{MRP}$  and  $M3P_{TP}$  showed highly significant positive relationships ( $P < 0.0001$ ) with  $DRP_{max}$  when all soils were considered, but these STP measurements were poorly related to  $DRP_{max}$  in low-P soils (Table 1). Although some of the DPS measures were significantly related to  $DRP_{max}$  in low-P as well as high-P soils, the same regression model did not fit both categories. Within the different DPS measures, DPS calculated using PSI as the P sorption capacity ( $DPS_{10}$ – $DPS_{15}$ ) often showed stronger relationships with the  $DRP_{max}$  across all Olsen P categories (Table 1).

Our results clearly indicate that STP concentrations in pre-flooded soils are poor predictors of the summer flooding-induced P release from low-P soils. In a recent study with paddy soils, similar observations were reported with weak relationships between total P concentrations in the field ponding water during 15 d of flooding and Olsen or Mehlich-3 P contents (Hua et al., 2017). In the current study, we observed that even soils with very low Olsen P concentrations can release substantial quantities of P to floodwater under prolonged periods of flooding. For example, in the first ex situ mesocosm study, the  $DRP_{max}$  was greatest in the Reinland soil, which had the lowest Olsen P concentration, 16.1 mg  $kg^{-1}$ . The DPS, on the other hand, is calculated taking into account both the P sorption capacity of soils and STP (Ige et al., 2005; Xue et al., 2014), thus integrating the effect of soil type with STP (Sharpley, 1995). Thus, the Reinland soil, which

had the lowest Olsen P in mesocosm Study 1, had relatively high DPS values since it had a lower P sorption capacity, due to its sandy texture and relatively low organic matter content. Thus, DPS can be considered as a soil-independent parameter (Fischer et al., 2018) and may predict P losses better than STP from a wide range of soils to floodwater under anaerobic conditions.

In previous studies, various DPS measures were found to be significantly correlated with P loss via leaching and runoff (Sharpley, 1995; Vadas et al., 2005) and used to assess the risk of P losses from soils (Nair, 2014; Fischer et al., 2018). Flooding-induced P release from soils and sediments under laboratory conditions also showed significant relationships with various DPS measures (Sallade and Sims, 1997; Young and Ross, 2001; Amarawansa et al., 2016). Young and Ross (2001) reported that DPS calculated as the ratio of fluoride-extractable P to PSI was able to predict the average pore water and floodwater DRP concentration over the flooding period reasonably well. With acidic ditch sediments, DPS calculated as the percentage of biologically available P to PSI was significantly correlated with P release after 21-d of flooding (Sallade and Sims, 1997). With unamended and manure-amended alkaline soils, the relative increase in DRP concentration of floodwater during 8 wk of flooding under laboratory conditions was significantly related to DPS calculated as the ratio of  $M3P_{TP}$  to  $[(2P_{150}) + M3P_{TP}]$  (Amarawansa et al., 2016). In the present study, conducted under field conditions, DPS calculated using either  $P_{150}$  ( $DPS_1$ ,  $DPS_2$ ,  $DPS_3$ ,  $DPS_7$ ,  $DPS_8$ , and  $DPS_9$ ) or PSI ( $DPS_{10}$ – $DPS_{15}$ ) as the capacity factor showed significant relationships with  $DRP_{max}$  in both low-P and high-P soils. The  $DPS_1$ ,  $DPS_7$ ,  $DPS_{10}$ , and  $DPS_{13}$ , all of which had Olsen P as the intensity factor, and either  $P_{150}$ - or PSI-based parameters as the capacity factor, often showed stronger relationships with the  $DRP_{max}$  across all soil categories (Table 1).

The predictive abilities of  $DPS_1$ ,  $DPS_7$ ,  $DPS_{10}$ , and  $DPS_{13}$  were similar, as evidenced by the relationship between predicted  $DRP_{max}$  obtained by cross validation, and observed  $DRP_{max}$  during flooding (Fig. 5). Predictions fit well with the 1:1 linear relationship when all soils were considered, indicating their high degree of predictive power. In low-P soils, however, even though all these DPS measures showed significant relationships with  $DRP_{max}$ , the predictive power was weaker, and the predicted versus observed values did not fit well with the 1:1 linear relationship. Since  $DPS_1$ ,  $DPS_7$ ,  $DPS_{10}$ , and  $DPS_{13}$  had similar predictive abilities, we suggest the use of  $DPS_7$  or  $DPS_{13}$ , as they can be simply calculated by expressing Olsen P as a percentage of  $P_{150}$  or PSI, respectively. We calculated the DPS thresholds for  $DPS_7$  and  $DPS_{13}$ , considering a floodwater DRP concentration of 0.1 mg  $L^{-1}$  as a critical concentration, which is 10 times greater than the lower threshold P concentration (10  $\mu g$   $L^{-1}$ ) in lake water for eutrophication of deep lakes (Sas, 1990). The calculated threshold values of  $DPS_7$  and  $DPS_{13}$  were approximately 3 and 7%, respectively.

### Conclusions

Ex situ and in situ field mesocosm studies with a total of 27 agricultural soils showed that prolonged flooding under summer temperature conditions increased P release from a majority of the soils. Potential risk of summer flooding-induced P release, indicated by the maximum DRP concentration in floodwater during the flooding period, was positively related to Olsen P and Mehlich 3 P in high-P soils, but not in low-P soils. However, several DPS indices

**Table 1. Regressions for floodwater maximum dissolved reactive P (DRP) concentration during the flooding period with soil test P and degree of P saturation (DPS) indices for all soils ( $n = 27$ ), low-Olsen-P soils (Olsen  $P < 30 \text{ mg kg}^{-1}$ ,  $n = 15$ ), and high-Olsen-P soils (Olsen  $P \geq 30 \text{ mg kg}^{-1}$ ,  $n = 12$ ).**

Predictor	All soils			Low-P soils			High-P soils		
	$r^2$	$P$ value	Equation†	$r^2$	$P$ value	Equation†	$r^2$	$P$ value	Equation†
Olsen P	0.73	<0.0001	$y = 0.029x - 0.190$	0.01	0.7642		0.63	0.0021	$y = 0.029x - 0.207$
$M3P_{MRP}^{\ddagger}$	0.77	<0.0001	$y = 0.026x - 0.377$	0.00	0.9816		0.70	0.0006	$y = 0.028x - 0.652$
$M3P_{TP}^{\S}$	0.87	<0.0001	$y = 0.021x - 0.448$	0.11	0.2181		0.85	<0.0001	$y = 0.022x - 0.618$
$DPS_1$	0.87	<0.0001	$y = 0.382x - 0.562$	0.50	0.0034	$y = 0.150x + 0.030$	0.87	<0.0001	$y = 0.434x - 0.994$
$DPS_2$	0.79	<0.0001	$y = 0.295x - 0.531$	0.36	0.0176	$y = 0.083x + 0.109$	0.77	0.0002	$y = 0.327x - 0.761$
$DPS_3$	0.76	<0.0001	$y = 0.216x - 0.432$	0.55	0.0016	$y = 0.060x + 0.102$	0.78	0.0001	$y = 0.236x - 0.424$
$DPS_4$	0.71	<0.0001	$y = 0.261x - 0.475$	0.15	0.1512		0.68	0.0010	$y = 0.297x - 0.792$
$DPS_5$	0.70	<0.0001	$y = 0.223x - 0.576$	0.11	0.2183		0.73	0.0004	$y = 0.275x - 1.088$
$DPS_6$	0.70	<0.0001	$y = 0.175x - 0.560$	0.23	0.0738		0.84	<0.0001	$y = 0.228x - 1.056$
$DPS_7$	0.89	<0.0001	$y = 0.164x - 0.442$	0.50	0.0030	$y = 0.072x + 0.035$	0.88	<0.0001	$y = 0.178x - 0.717$
$DPS_8$	0.81	<0.0001	$y = 0.123x - 0.408$	0.37	0.0161	$y = 0.039x + 0.116$	0.78	0.0001	$y = 0.131x - 0.509$
$DPS_9$	0.78	<0.0001	$y = 0.084x - 0.267$	0.57	0.0011	$y = 0.026x + 0.114$	0.79	0.0001	$y = 0.086x - 0.103$
$DPS_{10}$	0.85	<0.0001	$y = 0.213x - 0.658$	0.54	0.0019	$y = 0.074x + 0.033$	0.87	<0.0001	$y = 0.252x - 1.234$
$DPS_{11}$	0.75	<0.0001	$y = 0.166x - 0.609$	0.40	0.0117	$y = 0.043x + 0.106$	0.76	0.0002	$y = 0.192x - 0.938$
$DPS_{12}$	0.71	<0.0001	$y = 0.125x - 0.518$	0.58	0.0014	$y = 0.031x + 0.101$	0.77	0.0002	$y = 0.147x - 0.665$
$DPS_{13}$	0.88	<0.0001	$y = 0.080x - 0.431$	0.56	0.0014	$y = 0.034x + 0.044$	0.87	<0.0001	$y = 0.086x - 0.676$
$DPS_{14}$	0.80	<0.0001	$y = 0.059x - 0.375$	0.42	0.0093	$y = 0.018x + 0.119$	0.78	0.0002	$y = 0.063x - 0.423$
$DPS_{15}$	0.76	<0.0001	$y = 0.039x - 0.219$	0.60	0.0006	$y = 0.010x + 0.221$	0.77	0.0002	$y = 0.041x - 0.028$

† Regression equation indicated only when regression relationship is significant ( $P < 0.05$ ).

‡  $M3P_{MRP}$ , Mehlich-3 extractable molybdate reactive P.

§  $M3P_{TP}$ , Mehlich-3 extractable total P.

showed significant relationships with maximum DRP concentration in both low-P and high-P soils. Within the different DPS indices, DPS calculated using Olsen P as the intensity factor and PSI or  $P_{150}$  as the P sorption capacity often showed the strongest relationships with the maximum floodwater DRP across all soil categories and had a higher degree of predictive power. It should be noted that the current research investigated the P release under summer-flooding conditions; thus, for the northern Great Plains region in particular, relationships need to be further validated and refined for P release under spring snowmelt flooding conditions. Measuring an effective DPS index prior to an impending flooding event would help in developing strategies to mitigate P losses from flooded soils in our efforts to reduce the risk of eutrophication of surface water bodies.

## Supplemental Material

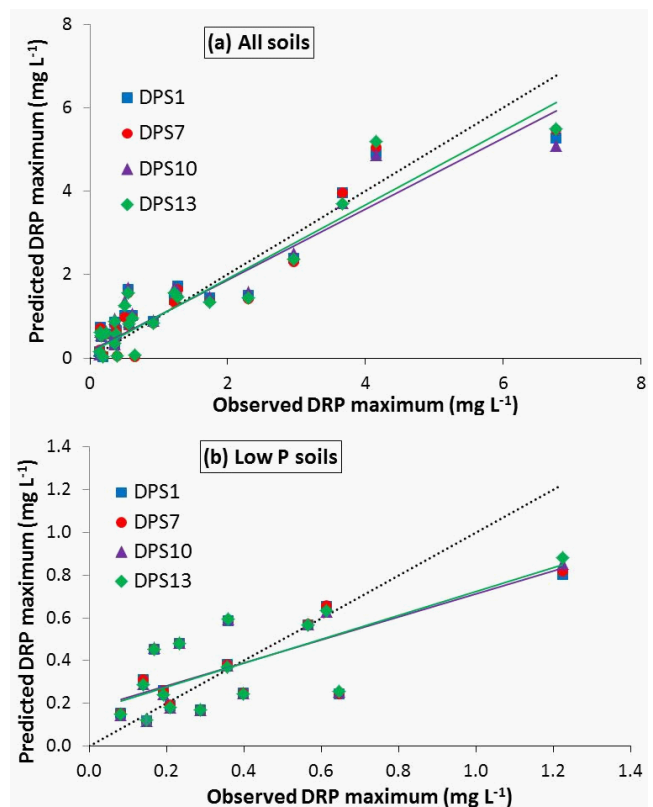
The supplemental materials provide information on the initial soil properties used for the two ex situ mesocosm studies with 12 soils each and the in situ mesocosm study with unamended, fertilizer-amended, and manure-amended plots (Supplemental Table S1), degree of P saturation of all soils used for the two ex situ and in situ mesocosm studies (Supplemental Table S2), pore water DRP concentrations with flooding time for the two ex situ mesocosm studies with mean comparisons (Supplemental Table S3), floodwater DRP concentrations with flooding time for the two ex situ mesocosm studies with mean comparisons (Supplemental Table S4), and pore water and floodwater DRP concentrations with flooding time in the in situ study for the unamended, fertilizer-amended, and manure-amended treatments (Supplemental Table S5).

## Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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**Fig. 5. Relationship between predicted and observed values of maximum dissolved reactive phosphorus concentration ( $DRP_{max}$ ) in floodwater during soil flooding for (a) all soils and (b) low-P soils. Values of  $DRP_{max}$  were predicted using degree of P saturation (DPS) values  $DPS_1$  [ $Olsen P / (2P_{150} + Olsen P) \times 100$ ];  $DPS_7$  [ $Olsen P / P_{150} \times 100$ ];  $DPS_{10}$  [ $Olsen P / (2PSI + Olsen P) \times 100$ ]; and  $DPS_{13}$  [ $Olsen P / PSI \times 100$ ], where  $P_{150}$  is the single-point P sorption capacity, and PSI is the P saturation index. The dotted line represents the 1:1 relationship. All relationships were significant at  $P < 0.05$ .**



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