The Effect of Flooding and Reducing Conditions on Phosphorus Dynamics in

Manitoba Soils

by

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ABSTRACT

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Anaerobic conditions resulting from flooding often lead to enhanced release of phosphorus (P) to overlying water. This study examined the effect of flooding and anaerobic conditions on soil P dynamics. A field ponding study using Scanterbury heavy clay soil (unamended, inorganic fertilizer- or manure-amended), and a laboratory incubation study using 12 soils (unamended or manure-amended) from Manitoba showed that P release to flood water under reduced conditions varied substantially. In the field ponding study, flooding and development of anaerobic conditions did not enhance P release into surface flood or soil pore water. In the incubation study, the response to flooding and anaerobic conditions ranged from a small decrease to a 15-fold increase in dissolved reactive P concentration (DRP) in flood water. Partial least squares analysis indicated that measures of degree of P saturation in soils can effectively predict DRP concentration changes in surface flood water under anaerobic conditions.

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FOREWORD

This thesis is prepared in manuscript format following the thesis guidelines of Department of Soil Science, University of Manitoba. Chapter 1 includes an introduction to literature review on P dynamics of flooded soils and objectives of the research. Chapter 2 describes a field study conducted to investigate the behavior of P release from a soil under waterlogged, anaerobic conditions in fields of relatively flat landscape with slowly permeable, heavy clay soils typical for the Red River Valley region of Manitoba. Chapter 3 describes a laboratory incubation study conducted to examine P dynamics of twelve different soils in Manitoba. Chapter 4 includes an overall synthesis which describes the general discussion on the findings, practical application of findings, and suggestions for further studies. Chapter 2 and 3 will be submitted to the Journal of Environmental Quality and therefore, formatting and reference style of this journal has been adapted throughout the thesis. Important tables and figures included in appendices will be submitted as supplemental information along with the manuscripts.

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ABBREVIATIONS

ΔDRP_{abs}	- Absolute change in DRP concentration in surface water (Maximum DRP - DRP concentration at day 1)
ΔDRP_{ratio}	- Relative change in DRP concentration in surface water (Maximum DRP / DRP concentration at day 1)
ANOVA	- Analysis of varience
CEC	- Cation exchange capacity
DCP	- Dicalcium phosphate
DCPD	- Dicalcium phosphate dihydrate
DF	- Degree of freedom
DOC	- Dissolved organic carbon
DOM	- Dissolved organic matter
DPS	- Degree of P saturation
DRP	- Dissolved reactive phosphorus
EC	- Electrical conductivity
EPC_0	- Equilibrium P concentration
EPC_w	- Equilibrium P concentration in overlying flood water
H_2O-Pi	- Water extractable inorganic P (in fractionation)
HCl-Pi	- 1 M HCl extractable P
ICP-AES	- Inductively coupled plasma membrane atomic emission spectroscopy
M3Al	- Mehlich-3 extractable Al
M3Ca	- Mehlich-3 extractable Ca
M3Fe	- Mehlich-3 extractable Fe
M3Mg	- Mehlich-3 extractable Mg
M3Mn	- Mehlich-3 extractable Mn
$M3P_{MRP}$	- Mehlich-3 extractable P measured by Molybdate blue method
$M3P_{Dry}$	- Mehlich-3 extractable P in air-dried soil
$M3P_{ICP}$	- Mehlich-3 extractable P measured by ICP-AES
MAP	- Mono-ammonium phosphate
$NaHCO_3$-Pi	- 0.5 M $NaHCO_3$ extractable inorganic P
NaOH-Pi	- 0.1 M NaOH extractable inorganic P
NaOH-Pt	- 0.1 M NaOH extractable total P
OC	- Organic carbon
OCP	- Octacalcium phosphate
Ols-P	- Olsen extractable P
OLS	- Ordinary least squares
$Ols-P_{Dry}$	- Olsen extractable P in air-dried soil
$Ols-P_{Wet}$	- Olsen extractable P in wet soil

P150	- Single point P adsorption capacity
PLS	- Partial least squares
RO	- Reverse Osmosis
SBCM	- Solid beef cattle manure
SDCM	- Solid dairy cattle manure
SE	- Standard error
Smax	- Phosphorus adsorption maximum
SOM	- Soil organic matter
STP	- Soil test P
TDP	- Total dissolved P
VIP	- Variable importance in the projection
WEP	- Water extractable P

1. INTRODUCTION

1.1. Phosphorus in the Environment

Phosphorus (P) is an essential macronutrient needed for optimum crop growth and production (Mengel et al., 2001). Soil P basically falls into one of three categories depending on the rate of equilibration with the soil particles: soil solution P, labile P, and non-labile P (Brady and Weil, 1999). The solution P pool is very important since it is the P pool from which plants take up P. This P pool typically contains about 2 μM of inorganic P concentrations, while in highly fertile soils it may exceed 10 μM (Bieleski, 1973). Labile P, which consists of moderately soluble P compounds, P adsorbed to the surface of silicate clay minerals, oxides and hydroxides of Fe and Al, calcium carbonates, humus particles and other minerals, and mineralizable organic P, has the ability to replenish the soil solution P pool. Non-labile phosphorus includes occluded P within the matrices of Fe and Al minerals, which are relatively insoluble, inorganic phosphate compounds that are sparingly soluble as well as organic P compounds that are resistant to microbial mineralization.

Phosphorus in soil exists in both inorganic and organic forms. Inorganic P forms present in soil are mainly orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-} depending on soil pH), Ca and Mg bound P, non-occluded Al and Fe bound P, and P occluded within Al and Fe oxides/hydroxide (Chang and Jackson, 1956; Vadas and Sims, 1998). In alkaline soils, Ca-based inorganic P is predominant, while Fe- and Al-bound inorganic P are predominant in acidic to neutral soils. All the groups slowly contribute to soil solution P

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pool, but most of the soil P exists in sparingly soluble forms and is therefore unavailable for plant uptake (Brady and Weil, 1999). Three main groups of organic P found in the soil are inositol phosphates, nucleic acids, and phospholipids. Soluble P compounds, HPO_4^{2-} or $H_2PO_4^-$, are released by microbial mineralization of organic P depending on soil pH and microbial activity.

The amount of P in soil solution at any one time is very low due to its tendency to form relatively insoluble compounds with soil components and ions present in the soil (Adams, 1980). Hence, P availability to plants is generally very low and fertilization of P is necessary to achieve an optimal level of crop production in most soils (Allen and Mallarino, 2006). Long-term continuous application of P fertilizers and other P sources, such as organic wastes and manure may cause P accumulation in the surface horizon due to low crop use efficiency ($< 25\%$) and high P retention ability of soils (Brady and Weil, 1999; Zhang, 2004).

From an environmental standpoint, excess P in agricultural soils may lead to eutrophication of surface water bodies (Sharpley, 1995). Nutrient losses, mainly losses of P and nitrogen (N) from agricultural lands through surface runoff, soil erosion, and leaching into aquatic environments have made agriculture the largest source of non-point water pollution (USEPA, 2000). Soil erosion, mainly water erosion (both sheet and rill erosion) and to a lesser degree, wind erosion is the major pathway of particulate P transport (Manitoba Phosphorus Experts Committee, 2006). It has been estimated that loss of P from the world's crop fields is about 19.3 MMT yr^{-1} (Liu et al., 2008). Erosion from pasture lands is generally less than that from agricultural lands. Surface runoff of

soluble or dissolved P is the main P transport process in relatively flat landscapes and snowmelt-dominated runoff of the Canadian Prairies (Salvano and Flaten, 2009). Worldwide, total of 0.5 MMT P yr^{-1} of applied P would loss through surface runoff (Liu et al., 2008).

Phosphorus leaching, the process of P loss through subsurface pathways, can also play an environmentally significant role. For example, Turner and Haygrath (2000) observed that P concentrations in drainage waters of lysimeters were at levels that could cause eutrophication in surface waters. Traditionally, it was considered that P losses from soil through leaching and subsurface flow were not significant compared with losses via surface pathways (Sparks, 1995) due to the presence of Al, Fe, Ca and Mg oxides and other soil components capable of adsorbing P in subsoils. However, the P losses through subsurface flow is becoming important not only under waterlogged conditions but also in sandy-textured soils with heavy fertilization, and clay soils with large cracks which facilitate preferential flow, and in tile drains (Sims et al., 1998; Turner and Haygarth, 2000).

Eutrophication is the process of stimulating the growth of aquatic plants and algae in a water body due to nutrient over-enrichment; however, P is often the most limiting nutrient controlling fresh water eutrophication since cyanobacteria (blue green algae) have the capability of fixing N. This algal over-growth finally leads to death and decomposition of aquatic fauna to make the water bodies anaerobic. This would cause a major environmental problem resulting in a biodiversity loss in aquatic systems (Dunne et al., 2005). Therefore, the reduction of lake eutrophication often requires restricting P

input to surface water bodies (Pote et al., 1996). Yates et al. (2011) reported that the largest source of nutrients, especially P, to Manitoba watersheds is fertilizer application. A recent study conducted by Schindler et al. (2012) suggested that Lake Winnipeg is becoming increasingly eutrophic altering the ecology of the lake.

Phosphorus release into surface water bodies is often related to soil test P content and the soil's ability to retain P in soil (Ige et al., 2005). Phosphorus retention of a soil has often been related to adsorption and/or precipitation reactions (Brady and Weil, 1999; Reddy et al., 1999). Phosphorus adsorption is a two-step process in which a rapid phase takes place during the first few minutes followed by a slower phase, which can occur over days or weeks. Rapid phase is characterized by an initial P retention on mineral surfaces (adsorption) and the slower phase corresponds to diffusion of P into a solid phase (absorption) after all the surface sites are filled (Reddy et al., 1999). Depending on the oxides/hydroxides present in the soils and soil pH, ligand exchange of phosphates on oxide/hydroxide surfaces results in formation of monodentate, bidentate or binuclear complexes (Torrent, 1997). Precipitation is the formation of new solid precipitates of PO_4^{3-} with Al^{3+}, Fe^{3+}, Ca^{2+} and Mg^{2+} cations if the activities of these cations are high (Adams, 1980).

Crystalline or amorphous Al and Fe oxides, which contribute positive charges for PO_4^{3-} adsorption, dominate P retention in acidic to neutral soils (Toor et al., 1997). For example, Van der Zee et al. (1986) reported that P sorption in sandy terrestrial soils in the Netherlands was linearly related to the sum of ammonium oxalate-extractable Fe and Al. Precipitation of PO_4^{3-} as Al or ferric phosphate is also dominant in acidic to neutral soils

with high ion activities (Hsu, 1965). In alkaline to calcareous soils, P retention is mainly governed by Ca and Mg in the soils even though Al and Fe may be involved to some extent (Von Wandruszka, 2006). A strong correlation was observed between P retention capacities and various measures of extractable Ca and Mg in alkaline to calcareous soils in Manitoba, confirming the effect of Ca and Mg on P retention (Ige et al., 2005). Calcium saturated conditions prevalent in Manitoba soils release Ca into solutions through ion exchange reactions and this Ca in the soil solution combines with phosphate to form precipitates (Akinremi and Cho, 1991). Retention of P in calcareous soils is governed mainly by the Ca^{2+} activity in the liquid phase, where adsorption predominates at low concentrations (below 0.5 mM) while above this level precipitation become dominant (Tunesi et al., 1999). The first product of precipitation is dicalcium phosphate dihydrate (DCPD, $Ca_2HPO_4 \cdot 2H_2O$), and consequently, octacalcium phosphate may be formed (Cole et al., 1953). The hydrolytic conversion of DCP to OCP and the cyclic process which produces DCP and stable hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) from OCP has also been observed in alkaline to calcareous soil (Von Wandruszka, 2006).

1.2. Phosphorus Availability and Release in Anaerobic Soil

Various environmental and soil factors can modify P retention in soils and release from soil to water. Seasonally flooded conditions change soil's oxidation-reduction status and may alter P dynamics in soils. In the Canadian Prairies, there are two main conditions under which soils could become saturated and anaerobic. Agricultural lands in areas with flat landscapes could become saturated or flooded for a period ranging from few days to several weeks after snowmelt in spring and after heavy precipitation in

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summer (Wang and Bettany, 1997). For example, large areas of Manitoba where agriculture is the main land use were flooded due to snowmelt followed by heavy rainfall during spring of 2011 (Lake Manitoba/Lake St. Martin Regulation Review Committee, 2013). Secondly, natural or constructed wetlands, which cover approximately 14% of Canada's total land area, also exhibit anaerobic conditions having the water table at, near, or above the land surface for a period long enough to promote hydric soils (Kennedy and Mayer, 2002). In other parts of the world, periodic flooding is a general practice in rice cultivation to optimize the harvest and to control weeds and insect pathogens (Ikehashi, 2007).

Flooding or excess water in soils with readily available organic matter causes anaerobic conditions, which alter both soil oxidation-reduction potential and soil pH, thereby directly or indirectly influencing solubility and sorption/desorption of P (Racz, 2006). Numerous studies have investigated the release of P from soils under flooded conditions. Most of the studies conducted have observed increases in P release from soil to surface flood water or soil pore water during submersion or anaerobic incubation (Ajmone-Marsan et al. 2006; Ann et al., 2000; Sallade and Sims, 1997a; Scalenghe et al., 2002; Scalenghe et al., 2012; Shenker et al., 2005; Vadas and Sims, 1998; Young and Ross, 2001). For example, Ajmone-Marsan et al. (2006) observed a dramatic increase of P in soil solution after two weeks of anaerobic incubation of solid hog manure amended soil and the amount of P released increased with the increase in manure application rate. Scalenghe et al. (2002) observed a significant increase in molybdate reactive P concentration in soil solution during the first week of submersion followed by a continuous increase up to a 32 days (complete Eh reduction) accompanying the

development of reducing conditions. Molybdate reactive P concentration attained a maximum that remained relatively stable for the rest of the incubation period. Results of another study showed that dissolved reactive P (DRP) concentration in soil solution, both in chemically amended ($CaCO_3$, $FeCl_3$ and alum) and unamended soils increased with the intensity of reduction (Ann et al., 2000). In contrast, a relatively stable dissolved P content over the period of 63 days of anaerobic incubation of Berks clay loam soil was observed by Shober and Sims (2009). Young and Ross (2001) observed a steady decline in surface flood water P over the first 55 days of submersion of low-P soils and three to six-fold reduction in flood water P from day 22 to day 25 in high-P soils. The increases of P concentrations under flooded and reduced conditions are attributed to reductive dissolution of Fe^{+3} while decreases of P are attributed to precipitation of dissolved P with Fe in the solution as discussed further in this chapter.

Phosphorus transformations under flooded and anaerobic conditions greatly affect the relative proportion of P forms (Scalenghe et al., 2012). For instance, Quintero et al. (2007) reported that flooding significantly changed the inorganic labile P fractions such as anion exchange resin extractable P, 0.5 M $NaHCO_3$ extractable P, and 0.1 M NaOH extractable P as well as most labile organic fraction (0.5 M $NaHCO_3$ extractable P) where the magnitudes of increase or decrease depended on the soil type. According to Vadas and Sims (1998), reduced conditions of cultivated subsoils with low P and wooded horizons significantly increased Ca-bound P but did not affect non-occluded Al- and Fe-bound P and occluded P. Reduced conditions of cultivated topsoils with high P significantly increased extractability of all P fractions except occluded P in some occasions.

1.3. Influence of Anaerobic Conditions on Soil P Dynamics

Iron plays a vital role in P dynamics by reductive dissolution, particularly in acidic to neutral soils where P retention is mainly governed by Fe^{3+}, Al^{3+} and Mn^{4+} (Ajmone-Marsan et al., 2006; Ann et al., 2000; Kröger et al., 2012; Scalenghe et al.,2012). It has been shown that Fe reduction is important in P release in alkaline to calcareous soils as well (Scalenghe et al., 2012). Redox potential (Eh) below 100 mV can cause microbial mediated reduction of Fe^{3+} to Fe^{2+} as follows (Gotoh and Patrick, 1974; Petruzzelli et al., 2005).

$$Fe_2O_3 + 6H^+ + 2e \rightleftarrows 2Fe^{2+} + 3H_2O$$
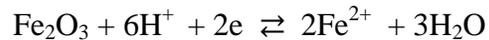
In soils where Mn is also responsible for P retention, reductive dissolution of Mn^{4+} would also control P release into solution at the initial stage of reduction (Olila and Reddy, 1997; Scalenghe et al., 2002; Shahandeh et al., 2003).

$$MnO_2 + 4H^+ + 2e \rightleftarrows 2Mn^{2+} + 2H_2O$$
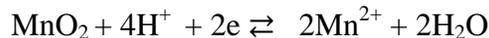
Changes in soil pH with decreasing redox potential also play an important role in P dynamics under flooded conditions (Racz, 2006). In general, soil pH of flooded soils increases in acidic soil (Ponnamperuma, 1972), and decreases in alkaline soils towards neutrality with time (Racz, 2006). The consumption of protons during the reduction process of Fe and Mn is responsible for the increase in soil pH in acidic soils while Eh reduction of soil and accumulation of CO_2 (i.e., increase CO_2 partial pressure) causes a soil pH decrease in alkaline soils. This pH change towards neutrality decreases the stability of oxides and other minerals. In acidic soils, increased pH decreases the stability of crystalline strengite ($FePO_4. 2H_2O$) releasing associated PO_4^{3-} ions into soil solution

(Racz, 2006). However, pH decrease in alkaline to calcareous soils enhances the solubility of apatite, b-tricalcium phosphate, octacalcium phosphate, brushite and monetite to release P to surface or pore water (Ann et al., 2000).

Changes in dynamics and release of P from anaerobic soils depend on other soil properties as well. In soils with high cation exchange capacities (CEC), release of P due to Fe and Mn reduction is further enhanced by scavenging Fe^{2+} and Mn^{2+} formed during the reductive dissolution which prevent the precipitation of new P sorbing Fe minerals (Amery and Smolders, 2012). In sulfate rich soils, reduction of sulfate into sulfide followed by formation of ferrous sulfides (FeS) may prevent P retention by Fe thus increasing P release (Caraco et al., 1991; Reddy and DeLaune, 2008; Roden and Edmunds, 1997). Soil organic matter plays a role as well, since reducing conditions increases the mineralization of soil organic phosphorus and the hydrolysis of pyro- and longer chain- phosphates to increase P concentration in soil solution (Campbell and Racz, 1975). Ligand exchange of P with soil organic matter produced during an anaerobic period would also enhance P release to soil solution (Zhang et al., 2010). Hutchison and Hesterberg, (2004) found a significant positive relationship (r^2 = 0.79) between DRP concentration in soil pore water and dissolved organic carbon (DOC) content indicating the importance of DOC produced by microbial reduction during flooding on P release to soil pore water. Further, they observed that dissolved organic matter (DOM) formed under reduced condition facilitates formation of ternery aqueous $DOM-Fe^{+3}-PO_4$ or $DOM-Al^{+3}-PO_4$ to increase dissolution of phosphate under reduced conditions. Soil/sediment temperature also influences P release to surface or pore water (Sallade and Sims, 1997b; Stevens, 2008). Soluble P concentrations were greater at 35 °C compared

to 7 °C after 42 days of anaerobic incubation of ditch sediments (Sallade and Sims, 1997b). High P release at elevated temperature has been attributed to more intense reduction of soil, which releases more Fe-bound P to water and increased mineralization of organic matter.

Mobility of P in flooded soils is often governed by P sorption capacity and P buffer intensity (Reddy et al., 1999). The effect of flooding and subsequent reduction on P sorption capacity varies from soil to soil. Many researchers have shown that P sorption capacity of a soil increases during flooding (Amer et al., 1991; Khalid et al., 1977; Patrick and Khalid, 1974; Zhang et al., 2010) and after flooding (Shober and Sims, 2009). Increased P sorption capacity could result in a decrease in P release from soil to water, or maintain a stable P concentration in overlying water (Shober and Sims, 2009; Young and Ross, 2001) if released P are re-sorbed during flooding. Zhang et al. (2010) observed an increase in P sorption maximum values for reduced surface soils with and without waste water addition whereas the P sorption maxima did not change due to reduction for subsurface soil. Shober and Sims (2009) also observed significant increases in single point P sorption capacity after 63 days of anaerobic incubation of unamended, biosolid- and manure-amended soils. Further, Amer et al. (1991) reported that P sorption capacity increased with time of submergence with most of the increase occurring between 0.16 and 70 days with a lower increase in P sorption after 70 days until 170 days of flooding. On the contrary, Vadas and Sims (1999) observed a decrease in maximum P sorption in A, B, and C horizons of two Inland Bay watershed soils after 28 days of flooding which was attributed to higher soil pH after incubation. Increases in P sorption in anaerobic soils may result from transformation of crystalline ferric oxides/hydroxides to poorly

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crystalline or amorphous ferrous/ferric oxides/hydroxides, which provide more reactive surface sites (Barber, 2002; Holford and Patrick, 1981; Vadas and Sims, 1999; Young and Ross, 2001; Zhang et al., 2010). As well as, Al^{+3}, which is not redox active (Chacon et al., 2006) would have more open reactive sites for P sorption after removal of the iron coat due to reductive dissolution of Fe (Shober and Sims, 2009). In alkaline soils, P sorption under flooded conditions is also associated with adsorption onto Ca and Mg carbonates (Reddy et al., 1999).

In acid soils, increased Fe and Mn concentrations resulting from reductive dissolution may cause precipitation of dissolved PO_4^{3-} (Reddy and DeLaune, 2008). This could lead to an increase in P sorption capacity in acid soils if dissolved Fe concentration is high enough (Holford and Patrick, 1981). Zhang et al. (2010) reported that precipitation of Fe and Mn minerals is possible even in alkaline soils; however, their contribution to P sorption was low ($< 2\%$) due to low concentrations in those soils. In alkaline soils, P retention through precipitation with Ca^{2+} to form Ca phosphate minerals is significant (Reddy et al., 1999; Zhang et al., 2010). Zhang et al. (2010) observed that Ca phosphate formation in alkaline soil solutions with high P (1-200 mg L^{-1}) and high Ca concentrations contributed $19\pm3\%$ of P sorption when using electrolyte solution (0.01 M KCl) as the P sorption solutions and $68\pm19\%$ of P sorption when using 0.01 M KCl plus waste water as the sorption solution. The increased precipitation of Ca phosphate when using diluted waste water as the sorption solution can be attributed to high Ca concentration in waste water.

Other than the changes in soil mineralogical composition, changes in soil physical and chemical properties under flooded and anaerobic condition could affect P sorption capacity. When soils undergo alternate wetting and drying cycles, soil aggregates can disintegrate exposing new soil surfaces for P sorption (Olsen and Court, 1982). Organic molecules capable of complexing released P would also increase P sorption capacity of flooded soils (Hutchison and Hesterberg, 2004).

Phosphorus sorption capacity of a soil does not, however, reflect the P retention and release from submerged soils, wetlands or sediments (Reddy et al., 1999) unless equilibrium phosphorus concentration (EPC_0) and bonding energy of the soil are considered. Equilibrium phosphorus concentration can be defined as the P concentration in solution where sorption equals desorption (Pierzynski et al., 2005; Reddy et al., 1999) and can be determined by P sorption data (Dunne et al., 2005). In general, soil solution concentrations greater than an EPC_0 value for a particular soil suggests that the soil will sorb P, whereas soil solutions lower than an EPC_0 suggest that the soil will desorb P, i.e., EPC_0 can be used to identify the effect of P loading on P release from flooded soil (Reddy et al., 1999). When the overlying flood water contains P concentrations above equilibrium P concentration in flood water (EPC_w), flooded soil would act as a sink for P. Alternatively, if flood water P concentration is lower than EPC_w, soil would act as a source of P. When the bonding energy is considered, ferrous oxide, which is the dominant form of oxides/hydroxides is responsible for P retention in anaerobic acidic to neutral soils, has a lower affinity and lower bonding energy to retain P compared to ferric oxides/hydroxides, which retain P more firmly in aerobic soils. Therefore, desorption

potential is frequently greater in anaerobic soils compared to aerobic soils (Barber, 2002; Patrick and Khalid, 1974).

Diffusive transport between soil and overlying water also plays an important role in controlling P release into surface water. For example, P in overlying water must diffuse into underlying soil to facilitate P retention by that soil in which the diffusion happens only when the concentration of P in overlying water is greater than the pore water P concentration (Reddy et al., 1999). Thus, P retention by flooded soil is controlled by P diffusion from surface water to soil, P concentration of the soil pore water and physicochemical characteristics of the soil/water interface.

1.4. Predicting Changes in Dissolved Reactive Phosphorus in Flooded Soils

There is a growing need to predict P release from flooded and anaerobic soils because of the environmental importance of releasing P into surface flood water and soil pore water during flooding. Despite its importance, only a few researchers have examined the capability of soil test P (STP) methods and degree of P saturation (DPS) to predict P release from flooded upland soils, wetlands and drainage ditch sediments. For example, Sallade and Sims (1997a) attempted to predict the soluble P (0.01 M $CaCl_2$ extractable) and EPC_0 in top drainage sediments using DPS calculated in different ways. They observed a significant correlation between DPS calculated using Langmuir P sorption capacity and biologically available P (BAP) and soluble P ($r = 0.38$, $P < 0.05$) and EPC_0 ($r = 0.34$, $P = 0.08$). However, these correlations are too low for a reliable prediction of DPS threshold, thus, emphasizing the need for a more appropriate method to determine DPS threshold. Sallade and Sims (1997b) showed that total Fe oxide

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(dithionate-citrate extractable) is a good predictor of P release from prolonged flooded and anaerobic ditch sediments. As well, a DPS (BAP/P sorption index*100) threshold of 40% was introduced with a reasonable accuracy ($r = 0.75$) as the upper environmentally based limit of ditch sediments to minimize release of P to overlying water bodies. In an attempt to identify predictors of P release to the surrounding water bodies, Mukherjee et al. (2009) found strong relationships of water extractable P with Mehlich-1 extractable P, Mehlich-3 extractable P and DPS (calculated using oxalate extractable P, Mehlich-1 extractable P, and Mehlich-3 extractable P as intensity factors and Fe + Al in each extractant as the capacity factor). Estimated STP threshold values for P release were 24 mg kg^{-1} for Mehlich-1 extractable P, 44 mg kg^{-1} for Mehlich-3 extractable P, and 0.079, 0.101 and 0.067, respectively, for DPS calculated using oxalate extractable P, Mehlich-1 extractable P, and Mehlich-3 extractable P as intensity factors with Fe + Al in each extractant as the capacity factor (Mukherjee et al., 2009). Young and Ross (2001) reported that pore water phosphate concentration of seasonally flooded upland agricultural, non agricultural, forest and wetland soils can be predicted using ammonium acetate extractable P ($r^2 = 0.74$) and DPS ($r^2 = 0.80$), where DPS was calculated as the ratio of fluoride extractable P to the P sorption index (PSI). Pant et al. (2002) observed that double acid (0.0125 M H_2SO_4 + 0.05 M HCl) extractable Ca, Mg, Al and P were able to predict 80% of variation of P release from diverse range of Lake Okeechobee watershed soils under anaerobic condition. Loeb et al. (2008) observed that the ratio between Fe-bound P extracted by Golterman (1996) P fractionation method and amorphous Fe extracted by oxalate extraction method was a strong predictor ($r^2 = 0.79$) of P release from floodplains in Netherlands and Poland.

1.5. Need and Research Objectives

Many studies investigating P release from flooded soils have been documented for acidic soils where P retention is mainly governed by Fe and Al. Most of these studies conducted elsewhere have indicated that Fe plays a vital role in P dissolution under reduced conditions. Less work has been carried out in alkaline to calcareous soils around the world to investigate the P release under flooded conditions with consequent occurrence of anaerobic conditions (Amer et al., 1991; Shenker et al., 2005; Zhang et al., 2010). In particular, only a few studies had been conducted to investigate the P behavior in flooded alkaline to calcareous soil in Manitoba where flooding increases P loadings to the main rivers during spring (McCullough et al., 2012). Therefore, to develop proper beneficial management practices associated with surface and subsurface drainage to reduce P mobilization from agricultural soils, it is important to identify the temporal pattern of P release, and to develop indicators to reliably predict the magnitude of P release from soils under temporarily waterlogged conditions with consequent occurrence of anaerobic conditions. This information is important for designing and operating drainage systems and beneficial management practices such as restored wetlands, to minimize P loadings to surface and groundwater.

Therefore, a one-site field experiment was conducted to (1) quantify P release to surface and soil pore water with flooding and development of anaerobic conditions in unamended, inorganic fertilizer- or manure-amended heavy clay soil, (2) correlate changes in soil solution and surface flood water chemistry to the changes in DRP and TDP concentrations in order to identify the causes of changes in P concentrations during

flooding, and (3) identify the effect of flooding on P sorption and extractability. A follow-up laboratory incubation study with 12 surface soils from different locations of Manitoba was conducted to (1) quantify and compare P release to surface and soil pore water with flooding and development of anaerobic conditions in manured and unamended soils having different physical and chemical properties, (2) monitor changes in P sorption ability of soils before and after flooding and identify factors affecting P sorption of the soils, (3) relate changes in soil solution and surface flood water chemistry to the changes in DRP concentration in order to identify the possible causes for P release during flooding, and (4) develop indices to predict P release from soils under flooded condition by determining the relationship between DRP concentrations in surface flood water after development of anaerobic condition and easily measurable soil parameters. The information gathered from this research project will help to reduce P losses from soils under anaerobic conditions and will benefit Manitoba's water resources, including lakes, wetlands, and aquatic habitat.

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2. PHOSPHORUS RELEASE FROM A HEAVY CLAY SOIL IN MANITOBA UNDER SIMULATED FLOODING

2.1. Abstract

Flooding and development of reducing conditions often lead to enhanced release of phosphorus (P) to flood water. A field ponding study was conducted to examine the behavior of P release from a Scanterbury heavy clay soil (Vertisol) in the Red River Valley of Manitoba. Unamended, manured, and fertilized plots were flooded for 42 days and surface flood and pore water samples were collected twice a week. Soil samples collected from inside and outside of ponds after flooding period were analyzed for soil test P and P sorption capacity. Flooding did not significantly change dissolved reactive P (DRP) release to surface flood water or to soil pore water. Concentrations of DRP in pore water slightly decreased in the manured treatment and remained relatively stable in the other treatments. Phosphorus fractionation of soils before and after flooding indicated a significant decrease in moderately labile P fractions ($NaHCO_3$- and NaOH-extractable P) with flooding. Olsen P and Mehlich-3 P concentrations were not significantly different between flooded soils and unflooded soils taken from outside the ponds, indicating that there was no significant change in chemical availability of soil P with flooding. The soil's capacity to sorb P, as indicated by the single point P sorption values was significantly greater in all treatments after the flooding period compared to initial values. Results suggest that development of anaerobic conditions with flooding did not pose a significant

risk in enhancing P release to surface water in this soil since the soil retained its capacity to act as a sink for P under anaerobic conditions.

2.2. Introduction

Phosphorus (P) is the nutrient limiting eutrophication of most surface freshwater bodies (Schindler, 1977). Phosphorus accumulated in the surface of agricultural soils is susceptible to losses through surface runoff, erosion, and leaching, and could be transported to water bodies, increasing their P concentrations and contributing to accelerated eutrophication in lakes and streams (Sharpley, 1995). As a result, the United States Environmental Protection Agency (USEPA) has identified agricultural non-point source pollution as the major source of stream and lake contamination that lowers water quality in the USA (USEPA, 2000).

Various environmental and soil factors can modify P retention and release (adsorption and desorption) of a soil. In the Canadian Prairies, areas with flat or depressional landscapes become saturated or flooded during snowmelt periods. Under such conditions, redox potential and associated pH changes may play an important role in controlling P sorption and release, directly and indirectly. The majority of studies conducted elsewhere showed that flooding increased P release to surface water (Ann et al., 2000; Ajmone-Marsan et al., 2006; Grunth et al., 2008; Scalenghe et al., 2002; Shenker et al., 2005; Young and Ross, 2001). However, in a few studies, a decrease, or a relatively steady P concentration in surface flood water over the flooding period was observed (Shober and Sims, 2009; Zhang et al., 2010).

Anaerobic soil conditions may enhance P solubility, which could result in a greater loss of P to water bodies. In a Quebec study, two weeks of anaerobic incubation of liquid hog manure-amended and unamended soil resulted in a significant increase of P

release from soil to the solution (Ajmone-Marsan et al., 2006). The increase in P release was a result of Fe reduction, which occurred within 7–10 days in those anaerobic soils. In addition, reducing conditions in the soil caused a shift in P from recalcitrant to more labile forms, eventually increasing the risk of P loss from manured soils (Ajmone-Marsan et al., 2006). Results of another study showed that dissolved P in soil solution, both in chemically amended ($CaCO_3$, $FeCl_3$ and alum) and unamended soils increased with the intensity of reduction (Ann et al., 2000). The authors suggested that this increase in P was due to the release of occluded phosphate and ferrous ions to the soil solution when Fe compounds are reduced. Concentrations of both dissolved P and dissolved Fe in pore water at a redox potential (Eh) of approximately -100 mV were about eight to ten times greater than those under aerobic conditions for unamended soils. In alkaline soils, the pH decrease associated with reducing conditions of soil also contributes to the increase in P solubility. Saleque and Kirk (1995) found that the decrease in pH in an alkaline soil under reducing conditions enhanced dissolution of calcium phosphates thus releasing more P into soil solution.

In contrast to the above findings, some researchers found a decrease in P concentrations in soil solution with reduction in a submerged rice soil (Holford and Patrick, 1981) and poultry litter-amended soil (Vadas and Sims, 1999). This was attributed to an increase in P sorption by soils under reduced conditions. Transformation of crystalline ferric hydroxide to amorphous forms of ferrous or ferric hydroxide under reducing conditions resulted in more reactive sites for P adsorption (Chacon et al., 2006), thus decreasing soil solution P concentration. Phosphorus compounds released under anaerobic conditions may get bound to already available Al in acidic soils, which is not a

redox active element, reducing the P concentration in the soil solution. Retardation of Fe^{3+} dissolution, probably through mechanisms that block electron transfer to Fe^{3+} mineral surfaces, can prevent an increase in P in soil solution by lowering the release of Fe^{+3} bound P under reduced conditions (Murray and Hesterberg, 2006).

Most of these previous studies have indicated that Fe plays a vital role in P dissolution under reduced conditions. However, even though Manitoba soils are generally characterized by low Fe and high Ca and Mg concentrations, an increase in P release to overlying water and pore water over a period of flooding has been observed in organic soils and a feedlot (Campbell and Racz, 1975; Racz, 1979). In both of these situations, there were large concentrations of organic P in soils. Therefore, the authors suggested that reducing conditions due to flooding may have increased the hydrolysis of polyphosphates in soil as well as increased mineralization of organic P.

To develop best management practices to minimize P loadings to water bodies, there is a need to understand the temporal pattern of P release under temporarily waterlogged conditions with consequent occurrence of anaerobic conditions in Manitoba soils and identify the factors responsible for the behaviour. The specific hypothesis of the experiment was that flooding and resulted anaerobic conditions change the P release from soils. Therefore, research was conducted to investigate the release of dissolved reactive P (DRP) and total dissolved P (TDP) from manured, fertilized and unamended soils under waterlogged, anaerobic conditions in a field of relatively flat landscape with slowly permeable, heavy clay soils typical for the Red River Valley region of Manitoba and to relate changes in DRP and TDP concentrations to the changes in soil pore water and surface flood water chemistry such as dissolved Ca and Mg under flooded, anaerobic

conditions. Such information is needed for the design and operation protocols for drainage systems and constructed/restored wetlands in Manitoba soils to minimize P loadings from agricultural land to surface water bodies.

2.3. Materials and Methods

A field site at the University of Manitoba's Glenlea Research Station was selected for the study. The soil at the site is a Scanterbury heavy clay (Vertisol) (Soil Classification Working Group, 1998). The soil has 60% clay and was alkaline with a pH of 7.4. The Olsen extractable P concentration in air-dried soil samples at the beginning of the experiment was 16.6 mg kg^{-1} (Table 2.1). The field site was established with three fertility treatments: solid beef cattle manure (SBCM)-amended, monoammonium phosphate (MAP) fertilizer-amended and unamended, with four replicates arranged in a randomized complete block design (Appendix 2.A). Solid beef cattle manure was analyzed for total P concentration prior to application. Both SBCM and MAP were applied at a rate of 100 kg total P ha^{-1}. All plots were 2 m x 2 m and were roto-tilled twice to thoroughly incorporate the manure and fertilizer into the soil. One month after treatment application, ponding basins (1 m x 1 m) were constructed at the centre of each plot by excavating the upper 15 cm soil, installing a watertight liner, then replacing the soil inside the liner. Each basin was enclosed within a wooden frame to hold the vinyl liner high enough to allow water ponding to a depth of 15 cm above the surface of each ponding basin (Figure 2.1). Two Rhizon flex soil solution samplers with a diameter of 2.5 mm (Rhizosphere Research Products, Wageningen, The Netherlands) were installed at 5 and 10 cm depths below the soil surface to extract samples of soil pore water.

Figure 2.1 A ponded basin with Rhizon flex samplers

Soil samples (0-15 cm depth) were taken from all plots immediately prior to flooding and were analyzed for Olsen P (Olsen et al., 1954) on a fresh (un-dried) basis. Soil samples were air-dried, sieved (2 mm) and analyzed for texture by the pipette method (Gee and Bouder, 1986), Olsen (Ols-P) P (Olsen et al., 1954), Mehlich-3 (M3P) extractable P (Mehlich et al., 1984),   water extractable P (Kuo, 1996), pH (1:2 soil: solution), and EC (1:2 soil: solution), and Mehlich-3 extractable Ca (M3Ca), Mg (M3Mg), Fe (M3Fe), Mn (M3Mn), and Al (M3Al). To determine Olsen extractable P, 20 mL of 0.5 M $NaHCO_3$ solution (pH = 8.5) was added to 1 g of soil together with 0.25 g P-free charcoal, shaken for 30 min and filtered through Whatman No 40 filter paper. Mehlich-3 P was extracted by shaking 2.5 g soil with 25 mL of Mehlich-3 extracting reagent (0.015 M NH_4F + 0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.013 M HNO_3 + 0.001

M EDTA) for 5 min and filtering the extract through Whatman No. 42 filter paper. Water

extractable P was extracted by shaking 2.0 g soil with 20 mL of de-ionized water for 1 h

and filtering using Whatman No. 40 filter paper. Phosphorus in extracts was determined

by the molybdate blue color method (Murphy and Riley, 1962) and absorbance was

measured at 882 nm wavelength using an Ultraspec 2100 pro UV/visible

spectrophotometer (Biochrom, Cambridge, UK). Mehlich-3 extractable Ca, Mg, Fe, Mn,

and Al were determined using inductively coupled plasma membrane atomic emission

spectroscopy (ICP-AES; Thermo Electron ICAP 6500, Cambridge, UK).

Table 2.1 Initial chemical and physical soil properties[†] for the field experiment

Soil property[†‡]	
Clay %	60
Silt %	30
Sand %	10
pH[§]	7.50 (0.07)
Ols-P (mg kg^{-1})[§]	16.6 (1.65)
M3P (mg kg^{-1})[§]	17.7 (3.15)
M3Fe (g kg^{-1})[§]	0.30 (0.04)
M3Mn (g kg^{-1})[§]	0.05 (0.01)
M3Al (g kg^{-1})[§]	0.84 (0.07)
M3Ca (g kg^{-1})[§]	6.70 (1.06)
M3Mg (g kg^{-1})[§]	1.90 (0.05)

[†]Initial soil properties were analyzed before treatment application
[‡]Abbreviations: M3Ca, M3Mg, M3Fe, M3Mn and M3Al - Mehlich-3 extractable Ca, Mg, Fe, Mn, and Al respectively; Ols-P - Olsen extractable P; M3P - Mehlich-3 extractable P
[§]Values are the average of four replicates with ± one standard error of the average given in the parenthesis

Each basin was ponded to a depth of 15 cm above the surface using a well water

source with low dissolved P concentrations (<0.003 mg L^{-1}). Water samples were

collected immediately after flooding and twice a week for a period of six weeks after flooding. Rhizon flex samplers were used to collect samples from soil pore water at 5 and 10 cm depths. Surface water in the basins was sampled using syringes and filtered through 0.45 μm membrane filters. Soil in the basins was sampled at the same time as water samples and analyzed for Ols-P throughout the flooding period. Redox potential (Eh) and soil pH in flooded soil were measured at each water sampling date using a portable Fisher Accumet Eh meter and a portable Fisher Accumet pH meter (Thermo Fisher Scientific Inc, Beverly, USA), respectively. Surface flood water and pore water samples were analyzed within 24 h for dissolved reactive P (DRP) by the molybdate blue method. Subsamples of surface flood water and soil pore water were analyzed using ICP-AES for concentrations of total dissolved P (TDP), Ca, Mg, Fe, Al and Mn to identify the possible reactions responsible for any changes in P release patterns under anaerobic conditions.

Soil samples collected over the flooding period and at the end of the flooding period from both inside (flooded) and outside the ponds (unflooded) were analyzed freshly for Olsen extractable P and then dried, ground, and sieved through a 2 mm sieve and were stored until further analysis. Olsen extractable P, water extractable P, and Mehlich-3 extractable P, Ca, Mg, Fe, Mn and Al concentrations were determined in the dried and ground soil samples using the same procedures described above. Soil pH and EC (1:2 soil: solution) were measured using Fisher Accumet AB15 pH meter and AB30 conductivity meter (Fisher Scientific Ltd, Ottawa, Canada), respectively. Soil samples collected from inside and outside of the ponds prior to flooding and at the end of the flooding period were also analyzed for single point (150 mg P L^{-1}) sorption capacity

(P150) (Bache and Williams, 1971). To determine the P sorption capacity, 2 g of air-dried, sieved (< 2 mm) soil were weighed into plastic vials and a 20 mL solution containing 150 mg P L^{-1} in 0.001 M KCl was added. The suspension was shaken at 120 epm for 24 h at room temperature (22±2˚C). The samples were filtered through Whatman No. 1 filter paper and the remaining P was determined colorimetrically by the molybdate blue method. The amount of P adsorbed, P150, was determined by the difference between the amount of P added to the soil and the equilibrium P concentration in the solution. Dried and ground soil samples were also subjected to P fractionation analysis by a modified Hedley procedure (Ajiboye et al., 2004; Dou et al., 2000). Soil samples (0.5 g) were sequentially extracted with deionized water, 0.5 M $NaHCO_3$, 0.1 M NaOH and 1 M HCl. For each extraction step, the soil with the extraction solution (1:60 soil: solution) was shaken at 120 epm for 16 h at room temperature (22±2˚C), and centrifuged at 12,500 g for 10 min. The supernatant was then collected through vacuum filtration (0.45 μm membrane filter) and the P concentration in each extract was determined by the molybdate blue method. Residual P content of the remaining soil at the end of sequential extraction was measured colorimetrically after digestion with a digestion mixture containing H_2O_2 and H_2SO_4.

2.3.1. Statistical analysis

The UNIVARIATE procedure (SAS Institute, 2011) indicated that residuals of DRP, TDP and total dissolved Fe and Mn concentrations in surface flood and soil pore water were not normally distributed, according to the Shapiro–Wilk statistic ($W < 0.9$). Therefore, analysis was conducted after natural log transformation of raw data. Analysis

of variance (ANOVA) was performed on properties analyzed in surface water and soil solution using the MIXED procedure for repeated measures in SAS Version 9.3 (SAS Institute, 2011) having treatment and depth as fixed effects and time (days after flooding) as the repeated measures factor. The spatial power [SP(POW)] covariance structure was used because time intervals were heterogeneous. The LSmeans statement with the pdiff option was used to compare least square mean differences with adjustments made using Tukey's method. To investigate the changes in extractable P, P fractions, and P sorption capacity in soils before and after flooding, the MIXED procedure was used. Soil, treatment, flooding condition, and their interactions were considered as fixed effects. Coefficients of variation % (CV%) for the transformed data were calculated using the equation, Sqrt((exp(MSE)-1)*100%, and for row data using the equation, Sqrt(MSE)/mean*100%. Correlation analysis was conducted to explore relationships between the changes in TDP and DRP concentrations and changes in Fe, Mn, Ca and Mg concentrations in surface flood and soil pore water samples For all statistical analyses, significance was determined at $P < 0.05$.

2.4. Results and Discussion

2.4.1.   Changes in redox potential (Eh) and pH of surface soils with time of flooding

Redox potential (Eh) of surface soils decreased rapidly during the first 14 days of flooding, and decreased from initial Eh of 263-279 mV to below +100 mV, the approximate threshold redox potential at which Fe^{3+} is reduced to Fe^{2+} at pH 7 (Gotoh and Patrick, 1974), after day 14 of ponding (Figure 2.2, Appendix 2.B). The redox

potential at a given time was not significantly different among treatments even though we expected a faster rate of reduction in manured soils, since readily decomposable organic material may enhance soil microbial respiration. Although not as consistent as the decrease in Eh, there was generally a decrease in pH during the flooding period, with the lowest pH values in manure amended soils and the highest in fertilized soils under flooded conditions (Figure 2.3, Appendix 2.B). The decreases in pH of alkaline soils during flooding have been attributed to the accumulation of CO_2, which dissolves in water to produce carbonic acid (Ponnamperuma, 1972).
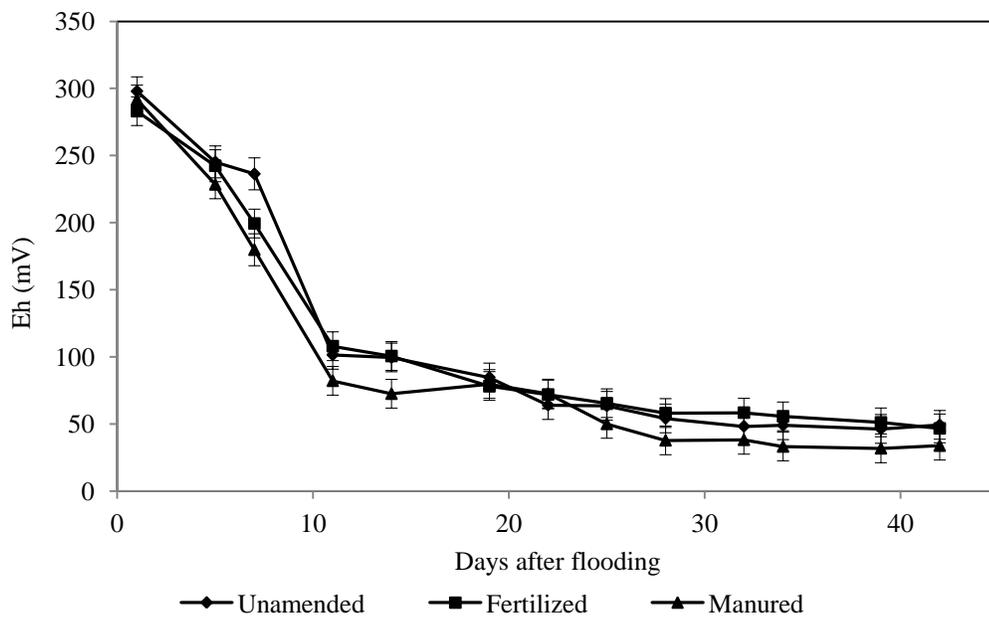
Figure 2.2 Changes in redox potential (geometric mean of four replicates) in unamended, manured, and fertilized soils over the flooding period.
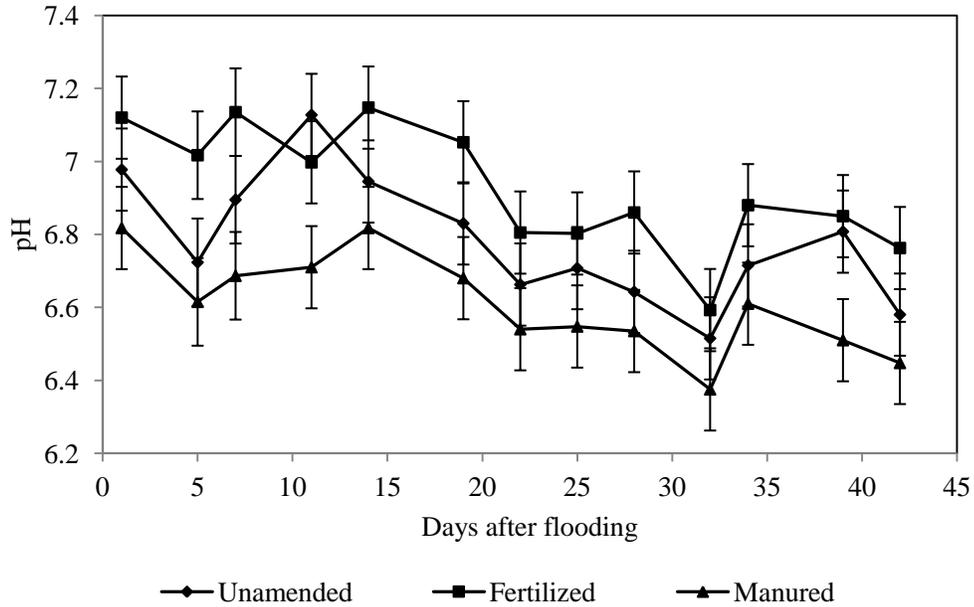
Figure 2.3   Changes in pH (geometric mean of four replicates) in unamended, manured, and fertilized soils over the flooding period.

2.4.2. Changes in dissolved reactive phosphorus (DRP) and total dissolved phosphorus (TDP) concentrations with time of flooding

The mean DRP concentration in surface water was significantly greater in the fertilized plots than in unamended plots, averaging around 0.06 mg L^{-1} on unamended soil, 0.11 mg L^{-1} on manured soils and 0.15 mg L^{-1} on fertilized soil. Concentration of TDP in surface water was greater in amended plots than in unamended plots, but this effect was significant only with fertilizer amendment. However, both DRP and TDP concentrations (means of four replicates) did not vary significantly during the 42 days of flooding regardless of the treatment (Table 2.2).

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Table 2.2 Variation of dissolved reactive phosphorus (DRP) and total dissolved phosphorus (TDP) concentrations in surface flood water over the flooding period (geometric least square means).

Treatment		DRP	TDP
		mg L^{-1}	
Unamended		0.06 b	0.08 b
Fertilized		0.15 a	0.18 a
Manured		0.11 ab	0.13 ab
ANOVA applied to log transformed values	df	$P > F$	$P > F$
Treatment	2	0.012	0.013
Time	12	0.061	0.115
Treatment*Time	24	0.061	0.090
CV‡ (%)		28	46

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]CV - coefficient of variation

Within treatments, mean DRP concentration in soil pore water was not significantly different at 5 cm and 10 cm depths. There was no significant treatment by depth interaction for DRP concentration. Mean DRP concentrations in pore water in unamended plots and fertilized plots did not vary significantly over the flooding period. Only the manured treatment showed significant differences in pore water DRP concentration over time, with DRP concentrations significantly less after 28 and 39 days of flooding than after one and five days of flooding (Table 2.3). With the exception of the first day of flooding, mean pore water DRP concentrations in manured and fertilized plots were not significantly greater than in unamended plots. Although this may suggest that manure or fertilizer addition does not result in any substantial increase in dissolved P concentration in pore water under flooded and anaerobic conditions, the lack of statistically significant difference is also due to the large variability in DRP measurements (CV = 57%). Even though there are some large differences in DRP concentration over

the flooding period, they were not statistically significant differences, which may be partly a result of some missing data, which affect the standard error.

Table 2.3 Variation of dissolved reactive phosphorus (DRP) concentration in 5 and 10 cm soil pore water over the flooding period (geometric least square means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
	mg L^{-1}		
1	0.07 aB[†‡]	0.39 aA	0.23 aAB
5	0.09 aA	0.23 aA	0.21 aA
7	0.05 aA	0.25 aA	0.14 abA
11	0.05 aA	0.22 aA	0.14 abA
14	0.05 aA	0.21 aA	0.16 abA
19	0.06 aA	0.22 aA	0.14 abA
22	0.06 aA	0.21 aA	0.08 abA
25	0.05 aA	0.20 aA	0.11 abA
28	0.06 aA	0.20 aA	0.07 bA
32	0.08 aA	0.22 aA	0.10 abA
34	0.06 aA	0.23 aA	0.11 abA
39	0.03 aA	0.16 aA	0.07 bA
42	0.05 aA	0.19 aA	0.13 abA

Analysis of variances applied to $\log_e$ transformed values	df	$P > \text{F}$
Treatment	2	0.012
Depth	1	0.877
Treatment*Depth	2	0.461
Time	12	0.0007
Treatment*Time	24	0.002
Depth*Time	12	0.159
Treatment*Depth*Time	24	0.628
CV§ (%)		57

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡] Mean values followed by the same uppercase letter within a row are not significantly different

[§]CV - coefficient of variation

Similar to the results for DRP, pore water TDP concentration was not significantly different between the 5 cm and 10 cm depths (Table 2.4). The effects of time and treatment were also similar at both depths. Mean TDP concentration in pore water of

unamended plots dropped after the first week of flooding and then increased from about

fourth week after flooding until the end of the flooding period (Table 2.4). However,

TDP concentration was relatively stable in fertilized and manured plots throughout the

flooding period. Similar to the DRP concentration, TDP concentrations were not

significantly affected by manure amendment and TDP concentration was significantly

greater in two out of 13 days fertilized plots compared to unamended plots.

Table 2.4 Variation of total dissolved phosphorus (TDP) concentration in 5 and 10 cm soil pore water over the flooding period (geometric least square means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
	mg L^{-1}		
1	0.091 abcdeA[†‡]	0.36 aA	0.19 aA
5	0.131 abcA	0.27 aA	0.15 aA
7	0.106 abcdA	0.30 aA	0.12 aA
11	0.049 bcdeA	0.25 aA	0.15 aA
14	0.052 bcdeA	0.22 aA	0.14 aA
19	0.034 deB	0.21 aA	0.11 aAB
22	0.031 eB	0.19 aA	0.08 aAB
25	0.047 cdeA	0.20 aA	0.13 aA
28	0.174 aA	0.15 aA	0.11 aA
32	0.135 abA	0.15 aA	0.12 aA
34	0.082 abcdeA	0.23 aA	0.17 aA
39	0.110 abcA	0.23 aA	0.21 aA
42	0.080 abcdeA	0.21 aA	0.16 aA

Analysis of variances applied to $\log_e$ transformed values	df	$P > \mathrm{F}$
Treatment	2	0.035
Depth	1	0.559
Treatment*Depth	2	0.144
Time	12	0.0002
Treatment*Time	24	<0.0001
Depth*Time	12	0.893
Treatment*Depth*Time	24	0.997
CV§ (%)		64

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]Mean values followed by the same uppercase letter within a row are not significantly different

[§]CV - coefficient of variation

In this study, anaerobic conditions did not enhance release of dissolved P to surface flood water or soil pore water in any of the treatments. These results are contrary to most previous work reporting increased DRP concentrations in surface flood and soil pore water after flooding (Ann et al., 2002; 2006; Scalenghe et al., 2012; Surridge et al., 2007; Young and Ross, 2001). However, Shober and Sims (2009) observed a steady DRP concentration in surface water even after 63 days of anaerobic incubation of unamended and organic P source (liquid slurry pit dairy manure and biosolids) amended soils.

The release of P that often occurs in anaerobic soils has serious implications for land drainage practices. Sanchez-Valero et al. (2007) found that the increased P load in managed tile drains compared to free flowing drains was caused mainly by the increased P solubility caused by shallow water table rather than by external addition of P. In addition, Sallade and Sims (1997) observed that sediments in drainage ditches released P to overlying water thereby increasing the P concentration in receiving water bodies.

The re-sorption of released P by soil components has been identified as one of the reasons for the relatively stable or decrease in DRP or TDP concentration in the soil solution following flooding (Chacon et al., 2006; Holford and Patrick, 1981; Vadas and Sims, 1999). In the present study, single point P sorption isotherm studies on dried and rewetted soil samples showed a significant ($P < 0.05$) increase in P retention capacity after 42 days of flooding compared to pre-flooding in all treatments (Table 2.5) while there was no significant treatment or interaction effect. Although P150 was not measured in anaerobic soil, the results suggest that the Scanterbury soil continues to act as an

effective sink for P when exposed to reducing conditions. In literature, increased P sorption with flooding has been commonly attributed to the transformation of crystalline ferric hydroxide to amorphous ferrous or ferric hydroxide resulting in more reactive surface sites (Holford and Patrick, 1981; Vadas and Sims, 1999). As well, soil Al^{3+}, which is not redox active, can also sorb P released due to Fe reduction (Chacon et al., 2006). In addition, anaerobic microorganisms may use released P for their metabolism, which may also reduce the P concentration in soil solution (Pant and Reddy, 2001). Organic molecules also have the ability to complex the released P and decrease P concentration in the soil solution (Hutchison and Hesterberg, 2004).

Table 2.5 Effect of flooding on single point phosphorus sorption capacity (P150) of soil (geometric least square means).

Treatment	Flooded condition		
	Prior to flooding	**After 42 days-unflooded soil**	**After 42 days-flooded soil**
		mg kg^{-1}	
Unamended	777.0	765.4	794.3
Fertilized	723.3	722.7	784.9
Manured	746.5	745.5	826.5
Mean	744.5 b†	748.9 b	801.9 a
ANOVA		df	$P >$ F
Treatment		2	0.487
Flooding condition		2	0.002
Treatment* Flooding condition		4	0.486
CV‡ (%)			22

†Mean values followed by the same lowercase letter within a row are not significantly different
‡CV - coefficient of variation

2.4.3. Changes in soil pore water and flood water chemistry and their effect on DRP and TDP concentration changes

In general, concentrations of dissolved Ca and Mg increased with flooding in surface flood water for all treatments. Dissolved Ca and Mg concentrations in surface flood water at 28 day of flooding increased by 6- and 18-fold, respectively, compared to day one concentrations (Appendix 2.C; Table I). Dissolved Fe concentrations in surface flood water did not show a consistent trend during the flooding period but generally declined to levels below detection limit by the end of the flooding period (Appendix 2.C; Table I). However, there was a significant treatment*time interaction, where concentrations of dissolved Fe were more variable with time in surface water of unamended and manured plots than in fertilized plots. Dissolved Mn concentration in surface water was also highly variable during the flooding period, with the lowest concentration in fertilized soils and the greatest in manured soils (Appendix 2.C; Table I). Concentration of Mn in surface water was significantly different from that of day 1 only on the 28th day of flooding, when Mn concentration increased by nearly six times. Dissolved Ca and Fe concentrations in pore water were not different for 5 cm versus 10 cm depths (Appendix 2.C; Table II and IV). However, dissolved Mg concentration was significantly different at 5 and 10 cm depths regardless of the treatment or time (Appendix 2.C; Table III). The depth*time interaction was significant only for dissolved Mn concentration in pore water at 5 and 10 cm depths (Appendix 2.C; Table V and VI). Dissolved Ca concentration in pore water periodically increased over the last half of the flooding period in manured and fertilized plots but remained relatively stable in

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unamended plots. Periodic increases in dissolved Mg concentrations were observed during the last four weeks of flooding for all treatments. Decrease in pH due to the anaerobic conditions may have increased the solubility of Ca and Mg compounds present in the soil. Reduction of soil leads to an increased solubility of Fe and Mn compounds, releasing these elements to the soil solution (Chacon et al., 2006; Surridge et al., 2007). As expected, dissolved Mn concentrations increased within the first few days of flooding for all the treatments and generally continued to increase throughout the flooding period. Iron concentrations increased periodically during the last half of the flooding period, except in fertilized soil, whereas in the manured treatment, dissolved Fe concentrations increased by 12- to 14-fold during the last two weeks compared to day 1. Dissolution of Fe and Mn under anaerobic conditions may significantly enhance the release of P (Ajmone-Marsan et al., 2006; Ann et al., 2000; Racz, 2006; Young and Ross, 2001). However, in this study, the increased concentrations of Fe and Mn in pore water during flooding did not result in increased concentrations of Fe and Mn in surface flood water or increased DRP or TDP concentrations in surface or soil pore water.

Since differences in DRP or TDP concentrations throughout the flooding period were not significant between pore water at 5 and 10 cm, only pore water at 5 cm depth along with surface water were considered for correlation analysis. Correlation analysis was conducted between changes in DRP or TDP concentrations in relation to previous sampling day and changes in dissolved Ca, Mg, Mn and Fe concentrations in relation to previous sampling day during flooding in unamended, fertilized and manured soils. Even though the release of DRP or TDP from this soil to surface water did not increase during the flooding period, the change in TDP was significantly correlated with changes in

concentrations of Ca, Mg, Fe, and Mn in several cases, especially for soil pore water

sampled in the manured treatment (Table 2.6).   Changes in Fe, Mg, and Ca

concentrations in surface or pore water were generally not significantly correlated with

changes in DRP concentrations, except for Mn, which was negatively correlated with

DRP in pore water of fertilized soil.

Table 2.6   Correlation coefficients (*r*) between changes in dissolved reactive phosphorus (DRP) or total dissolved phosphorus (TDP) concentrations in relation to previous sampling day and changes in dissolved Ca, Mg, Mn and Fe concentrations in relation to previous sampling day in surface flood and soil pore water of unamended, fertilized and manured soils.

Dissolved P form	Treatment	Depth	Fe	Mn	Ca	Mg
			Correlation coefficients (*r*)			
DRP	Unamended	Surface	0.06	-0.18	0.15	0.05
		5 cm	0.18	0.24	0.36	0.27
	Fertilized	Surface	-0.34	-0.31	-0.01	-0.10
		5 cm	-0.03	-0.63*	-0.14	-0.24
	Manured	Surface	0.06	0.10	0.27	0.22
		5 cm	0.41	0.31	-0.29	-0.14
TDP	Unamended	Surface	0.16	-0.10	0.43	0.38
		5 cm	0.58	0.84***	0.41	0.71**
	Fertilized	Surface	-0.38	-0.29	-0.01	-0.19
		5 cm	0.08	0.42	0.01	0.12
	Manured	Surface	-0.07	0.05	0.38*	0.37
		5 cm	0.76**	0.68*	0.46	0.68*

*,**,*** Significance at 0.05, 0.01, and 0.001 probability, respectively

2.4.4. Changes in extractable phosphorus concentrations in response to reducing conditions

Concentration of Olsen P in air-dried soils (Ols-P_{Dry}) was generally greater for the

fertilized and manured soils than for the unamended soils (Appendix 2.D; Table II).

However, concentrations of Mehlich-3 extractable P in air-dried soils (M3P_{Dry}), and

Olsen P in wet soil (Ols-P_{Wet}), were significantly greater only for a few days in fertilized

and manured treatments compared to the unamended treatment (Appendix 2.D, Table I, III). Concentrations of Ols-P$_{Wet}$ (Appendix 2.D; Table III) did not change significantly throughout the flooding period except for a significant increase on the 11th day in manured soil. Olsen extractable P concentrations measured in wet soils were significantly smaller ($P < 0.0001$) in soils sampled after flooding than in soils sampled prior to flooding on three occasions during the flooding period.

Several researchers have previously reported that flooding significantly decreases the "chemical availability" of P in soil (Willet, 1989; Zhang et al., 2003). For example, Zhang et al. (2003) measured decreased concentrations of easily available P and increased concentrations of slowly available P after flooding. However, Ajmone-Marsan et al. (2006) observed a large increase in P availability measured using anion exchange membrane. In this study, however, soil test P values in air-dried anaerobic and aerobic soils were similar, when measured either as Mehlich-3 P or as Olsen P. It is possible that the extractable P from soils was increased by air drying soils prior to analysis (Baldwin, 1996; Blackwell et al., 2009; Turner and Haygarth, 2003; Xu et al., 2011). Turner and Haygarth (2001) suggested that the rewetting of dried soils during analysis increases extractable P due to the release of microbial P into the soils as a result of killing microorganisms by osmotic shock and cell rupture. In Manitoba soils, Racz (1979) reported that flooding and resulting anaerobic conditions increased the NH_4Cl and NH_4F extractable P concentration. He suggested that the underlying reason for the increased extractable P concentration was the hydrolysis of polyphosphates in soil and increased mineralization of organic P. For the air-dried soil samples taken before and after flooding in our experiment, the concentration of inorganic P in the water extractable

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fraction was significantly greater in the fertilized treatment than in the manured treatment but was not affected by the flooded condition. Concentrations of moderately labile inorganic P (P in NaHCO$_3$ and NaOH extractable fractions) were significantly lower in soils after flooding compared to the respective amounts before flooding (Table 2.7). Thus, flooding seems to have decreased the concentration of easily extractable P regardless of the treatment likely due to increase in P sorption. The more stable HCl-Pi and residual fractions of P were similar in soils before and after flooding regardless of the treatment. However, all these soil test P analyses were conducted after re-exposing flooded soils to oxygen, which might have altered P extractability.

Table 2.7 Inorganic phosphorus fractions in soils before and 42 days after flooding (geometric least square means).

Effect		H$_2$O-Pi	NaHCO$_3$-Pi	NaOH-Pi	HCl-Pi	Residual P
				mg kg^{-1}		
Treatment						
Unamended		4.82 b[†]	29.19	38.8	128.3	378.6
Fertilized		11.1 a	43.0	43.6	163.6	373.5
Manured		6.33 ab	47.1	49.2	125.9	369.9
Flooding condition						
Before flooding		5.98	46.7 a	49.3 a	142.0	369.1
After flooding		8.12	32.9 b	38.4 b	136.6	378.9
ANOVA	df	---------------------------- $P >$ F ----------------------------				
Treatment	2	0.023	0.088	0.254	0.371	0.651
Time	1	0.052	0.019	0.012	0.630	0.212
Treatment*Time	2	0.856	0.862	0.173	0.463	0.655
CV[‡] (%)		35	30	11	19	2

[†]Mean values followed by the same lowercase letter within a column are not significantly different
[‡]CV - coefficient of variation

2.5. Conclusions

Concentrations of DRP and TDP in surface flood water during the flooding period were low and did not significantly change for unamended, manured, and fertilized Scanterbury clay soil. Concentrations of DRP in soil pore water decreased slightly but significantly during the flooding period in manure amended plots, but not in fertilized or unamended soils. Flooding and resulting anaerobic conditions in this soil, therefore, did not enhance P release to surface water or soil pore water.

The moderately labile P fraction in soil decreased with flooding in all treatments. Furthermore, the single point sorption isotherm indicated an increase in P sorption capacity with flooding, suggesting that this soil's capacity to act as a sink for P may increase when exposed to reducing conditions. However, soil preparation prior to analysis, which involves air drying and re-oxidizing flooded soils, may alter the P extractability and P sorption of soils. Nevertheless, mineralogical studies are needed to provide more definitive information on P sink effect resulting from flooding and consequent occurrences of anaerobic conditions.

Increased concentrations of dissolved Fe, Mn, Ca, and Mg in soil pore water during the flooding period along with stable to slightly reduced P concentration indicates that reductive dissolution of Fe or Mn or dissolution of Ca and Mg due to decreases in pH did not result in the release of P to ponded surface or soil pore water. However, more research is needed to assess the P retention mechanisms and governing factors of increased P retention under anaerobic conditions.

These findings show that flooding and resulting anaerobic conditions did not affect P release from Scanterbury heavy clay soil. If this type of soil is not susceptible to large releases of soil P during flooding, drainage systems on these soils could be managed in a flexible manner from a water quality perspective, with a low risk of elevating concentrations of dissolved P in surface water during flooding periods. However, since this study was limited to one soil type, one site, and one flooding period there is a need to study P release patterns under anaerobic conditions with different soils in Manitoba with varying soil properties.

2.6. References

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3. PHOSPHORUS RELEASE FROM SIMULATED FLOODING OF ALKALINE TO CALCAREOUS SOILS IN MANITOBA

3.1. Abstract

Prolonged flooding and development of reducing conditions often lead to enhanced release of phosphorus (P) to flood water. A laboratory study examined the effect of flooding on release of resident and applied P to surface and pore water from 12 unamended and manured soils from Manitoba. Surface flood water and soil pore water samples were collected weekly over eight weeks of simulated flooding. Concentrations of dissolved reactive P (DRP) in soil pore water increased in all soils with flooding. Concentrations of DRP in surface water increased 2- to 15- fold after flooding in ten soils but were stable or slightly decreased in the two heavy clay soils. Despite increased P release into surface flood and soil pore water during the flooding period, P sorption capacity calculated as single point isotherm (P150), as well as Olsen, Mehlich-3 (M3P) and water extractable P of most unamended soils remained unchanged. In manured soils, P150 increased in six soils but remained relatively unchanged in the others.

Partial least squares (PLS) analysis showed that the absolute change in DRP concentration in surface flood water was related to soil test P in soils while relative change in DRP concentrations was related to soil test P and other soil chemical and physical properties. The PLS analysis indicated that degree of P saturation calculated as $M3P_{ICP}/(2*P150)+M3P_{ICP}$ and clay % can be effectively used to predict relative change in DRP concentration (r^2=0.74). Absolute change in DRP concentration in surface flood water can be predicted using DPS calculated as $(M3P/(2*P150)+M3P*100)$ (r^2=0.79).

3.2. Introduction

Lake Winnipeg, the 10th largest freshwater lake in the world, has been declared "Threatened Lake of the Year, 2013" by the Global Nature Fund due to excessive growth of toxic blue-green algae caused by overabundance of phosphorus (P) and nitrogen (N) (Global Nature Fund, 2013). Phosphorus runoff from agricultural activities in Manitoba contributes an estimated 15% of P enrichment to the lake (Lake Winnipeg Stewardship Board, 2006). To reduce agricultural P losses in Manitoba, a substantial effort has been invested into understanding the unique challenges of nutrient management in our soils, landscapes, climate, crop, and livestock management systems. However, water management is also a concern because periodic or continuous flooding conditions in soils often increase the risk of P release from soil to overlying or drainage water (Amery and Smolders, 2012; Ma et al., 2010).

Numerous studies have been conducted worldwide to investigate P release from flooded, anaerobic soils (Ajmone-Marsan et al., 2006; Liikanen et al., 2004; Scalenghe et al., 2012; Shenker et al., 2005; Surridge et al., 2007; Zhang et al., 2003). In most of the studies, anaerobic conditions increased P availability in soils, which could accelerate P loss to water bodies (Ajmone-Marsan et al., 2006; Hoffman et al., 2009; Kröger et al., 2012; Scalenghe et al., 2012). In a study with manured soils in Quebec, a ten-fold increase in soluble P in the soil solution was observed after two weeks of anaerobic incubation (Ajmone-Marsan et al., 2006). Hoffman et al. (2009) summarized numerous cases where re-flooding cropped lands to restore wetlands substantially increased concentrations of soluble P in soil pore water, resulting in the wetland adding more P to

outflow than it receives in inflow. Scalenghe et al. (2012) and Kröger et al. (2012) observed that periodic anaerobic conditions increase P release from soil, and more importantly, the reduced conditions shift P forms from less mobile P fractions to P more mobile fractions. Generally, flooding and anaerobic conditions decrease the redox potential of soil to <100 mV, converting less soluble Fe^{3+} compounds into easily soluble Fe^{2+} compounds, thereby releasing Fe-bound P into soil solution (Ann et al., 2000; Kröger et al., 2012; Scalenghe et al., 2012). At the initial stage of reduction, Mn may also be responsible for release of P in soils with relatively high Mn contents (Scalenghe et al., 2002; Shahandeh et al., 2003).

Increase in P release due to Fe and Mn reduction under anaerobic conditions is further enhanced in soils with higher cation exchange capacity (CEC) by scavenging Fe^{2+} and Mn^{2+} formed during the reductive dissolution (Amery and Smolders, 2012). Soil organic matter and pH are also important factors governing P release from anaerobic soils, since oxidation of low molecular weight organic matter and pH reduction may lead to changes in surface charges of minerals and organic particles (Ponnamperuma, 1972). In alkaline and calcareous soils, dissolution of Ca-bound P due to the decrease in pH under reduced conditions would also be an underlying reason to increase P release (Racz, 2006; Scalenghe et al., 2012).

In contrast to the above findings, relatively stable P concentration in soil solution has also been observed under anaerobic conditions (Shober and Sims, 2009), which was attributed to an increase in P sorption due to an increase in amorphous Fe in soil, which effectively increased the soil P sorption capacity. Ma et al. (2010) also found that

maximum adsorption of P in soils increased under flooded conditions while Olsen extractable P content decreased. Kröger et al. (2012) reported that prolonged flooding (130 days) of a northwestern Mississippi soil decreased water extractable P and Ca-bound P due to transformation of easily soluble P into less soluble P forms under longer flooding periods. This may suggest that increased hydraulic residence time decreases the chemical availability of P in soils.

A number of studies have been conducted to investigate changes in P release under flooded and anaerobic conditions in lowland soils including paddy fields, water table fluctuation zones of reservoirs, riparian buffer strips and natural and constructed wetlands. However, few studies were focused on studying P release during spring flooding in agricultural soils, where substantial amounts of P may be applied to enhance crop growth (Shober and Sims, 2009; Young and Ross, 2001). In addition, most of the studies reported earlier have been conducted using iron-rich soils where Fe plays a vital role in P retention in soil and therefore, affects P dissolution under reduced conditions. Limited information is available on P release under flooded conditions from Ca and Mg rich soils. Hence, there is a need to study the P release pattern from Ca and Mg dominated soils where P retention is largely controlled by Ca and Mg concentrations and not by Fe or Al.

As P is an important nutrient causing eutrophication in aquatic systems, it is important to identify soils that are prone to releasing substantial quantities of P under flooded, anaerobic conditions and to develop a tool to predict potential P release to flood water. Despite its importance, only a few researchers have examined the capability of

soil P measures and other soil/sediment properties to predict P release from wetland and drainage ditch sediments (Mukherjee et al., 2009; Sallade and Sims, 1997a; Sallade and Sims, 1997b) and soils (Loeb et al., 2008; Pant et al., 2002; Young and Ross, 2001). Therefore, there is a growing need to develop indices to predict P release from flooded and anaerobic soils especially for alkaline to calcareous soils.

In the above context, this laboratory research was conducted to investigate the release of P from manured and unamended Manitoba soils under flooded, anaerobic conditions. The study also aimed to identify the relationship between P release from soil and pH changes and the release of other elements (Ca, Mg, Fe, Mn, and S) into surface flood water. The effects of flooding and development of anaerobic conditions on P sorption capacity, extractable P, and extractable elements were also aimed to investigate. In addition, this study attempted to develop indices based on simple soil characteristics that could predict the P release from soils under flooded conditions by determining the relationship between changes in DRP released to flood water with soil test P (STP), degree of P saturation (DPS) and other chemical and physical properties.

3.3. Materials and Methods

Twelve soils covering four soil orders, Chernozem, Gleysol, Vertisol, and Regosol, were selected from different locations in Manitoba that are prone to flooding during snowmelt. During October and November, 2011, bulk soil samples (0-15 cm) were obtained from fields where manure or P fertilizer was not applied for the last 4 months and stored at room temperature and field moisture contents. Solid dairy cattle manure was collected from the University of Manitoba's Glenlea Research Station,

analyzed for total P, and then stored frozen until further use. To determine total P in fresh manure, five subsamples were digested with H_2SO_4–H_2O_2 acid digestion mixture (Akinremi et al., 2003).   Phosphorus in neutralized digests was determined colorimetrically by the molybdate blue color method (Murphy and Riley, 1962), using a UV/visible spectrophotometer (Biochrom, Cambridge, UK) at a wavelength of 882 nm.

3.3.1. Initial soil characterization

Field moist soil samples were sieved through a 10 mm sieve and separated into two sets. One set of soils was treated with solid cattle manure to provide 100 kg of P ha^{-1} (based on total P content in manure) and thoroughly mixed with the soil. This rate of P is comparable to P supplied at the normal agronomic nitrogen-based rate of manure application in Manitoba. The other set of soils was unamended and kept as the control. Soil samples were incubated for four weeks prior to flooding, to allow manure to interact with soil at field moisture and room temperature.

Subsamples from unamended soils were air-dried, sieved (2 mm) and analyzed for texture (Pipette method; Gee and Bouder, 1986). Representative samples were taken from each treatment after one month of incubation, air-dried and sieved (2 mm), then analyzed for Olsen extractable P (Ols-P) (Olsen et al., 1954), Mehlich-3 ($M3P_{MRP}$) extractable P (Mehlich et al., 1984), water (WEP) extractable P (Kuo, 1996) and Mehlich-3 extractable Ca (M3Ca), Mg (M3Mg), Fe (M3Fe), Mn (M3Mn), and Al (M3Al) concentrations. To determine Olsen extractable P, 20 mL of 0.5 M $NaHCO_3$ solution (pH = 8.5) was added to 1 g of soil together with 0.25 g P-free charcoal and shaken for 30 min and filtered through Whatman No 40 filter paper. Mehlich-3 P was extracted by shaking

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2.5 g soil with 25 mL of Mehlich-3 extracting reagent (0.015 M NH_4F + 0.2 M

CH_3COOH + 0.25 M NH_4NO_3 + 0.013 M HNO_3 + 0.001 M EDTA) for 5 min and

filtering the extract through Whatman No. 42 filter paper. Water extractable P was

extracted by shaking 2.0 g soil with 20 mL of de-ionized water for 1 h and filtering using

Whatman No. 40 filter paper. Phosphorus in extracts was determined by the molybdate

blue color method (Murphy and Riley, 1962) and absorbance was measured at 882 nm

wavelength using an Ultraspec 2100 pro UV/visible spectrophotometer (Biochrom,

Cambridge, UK). Mehlich-3 extractable total P ($M3P_{ICP}$), Ca, Mg, Fe, Mn, and Al were

determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES;

Thermo Electron ICAP 6500, Cambridge, UK). Soil pH and electrical conductivity (EC)

(1:2 soil: solution) were measured using a Fisher Accumet AB15 pH meter and Fisher

Accumet AB30 conductivity meter (Fisher Scientific Ltd, Ottawa, Canada), respectively.

Organic carbon (OC) contents of the soils were analyzed by the loss-on-ignition method

(Ball, 1964) and converted into soil organic matter (SOM) content using a factor of 1.72.

Ammonium acetate (1 M) extractable Ca, K, Mg, and Na in dried and ground samples

were measured by ICP-AES and the summation was reported as the cation exchange

capacity (CEC) of the soils.

A single point P sorption study (P150) (Bache and Williams, 1971) was conducted

using two grams of air-dried, sieved (< 2 mm) soil and 20 mL of solution containing 150

mg P L^{-1} in 0.001 M KCl. The suspension was shaken at 120 epm (excursions per min)

for 24 h at room temperature. The samples were filtered through Whatman No. 1 filter

paper and the remaining P was determined colorimetrically by the molybdate blue

method. The amount of P adsorbed, P150, was determined by the difference between the

amount of P added to the soil and the equilibrium P solution concentration. Soil samples were also subjected to P fractionation analysis by a modified Hedley procedure (Ajiboye et al., 2004; Dou et al., 2000). Soil samples (0.5 g) were sequentially extracted with deionized water, 0.5 M NaHCO$_3$, 0.1 M NaOH and 1 M HCl. For each extraction step, the soil with the extraction solution (1:60 soil: solution) was shaken at 120 epm for 16 h at room temperature, and centrifuged at 12,500 g for 10 min. The supernatant was then collected through vacuum filtration (0.45 µm membrane filter) and the inorganic P concentration in each extract was determined by the molybdate blue method (Murphy and Riley, 1962). Total P was measured using ICP-AES only for 0.1 M NaOH and 1 M HCl extracts. Residual P content of the remaining soil at the end of sequential extraction was measured colorimetrically after digestion with a digestion mixture containing H$_2$O$_2$ and H$_2$SO$_4$. The degree of P saturation (DPS), which is generally explained as the ratio between extractable or labile P concentration as a percent of P sorption capacity of a soil, was calculated using the following equations (Akinremi et al., 2007).

$$DPS1 = \frac{Ols - P}{(2 * P150) + Ols - P} * 100$$

$$DPS2 = \frac{M3P_{MRP}}{(2 * P150) + M3P_{MRP}} * 100$$

$$DPS3 = \frac{M3P_{ICP}}{(2 * P150) + M3P_{ICP}} * 100$$

$$DPS4 = \frac{Ols - P}{\propto (M3Ca + M3Mg) + Ols - P} * 100$$

$$DPS5 = \frac{M3P_{MRP}}{\propto (M3Ca + M3Mg) + M3P_{MRP}} * 100$$

$$DPS6 = \frac{M3P_{ICP}}{\propto (M3Ca + M3Mg) + M3P_{ICP}} * 100$$

Where, α is the slope of the regression line of 2*P150 against (M3Ca+M3Mg) through the origin and has a value of 0.1 for soils in Manitoba (Akinremi et al., 2007).

3.3.2. Incubation study with simulated flooding

After four weeks of incubation, manure amended and unamended soils were packed into incubation jars to a depth of 8 cm so as to attain a density of 1.1 g cm^{-3}. Each treatment was replicated three times within the experimental setup. One Rhizon flex soil solution sampler with a diameter of 2.5 mm (Rhizosphere Research Products, Wageningen, The Netherlands) was installed at the 5 cm depth in each incubation jar during packing to extract the soil solution after flooding. A Pt electrode was installed at 5 cm depth from the surface in one replicate of each treatment to measure the redox potential of the soil. Soil was then gradually flooded with reverse osmosis (RO) water to a depth of 8 cm above the surface to simulate the development of anoxic conditions. The incubation jars were covered with Parafilm$^{®}$M to minimize evaporation, and the water level was maintained by adding RO water after every sampling. The simulated flooding was conducted for eight weeks under room temperature. Surface flood water and soil pore water were sampled one day after flooding and once a week for a period of eight weeks.

Surface water samples were filtered through 0.45 μm membrane filters using vacuum suction. Filtered surface flood water samples and soil solutions extracted by the Rhizon flex samplers were analyzed within 24 h for pH and dissolved reactive P by the molybdate blue method. Subsamples of surface water and soil solution were stored at

4°C and analyzed later for total dissolved Ca, Mg, Fe, Mn, Al and S concentrations using ICP-AES. Redox potential in soil was measured using the permanently installed Pt electrodes coupled with temporarily installed reference electrodes after giving ten minutes of stabilizing time. At the end of the incubation period, soil samples from each incubation jar were obtained and stored frozen at -18 °C until further analysis. Soil samples collected at the end of the inundation period were air-dried, ground, and sieved through a 2 mm sieve and were analyzed for pH, EC, P150, Olsen extractable P, water extractable P, and Mehlich-3 extractable P, Ca, Mg, Fe, Mn and Al contents using the same procedures described above for analysis of the samples collected prior to flooding.

3.3.3. Statistical analysis

Analysis of Variance (ANOVA) was performed for concentrations of DRP and dissolved ions using the MIXED procedure in SAS Version 9.3 (SAS institute, 2011) having soil and treatment as fixed effects and time (days after flooding) as the repeated measures factor. Residuals of DRP, and total dissolved Fe, Mn, and S in both surface flood and soil pore water were not normally distributed, according to the Shapiro Wilks test from Proc Univariate ($W < 0.9$). Therefore, the data were analyzed after natural log transformation of raw data to meet the assumption of normality whenever necessary. Spatial power covariance structure [SP(POW)] was used (Littell et al. 1996) for repeated measure MIXED procedure because time intervals were heterogeneous. The LSmeans statement with the diff option was used to compare mean differences with adjustment made using the Tukey-Kramer test. To investigate the changes in extractable P and cations in soils before and after flooding, Proc MIXED procedure was used. Soil,

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treatment, redox status, and their interactions were considered fixed effects. Coefficient of variation % (CV%) for the transformed data were calculated using the equation, Sqrt((exp(MSE)-1)*100%, and for row data using the equation, Sqrt(MSE)/mean*100%.

Multiple backward regression analysis was conducted between maximum absolute and relative changes in DRP and the changes in pH, dissolved Ca, Mg, Fe, Mn and S concentrations on the sampling date at which the maximum DRP concentration was reported and day 1 of flooding to identify the influence of each element on DRP increase during flooding. Correlation analysis was conducted between extractable P, P150, and extractable cations to identify the cations most likely to be responsible for P retention under anaerobic condition.

The partial least squares (PLS) procedure of SAS 9.3 (SAS Institute, 2011) was used to explore quantitative relationships between the amount of P released from soil during the flooding period and initial soil properties. All soil parameters (30), including soil test P (STP), degree of P saturation (DPS), chemical and physical properties were included as predictors in the initial model. Soil parameters having the greatest influence on the response variable were determined based on the variable importance in the projection (VIP). The VIP > 0.8 was used as the significance level for PLS (Wold, 1995) to select the predictors with significant contribution to the variability in the increase in DRP concentration in surface flood water. Selected soil properties were then included in the reduced model and this was followed by the sequential exclusion of predictor variables with the least impact on the model, based on the loading weights and scores, until the highest r^2 was obtained. The number of PLS factors were selected using split

cross validation method (CV = SPLIT option of PROC PLS) in which successive groups of widely separated observations were held out as the test set. The number of extracted factors with the minimum predicted residual sum of squares (PRESS) statistic was chosen as the optimum. Using the CVTEST option of PROC PLS, the optimum or minimizing number of factors was compared to the PRESS for fewer factors to test whether there was a significant difference. If there was no significant difference, the model with fewer factors was chosen. Using the linear regression of measured values in the response variable and the predicted values obtained in the cross-validation procedure, the predictive strength of the model was assessed. In order to interpret results in terms of original variables, the PLS solution was transformed into an ordinary least squares (OLS) form using the SOLUTION option in PROC PLS. The result was a set of "pseudo" regression coefficients in the original dependent variables.

3.4. Results and Discussion

3.4.1. Soils used for the study

Soils collected from different locations of Manitoba were alkaline (pH ranged from 7.3 to 8.4), non-saline and covered a wide range of available soil P, organic matter, CEC, and textural properties (Table 3.1). The texture of the soils ranged between heavy clay (77% clay in Osborne soil) to loamy sand (8.6% clay in Reinland soil). Organic carbon content varied from 2.3% in Almasippi soil to 9.7% in Lakeland 2 soil. Cation exchange capacity ranged from 18.1 in Reinland soil to 52.6 cmol(+) kg^{-1} in Fyala soil. Sprague soil had the most M3Fe (463 mg kg^{-1}) while Niverville soil had the least (119 mg kg^{-1}). Mehlich-3 extractable Al ranged between 5.75 mg kg^{-1} in Alamasippi soil and

742.7 mg kg^{-1} in Osborne soil whereas M3Mn ranged between 37.0 mg kg^{-1} in Fyala soil and 244.3 mg kg^{-1} in Newdale soil. Smallest M3Ca and M3Mg concentrations were measured in Reinland soil (3267 and 565 mg kg^{-1}, respectively). The greatest M3Ca concentration was measured in Niverville soil (8037 mg kg^{-1}) while the greatest M3Mg concentration was measured in Osborne soil (1973 mg kg^{-1}). Initial Olsen extractable P contents in the studied soils also varied greatly. According to the rating system in Manitoba (Manitoba Soil Fertility Guide, 2007), Ols-P concentration in ten soils were greater than "medium" (15 mg kg^{-1}) while the other two soils (Almasippi and Reinland) were having medium Ols-P concentration (10 - 15 mg kg^{-1}).

Table 3.1 Different soils used in the study, their taxonomic classification, and basic soil properties.

Soil series	Taxonomic order	Clay	Silt	Sand	pH (1:2, soil:H$_2$O)	EC (1:2, soil:H$_2$O) dS m^{-1}	OC %	CEC cmol(+)kg^{-1}	Olsen P	Al[†]	Ca[†]	Fe[†]	Mg[†]	Mn[†]
		―― % ――								――――――mg kg^{-1}――――――				
						Unamended								
Newdale	Chernozem	32.3	32.7	34.9	7.3	0.48	3.94	27.7	23.7	315	4323	235	981	244
Lakeland 1	Chernozem	49.8	40.9	9.30	7.7	0.66	6.26	45.3	19.9	234	7250	135	1603	77
Lakeland 2	Chernozem	34.1	42.4	23.5	7.4	1.48	9.74	48.9	65.7	77	7793	232	1750	52
Arborg	Chernozem	65.1	29.1	5.80	7.9	0.69	4.41	40.4	77.1	736	6400	292	1750	70
Almasippi	Chernozem	13.1	8.20	78.7	8.4	0.51	2.26	25.3	12.6	6	5820	187	1427	77
Reinland	Chernozem	8.60	7.30	84.2	7.8	0.35	2.44	18.1	13.8	241	3267	192	565	141
Niverville	Chernozem	61.6	30.3	8.10	8.0	0.75	3.02	44.2	31.6	73	8037	119	1777	86
Fyala	Gleysol	50.6	44.4	4.90	7.5	0.91	9.34	52.6	43.4	220	7627	208	1670	37
Sprague	Gleysol	15.9	19.8	64.4	7.9	0.72	3.25	25.1	23.5	134	3823	463	742	53
Long Plain	Regosol	10.6	11.0	78.4	7.8	0.47	3.77	31.7	16.7	24	5543	200	665	97
Scanterbury	Vertisol	72.8	22.2	5.00	7.4	0.62	3.65	43.0	22.7	680	5573	189	1513	48
Osborne	Vertisol	77.0	17.2	5.80	7.7	0.65	2.96	43.7	37.2	743	5157	272	1973	47
						Manured								
Newdale	Chernozem	32.3	32.7	34.9	7.2	0.85	3.83	27.5	33.9	206	4280	224	986	217
Lakeland 1	Chernozem	49.8	40.9	9.30	7.6	1.06	6.09	48.5	28.0	74	7633	230	1780	51
Lakeland 2	Chernozem	34.1	42.4	23.5	7.3	1.73	9.63	51.9	79.5	214	7400	129	1660	74
Arborg	Chernozem	65.1	29.1	5.80	7.7	1.05	4.23	42.8	96.2	699	6313	270	1750	66
Almasippi	Chernozem	13.1	8.20	78.7	8.1	0.56	1.97	26.7	36.1	8	5923	211	1483	79
Reinland	Chernozem	8.60	7.30	84.2	7.6	0.45	2.20	18.1	23.6	234	3567	189	630	138
Niverville	Chernozem	61.6	30.3	8.10	7.8	1.13	2.78	46.1	44.1	94	8100	143	1873	97
Fyala	Gleysol	50.6	44.4	4.90	7.5	1.21	9.22	53.2	52.7	224	7827	200	1750	40
Sprague	Gleysol	15.9	19.8	64.4	7.4	1.18	3.19	23.3	34.6	134	3880	472	806	50
Long Plain	Regosol	10.6	11.0	78.4	7.7	0.52	3.83	29.2	25.3	18	5970	289	767	85
Scanterbury	Vertisol	72.8	22.2	5.00	7.3	1.02	3.36	40.4	30.6	720	5677	209	1610	54
Osborne	Vertisol	77.0	17.2	5.80	7.6	1.15	2.61	41.3	44.2	737	5230	279	1967	46

[†]Mehlich-3 extractable Al, Ca, Fe, Mg and Mn contents in soils

3.4.2. Changes in redox potential (Eh) and pH over the flooding period

The redox potential of the flooded soils was measured in one replicate for each treatment, using a Pt electrode at 5 cm depth. Even though the measurement is highly depth sensitive, we used it as an indicator of the degree of reduction of the soil with flooding period. The redox potential (Eh) initially ranged from 424 to 247 mV and decreased with time to values between -93 to -122 mV (Figure 3.1, 3.2, and 3.3) at the end of the incubation period. The redox potential of 10 out of 12 soils decreased rapidly during the flooding period to below 100 mV, which is the approximate Eh threshold for Fe^{3+} reduction at pH 7 (Gotoh and Patrick, 1974), within the first three weeks of flooding in both unamended and manure amended soils. The Sprague and Lakeland 2 soils showed the highest values of Eh during the incubation regardless of the treatment and required approximately 42 days to fall below 100 mV. Flooded incubation of soils may not necessarily produce an intense reduction of soil (Racz, 1979; Vadas and Sims, 1999), especially in soils with low organic carbon (OC) content. However, the reason for the slow rate of reduction in these two soils for most part of the flooding period is unclear. The Sprague soil had 3.2% OC while Lakeland 2 soil had the greatest OC (9.74%) of the studied soils (Table 3.1); however, the OC in these soils would not necessarily be readily available for microbial activities. Also, nitrate reduction, which occurs in the Eh range of +200 to +300 mV, has the ability to poise soil Eh for several days in soils containing high nitrate levels (Reddy and DeLaune, 2008). Nitrate concentrations between 25 - 50 mg L^{-1} have the ability to maintain soil Eh stable around +300 mV (Reddy and DeLaune, 2008).

A paired t-test conducted using soils as replicates showed that there was no significant difference ($P = 0.89$) in Eh between unamended and manured treatments after the first week of flooding. Zelasko et al. (2007) found that reduction rates of soils depend on OC content of soil only when OC content is less than 2.7%, whereas for soils with OC content greater than 2.7%, the effect of OC content on reduction rate disappeared. Therefore, the lack of Eh response to the addition of manure in the present study may be due to the high concentrations of OC (1.97 to 9.74%) in our soils.

Soil pore water pH was measured periodically as an indicator of pH changes in soils. The relationships between changes in pH with the decrease in redox potential varied from soil to soil (Figure 3.4 3.5, and 3.6 and Appendix 3.A; table I). In eight unamended soils and seven manured soils pH decreased slightly by approximately by 0.43 to 1.2 units during the flooding period, a common phenomenon in alkaline to calcareous soils under anaerobic conditions (Ponnamperuma, 1972). Out of those soils, only four unamended and one manured soils showed significant correlations between pH decrease and Eh decrease (Table 3.2). Only one soil (manured Lakeland 2 soil) showed a significant increase in soil pore water pH whereas other soils did not show a significant change in pH during flooding period (Appendix 3.A; Table I). In most of the soils, pH of surface flood water increased in both unamended and manured treatments (Figure 3.4 3.5, and 3.6 and Appendix 3.A; table II).
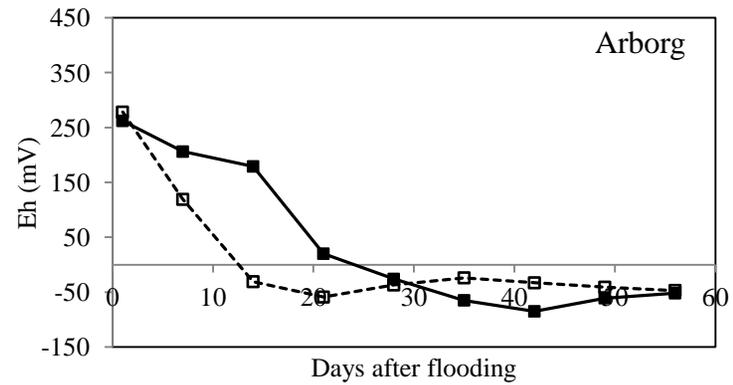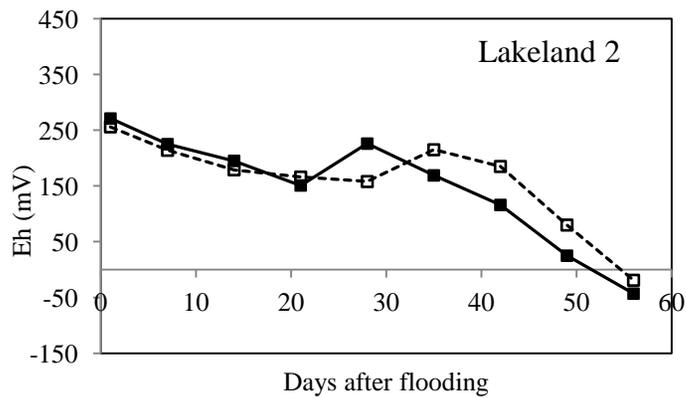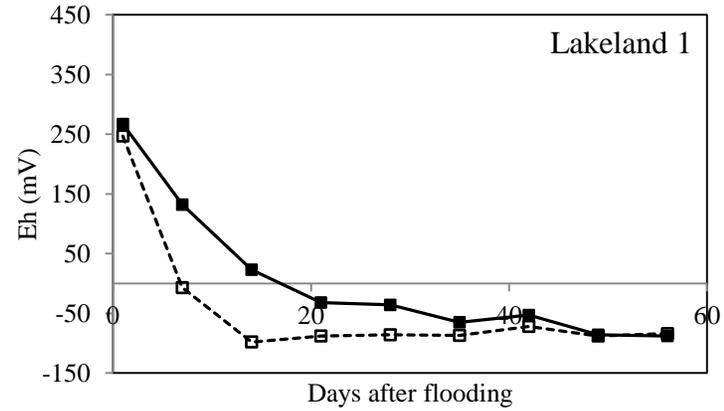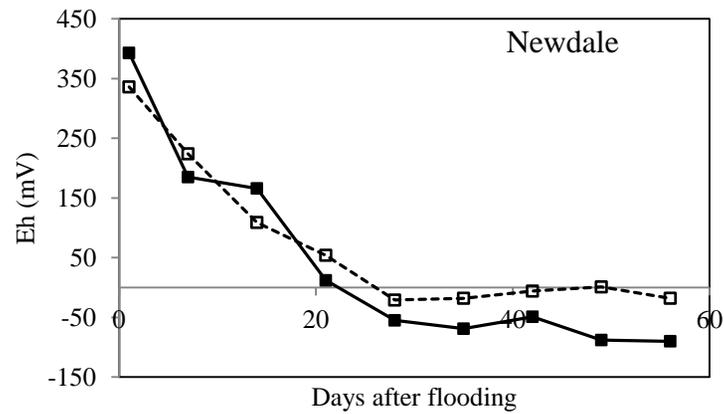
Figure 3.1 Changes in redox potential (Eh) over the flooding period for unamended and manured Newdale, Lakeland 1, Lakeland 2 and Arborg soils (arithmetic means).
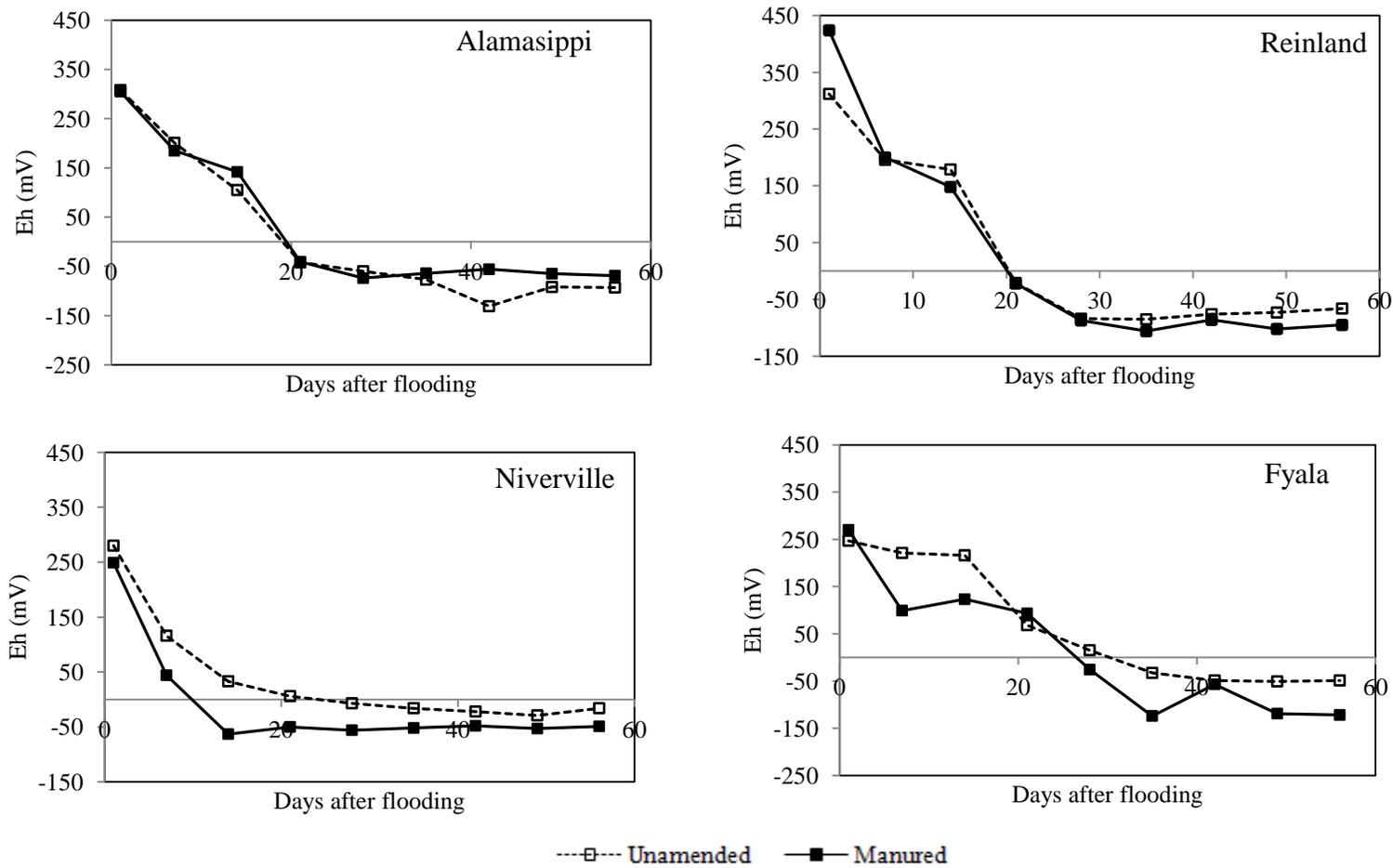
Figure 3.2 Changes in redox potential (Eh) over the flooding period for unamended and manured Almasippi, Reinland, Niverville, and Fyala soils (arithmetic means).
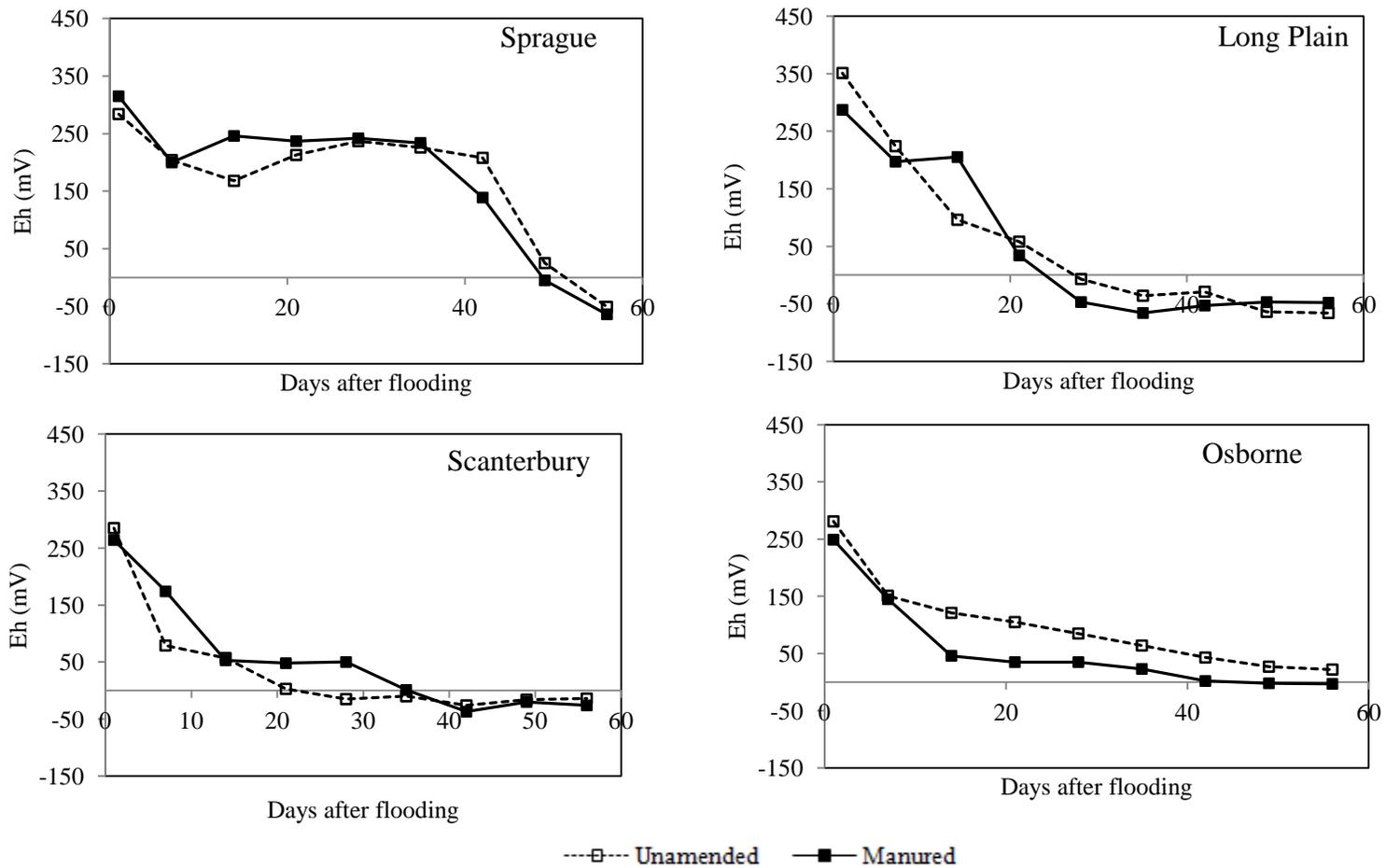
Figure 3.3 Changes in redox potential (Eh) over the flooding period for unamended and manured Sprague, Long Plain, Scanterbury, and Osborne soils (arithmetic means).

Table 3.2 Correlation coefficients between redox potential (Eh) in soil and and soil pore water pH changes over the flooding period.

Soil Series	Correlation coefficient (*r*)	
	Unamended	**Manured**
Newdale	0.62	-0.45
Lakeland 1	0.53	-0.08
Lakeland 2	0.43	0.33
Arborg	0.84**	0.81**
Almasippi	0.64	0.58
Reinland	-0.03	-0.52
Niverville	0.56	0.56
Fyala	0.34	0.24
Sprague	0.00	-0.35
Long Plain	0.87**	0.34
Scanterbury	0.85**	0.08
Osborne	0.87**	0.24

*,**,*** Significant at the 0.05, 0.01 and 0.001 probability levels, respectively.
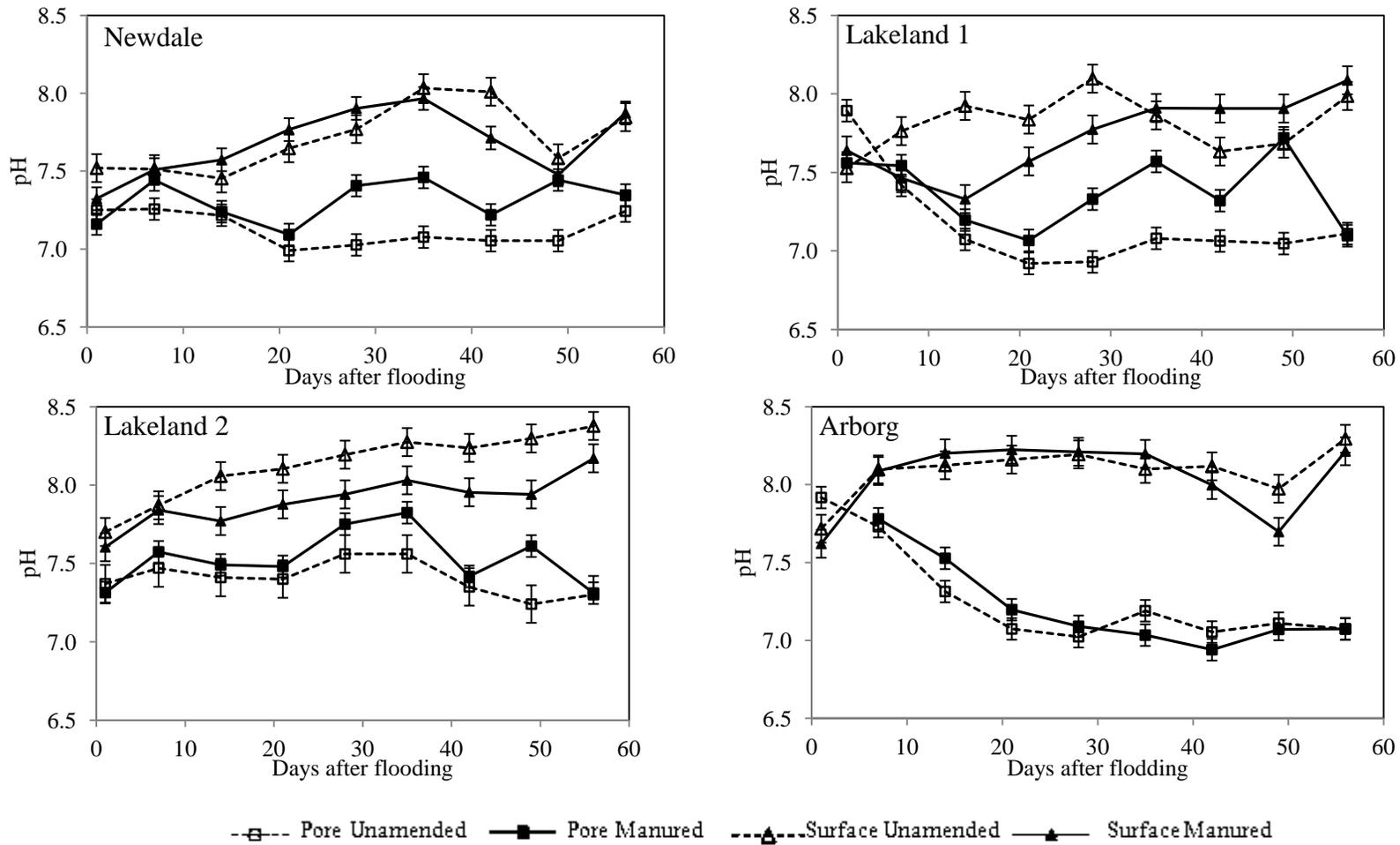
Figure 3.4 Changes in pH in surface flood and soil pore water over the flooding period for unamended and manured Newdale, Lakeland 1, Lakeland 2, and Arborg soils (arithmetic means).

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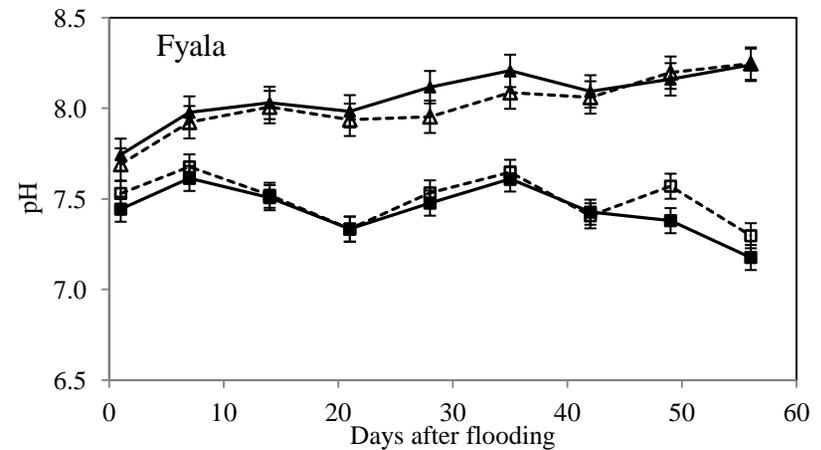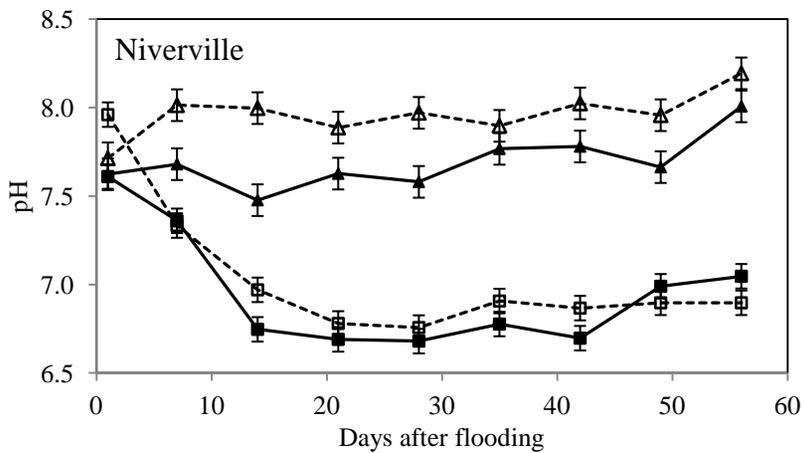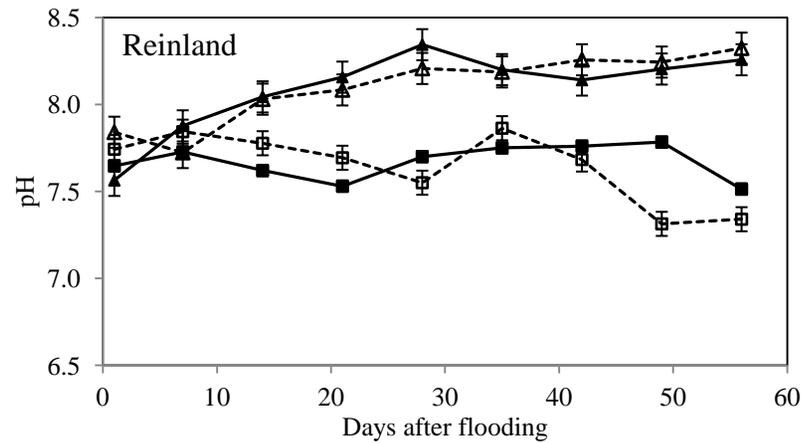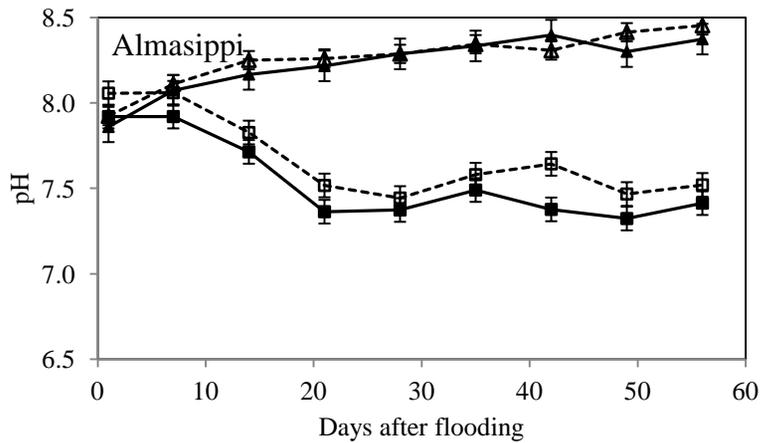
Figure 3.5 Changes in pH in surface flood and soil pore water over the flooding period for unamended and manured Almasippi, Reinland, Niverville, and Fyala soils (arithmetic means).
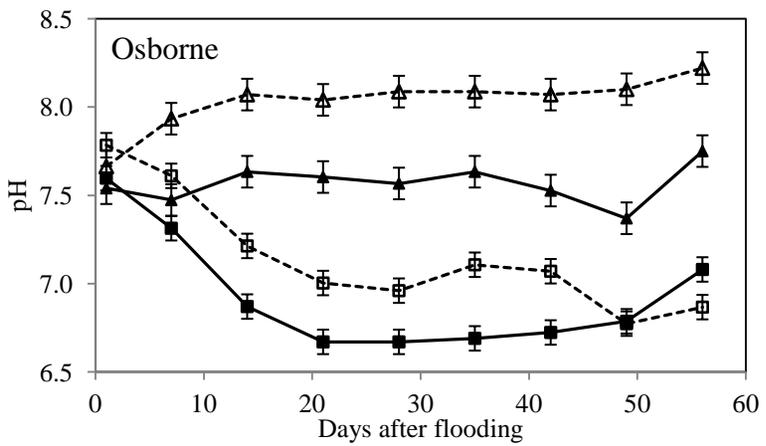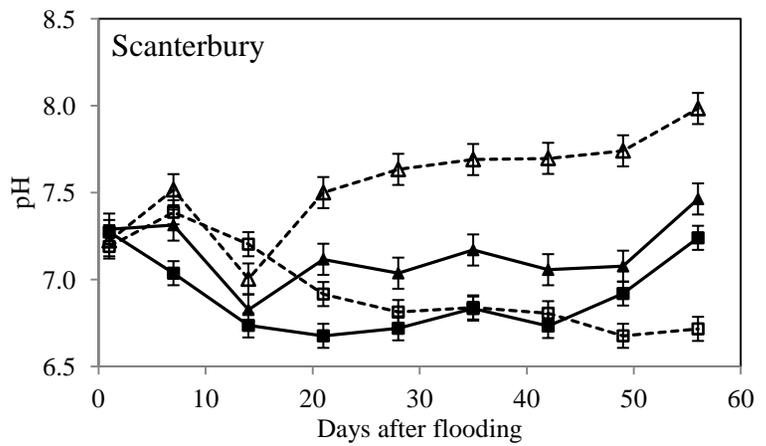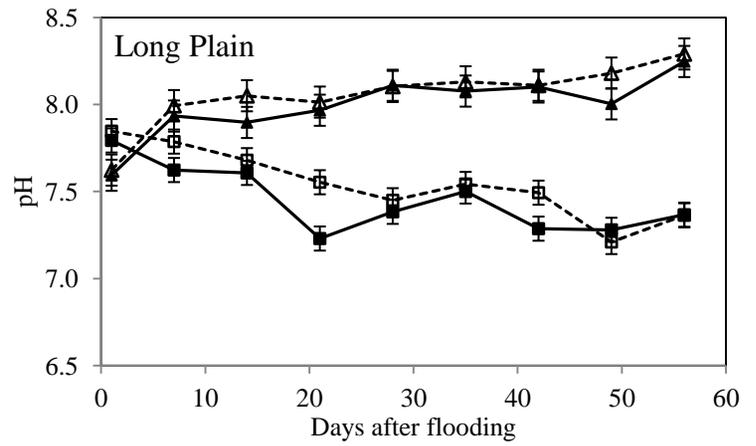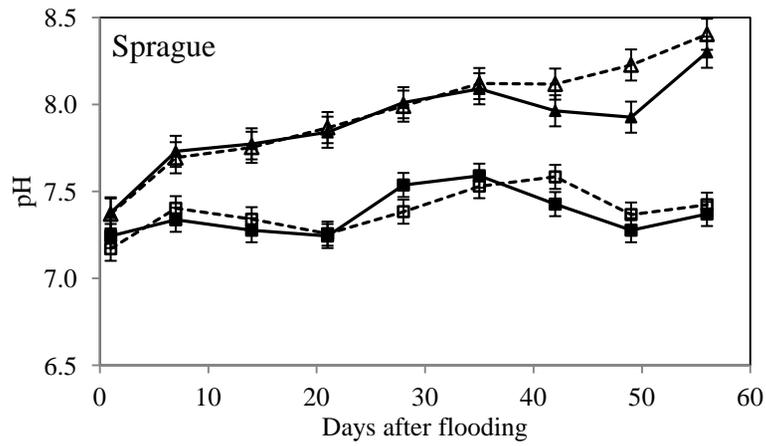
Figure 3.6 Changes in pH in surface flood and soil pore water over the flooding period for unamended and manured Sprague, Long Plain, Scanterbury, and Osborne soils (arithmetic means).

3.4.3. Release of dissolved reactive phosphorus to soil pore water and surface flood water over the flooding period

The patterns of P release to soil pore water over the flooding period varied among soils (Figure 3.7, 3.8, and 3.9 and Appendix 3.B; Table I). Unamended and manured treatments in most soils followed a similar pattern of P release into pore water; however, pore water DRP concentration was significantly greater in most of the manured soils compared to the unamended soils (Appendix 3.B; Table I). Pore water DRP concentrations in six out of 12 manured soils and 10 out of 12 unamended soils continuously increased up to the end of the incubation period. In three manured soils (Niverville, Long Plain, and Osborne), DRP concentration increased initially and then remained relatively stable for the remainder of the flooding period. In both unamended and manured Almasippi and Newdale soils, and manured Scanterbury soil, DRP concentrations increased initially and then declined towards the end of the flooding period. Even though the Sprague and Lakeland 2 soils did not show a substantial Eh decrease until day 42, these two soils also started releasing P into the soil solution from the first week of flooding. Similar to our results, Young and Ross (2001) also reported increases in dissolved P concentrations in soil pore water in both low P and high P soils over a period of 85 and 60 days of flooding, respectively. They observed that the increase in pore water P concentration was accompanied by an increase in pore water Fe^{2+} ions, suggesting that reduction of Fe^{3+} has an important role in P release to soil pore water.
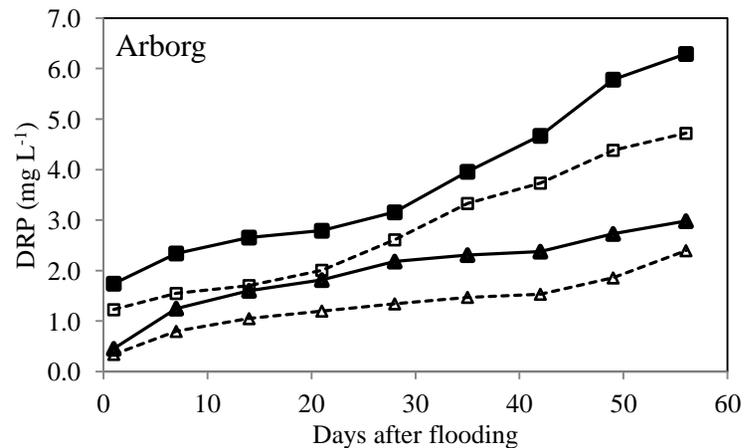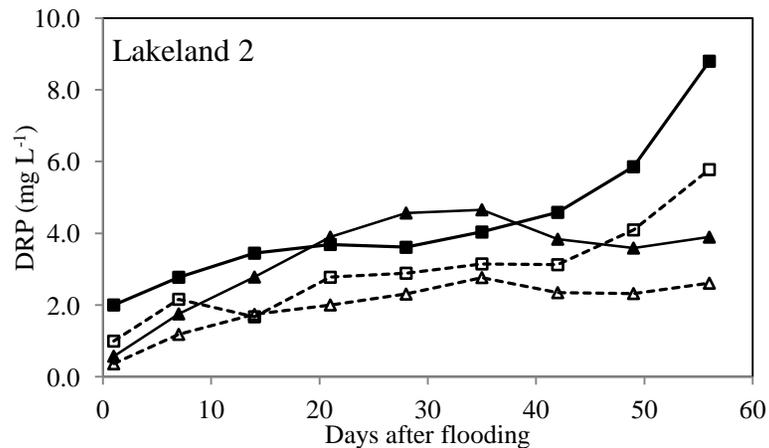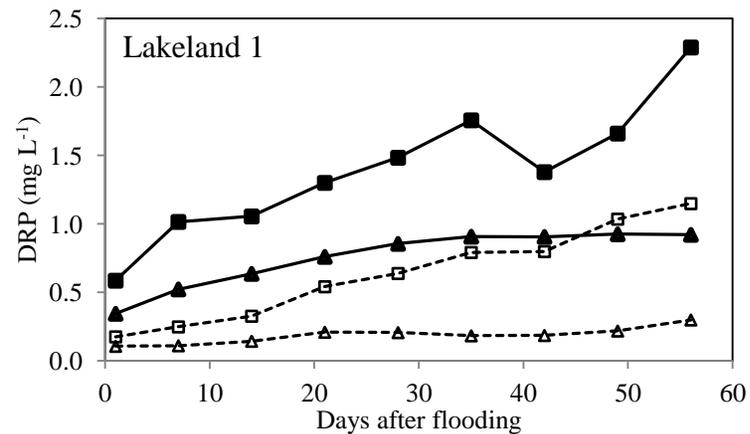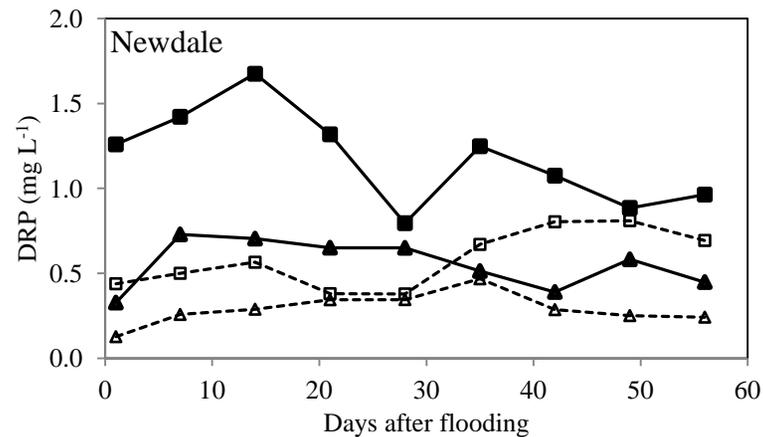
Figure 3.7 Changes in soil pore water and surface flood water dissolved reactive phosphorus (DRP) concentration over the 56 days of flooding in unamended and manured Newdale, Lakeland 1, Lakeland 2, and Arborg soils (geometric LSmeans).

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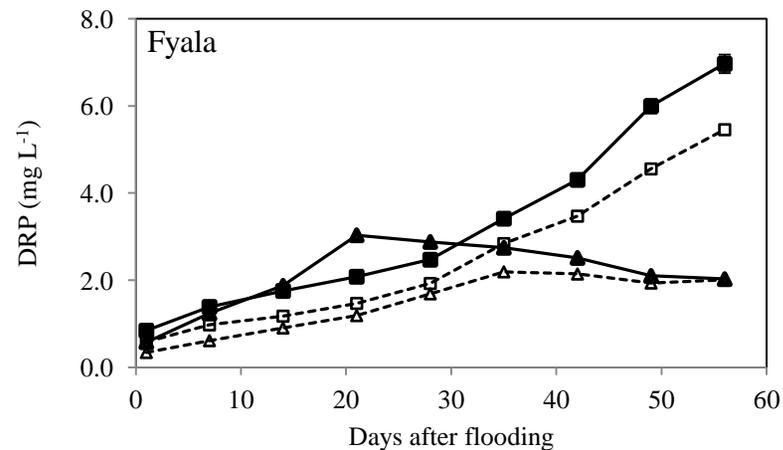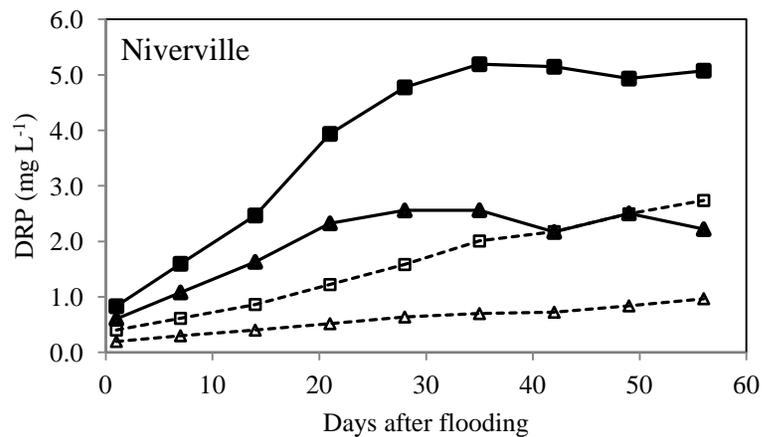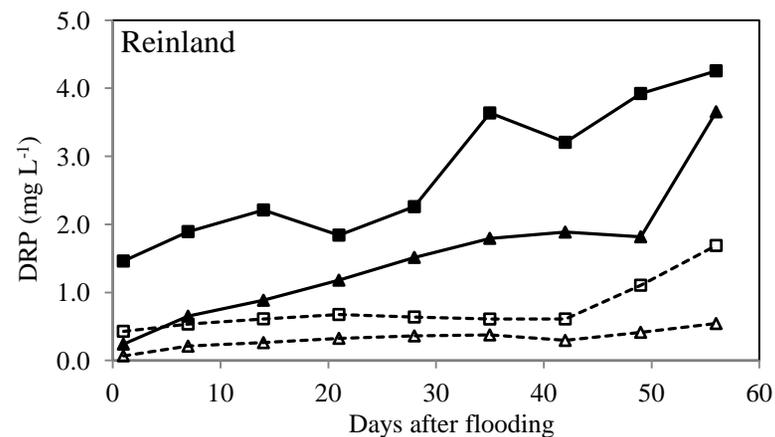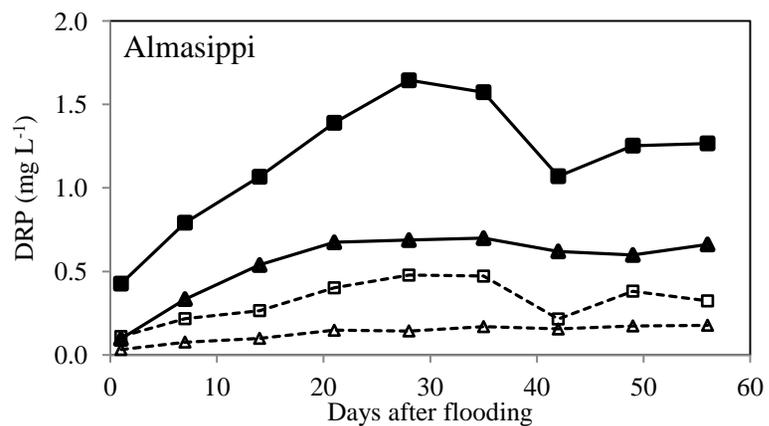
Figure 3.8 Changes in soil pore water and surface flood water dissolved reactive phosphorus (DRP) concentration over the 56 days of flooding in unamended and manured Almasippi, Reinland, Niverville, and Fyala soils (geometric LSmeans).

80
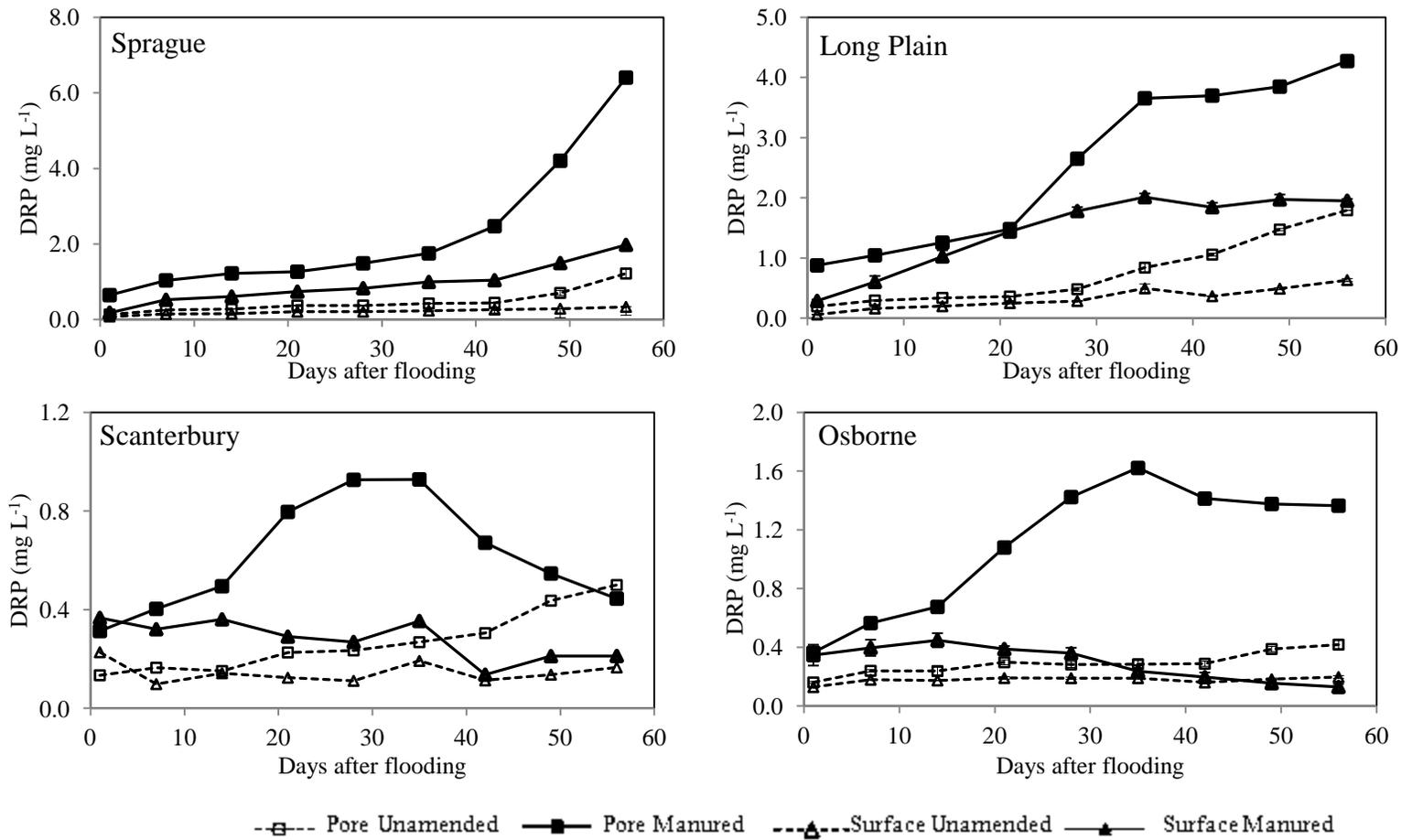
Figure 3.9 Changes in soil pore water and surface flood water dissolved reactive phosphorus (DRP) concentration over the 56 days of flooding in unamended and manured Sprague, Long Plain, Scanterbury, and Osborne soils (geometric LSmeans).

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The release of DRP to surface flood water during flooding also varied among soils (Figure 3.7, 3.8, and 3.9). In unamended soils, the changes in DRP concentration with duration of flooding in surface water varied from little or no increase to large increases up to 10 times of the DRP concentration after one day of flooding within few weeks (Appendix 3.B; Table II). Generally, the two Vertisols, Scanterbury and Osborne heavy clay soils, showed little or no increase in DRP concentration. After addition of manure, surface water DRP concentrations in these two Vertisols were relatively stable for 28 to 35 days of flooding and then gradually decreased. These are the soils that have a clay content of over 70%, mainly containing smectites, a highly active group of clay minerals (Soil Classification Working Group, 1998). Concentrations of DRP in other soils increased significantly by as much as 15 times compared to the DRP concentration at one day after flooding (Appendix 3.B; table II). Almost all soils started to release significantly greater amounts of P into surface water within the first week of flooding. Even though the pattern of DRP release from unamended and manured soils into both surface flood and soil pore water was similar, DRP concentrations were significantly greater ($P < 0.0001$) in manure amended soils compared to unamended soils. The relatively stable DRP concentration in surface water under reducing conditions for the unamended Scanterbury heavy clay was consistent with the results of the field study and is similar to the findings of Shober and Sims (2009). They observed relatively stable concentrations of dissolved P in surface flood water over a period of 63 days of anaerobic incubation in an unamended Berks clay loam soil. The decrease of DRP in surface water of manure amended Scanterbury and Osborne soils is also similar to the decrease in dissolved P after reduction of organic P source amended soils in a study by Shober and

Sims (2009). However, in most other studies, DRP concentration in surface flood water increased under anaerobic conditions (Hoffman et al., 2009; Kröger et al., 2012; Scalenghe et al., 2012).

The differences in DRP concentrations observed in surface flood and soil pore water under flooded conditions in unamended and manured soils have been attributed to a variety of changes in soil properties and transformation of soil constituents under anaerobic conditions and their effect on P retention and release of soils (Ajmone-Marsan et al., 2006; Scalenghe et al., 2012; Shenker et al., 2005; Surridge et al., 2007; Zhang et al., 2003). Therefore, differences observed in DRP concentration among soils and between the two treatments indicate the need to further investigate chemical reactions responsible for P release in different Manitoba soils under flooded and anaerobic conditions.

Flood water and pore water DRP concentrations in most of the soils showed highly significant positive correlations, indicating continuous mobilization of P from pore water to surface water over the flooding period (Table 3.3). Sallade and Sims (1997a) suggested that if equilibrium phosphate concentration at zero sorption (EPC_0) of a soil is greater than the P concentration in surface flood water, soil would continue to release P into flood water until EPC_0 equals to P in flood water. It appears that the above hypothesis is true for most of the flooded soils in this study assuming that pore water P concentration is similar to EPC_0. However, the correlations between P in pore water and surface water were poor for the unamended and manured Newdale clay loam and Scanterbury heavy clay soils, manured Fyala, and Osborne soils as well as in unamended

Almasippi soil (Table 3.3). In these situations, the mobilization of P from soil pore water to surface water essentially did not occur. This could be a result of sorption and/or re-precipitation of P by oxidized side of the soil - water interface (Young and Ross, 2001), approaching the equilibrium P concentration, or restricted diffusion of pore water P to the surface water in the small pores of swelling clay with their high degree of tortuosity.

Table 3.3 Correlation coefficients between dissolved reactive phosphorus concentrations in pore water and flood water.

Soil Series	Correlation coefficient (r)	
	Unamended	**Manured**
Newdale	-0.32	0.45
Lakeland 1	0.85**	0.93***
Lakeland 2	0.92***	0.55
Arborg	1.00***	1.00***
Almasippi	0.43	0.97***
Reinland	0.80**	0.90***
Niverville	0.90***	0.72**
Fyala	0.85**	0.42
Sprague	0.99***	1.00***
Long Plain	0.95***	0.88**
Scanterbury	-0.05	-0.28
Osborne	0.70*	-0.45

*,**,*** Significant at the 0.05, 0.01 and 0.001 probability levels respectively

3.4.4. Changes in soil pore water and surface flood water Ca, Mg, Fe, Mn and S concentrations during the flooding period

Dissolved Ca concentration in pore water was highly variable over the flooding period for almost all soils but decreased most of the time in Sprague and Lakeland 2 soils (Appendix 3.C; Table I). In general, dissolved Ca concentrations in surface flood water increased over the flooding period in all soils (Appendix 3.C; Table II). Magnesium concentration in pore water increased during the last half of the flooding period for six

unamended and four manured soils but decreased in unamended and manured Sprague and Lakeland 2 soils as well as during last two weeks of flooding for manured Lakeland 1 soil (Appendix 3.C; Table III). In five manured and four unamended soils, which included Scanterbury and Osborne soils, pore water Mg concentration did not change significantly during flooding. However, dissolved Mg concentration in surface flood water increased over the flooding period for all the soils (Appendix 3.C; Table IV).

The pore water Ca concentrations in manured soils were significantly greater in six of the soils at one day after flooding compared to unamended soils. However, from the 7th day onwards, the effect of manure addition on pore water Ca concentration disappeared from 11 out of 12 soils, but continued up to 21 days of flooding in Newdale soil. Pore water Mg concentrations in manured Scanterbury and Osborne soils were significantly greater than in unamended soils. Concentration of Ca in surface water was not significantly different between unamended and manured treatments in any of the soils. However, Mg concentrations in surface water of manured treatment were greater than in unamended treatment in most days starting generally from the 7th day of flooding, except for Lakeland 2, Sprague, and Fyala soils.

In Sprague and Lakeland 2 soils, changes in pore water Mg were highly correlated with changes in Ca ($r = 0.92$ and 0.84, $P < 0.0001$, respectively for unamended and manured pore water), which would be expected for soils such as these which are developed from dolomitic parent material. Lakeland 2 soil followed by Sprague soil had the highest concentration of dissolved Ca and Mg in soil pore water one day after flooding. The increase in DRP concentration from the first week of flooding without

reduction of soils would be a result of dissolution of Ca and Mg compounds present in the soils. Even though there was no pH decrease in these two soils during flooding, decreases in soil pH due to development of anaerobic conditions generally increase the solubility of Ca and Mg compounds (Racz, 2006) However, the form of $CaCO_3$ present in the soil is also an important factor for Ca dissolution. For example, the solubility of $CaCO_3 \cdot 6H_2O$ is two to three times greater than that of the solubility of calcite (Olsen and Watanabe, 1959). The decrease in Ca and Mg concentrations in soil pore water of the two soils which had the highest initial concentration of dissolved Ca and Mg might be a result of super saturation of Ca and Mg leading to precipitation of $CaCO_3$ and $MgCO_3$ (Olsen and Watanabe, 1959).

Concentrations of dissolved Fe and Mn in pore water of most soils increased over the flooding period, probably due to reductive dissolution under anaerobic conditions developed during flooding (Appendix 3.C; Table V and VII). Dissolved Mn concentrations in soil pore water significantly increased within the first week of flooding in eight unamended and seven manured soils while the rest of the soils took 21 to 28 days to show a significant increase in pore water Mn concentration. Iron concentrations in pore water were stable up to 14 to 28 days after flooding except in Sprague and Lakeland 2 soils. Concentrations of Fe in these two soils remained stable for up to 42 days, until soil Eh fell below 100 mV. In surface water, Fe concentrations were generally stable in most of the soils (Appendix 3.C; Table VI). However, in a few soils Fe concentrations were stable for the first four to seven weeks of flooding and increased or decreased during the last two weeks of flooding. Manganese concentrations in surface flood water significantly increased in three unamended soils and 11 manured soils while the Mn

concentration in other soils did not change significantly (Appendix 3.C; Table VIII).

Pore water Fe concentration in manured Scanterbury and Osborne soils were greater than unamended soils up to 21 days of flooding, while in other soils, there were a few occasions where pore water Fe concentration is greater in manured soil than in unamended soil. However, pore water Mn concentration did not show significant differences between manured and unamended soils except at 14th day of flooding of Newdale soil. Manured treatments in six soils had significantly greater Fe concentrations in surface flood water compared to unamended treatment during the last half of the flooding but there was no significant effect of manure addition on surface water Fe concentration in other soils. During the last half of the flooding period, surface water for six manured soils had significantly greater Mn concentrations than in the unamended treatment. However, manured treatment of Lakeland 1 soil showed significantly greater Mn concentration than the unamended treatment during the first half of the flooding period. Manganese concentrations in other soils were not significantly greater in manured soils than the unamended treatment during flooding.

Dissolved S concentration in soil pore water significantly decreased towards the end of the flooding period in ten soils while changes in pore water S concentration were not statistically significant in Sprague and Lakeland 2 soils (Appendix 3.C; Table IX). Dissolved S concentration in surface flood water increased in most of the soils but was not significantly different in three unamended and two manured soils (Appendix 3.C; Table X). The concentration of sulfate, which is the mobile form of sulfur, is controlled by the gypsum-calcite equilibrium in Manitoba soils. Under excess water condition, declining pH and increasing solubility and release of Ca from calcite, could decrease the

concentration of S in the soil solution via the common ion effect of Ca in calcite and gypsum (Racz, 2006). However, the Ca concentrations in soil pore water in studied soils were virtually unchanged and therefore, the effect of Ca on retention and release of S might be minimal. Therefore, the reason for increases and decreases in dissolved S is not known.

3.4.5. Relationship of changes in surface flood water dissolved reactive phosphorus concentration and changes in pH and other elements

Multiple backward regression analyses were conducted to assess the contribution of changes in pH and dissolved Ca, Mg, Fe, Mn, and S on maximum absolute changes (ΔDRP_{abs}; maximum DRP concentration - DRP concentration at day 1 of flooding) and relative changes (ΔDRP_{ratio}; maximum DRP concentration / DRP concentration at day 1 of flooding) in DRP concentrations in surface flood water. Regression analysis indicated that the absolute changes in DRP concentration was significantly related with the changes in dissolved Ca concentration suggesting the importance of Ca dissolution in releasing P into surface flood water during flooding (Table 3.4). No other measurements significantly improved the relationship between dissolved elements and absolute increases in DRP concentration in flood water. The relative changes in surface water DRP concentration were also significantly related with the changes in Ca concentration as well as with changes in Mn concentrations.

Table 3.4 Multiple backward regression between relative and absolute changes in dissolved reactive P in surface flood water and changes in pH and dissolved Ca, Mg, Fe, Mn, and S in surface flood water of flooded soils.

Response variable[†]	Fitted model equation[‡]	r^2	SE[§]	P
ΔDRP_{abs}	$\Delta DRP_{abs} = -5.56 + 0.063\ \Delta Ca_{abs}$	0.46	2.27	0.0002
ΔDRP_{ratio}	$\Delta DRP_{ratio} = 0.065 + 0.242\ \Delta Ca_{ratio} + 0.289\ \ln \Delta Mn_{ratio}$	0.43	2.68	0.0011

[†]ΔDRP_{abs} = Maximum DRP concentration - DRP concentration at day 1; ΔDRP_{ratio} = Maximum DRP concentration / DRP concentration at day 1

[‡]ΔCa_{abs} = [Ca] on sampling date for maximum [DRP] - [Ca] on Day 1 of flooding; ΔCa_{rato} = [Ca] on sampling date for maximum [DRP] / [Ca] on Day 1 of flooding; ΔMn_{ratio} = [Mn] on sampling date for maximum [DRP] / [Mn] on Day 1 of flooding

[§]Model standard error

A consistent significant relationship between changes in dissolved Ca concentration with the changes in DRP concentrations suggests that Ca dissolution plays a major role in P release into surface flood water in alkaline to calcareous Manitoba soils. Decreases in pH during flooding in alkaline to calcareous soils enhances the solubility of apatite, b-tricalcium phosphate, octacalcium phosphate, brushite and monetite to release P to surface flood or soil pore water (Ann et al., 2000). Precipitation of dissolved P with Ca^{2+} to form Ca phosphate minerals (Zhang et al., 2010) may have decreased the pore water DRP concentration during the last half of flooding period. The effect of Mn dissolution and re-precipitation of manganous minerals would also be a dominant process in P release and retention in these flooded soils, which exists over the entire flooding period. Shahandeh et al. (2003) also reported that Mn dissolution could be a significant factor controlling P release into soil solution especially in soils with high amount of "reactive Mn oxides".

In literature, it is largely reported that reduction of Fe^{3+} to Fe^{2+} releases Fe-bound P into solution under anaerobic conditions, especially in acidic soils (Ajmone-Marsan et

al., 2006; Ann et al., 2000; Kröger et al., 2012; Scalenghe et al., 2012). If this dissolved Fe^{2+} re-precipitates to form ferrous minerals that possess greater surface sites for P adsorption compared to ferric minerals, P adsorption would increase in soils and may lead eventually to a decrease in DRP concentrations in surface and soil pore water. In some soils, the conditions may be conducive for re-precipitation, thus decreasing P concentrations, while in others where re-precipitation is unlikely, P release will continue, increasing DRP concentrations further (Vadas and Sims, 1999). However, in the present study, there was no relationship between changes in DRP concentration and changes in dissolved Fe concentration suggesting that reductive dissolution of Fe did not play a major role in P release from these soils under flooded conditions. This may be because all the soils used in this study are alkaline in reaction and P retention is dominated by Ca and Mg ions, not by acidic cations (Ige et al., 2005).

Results suggest that dissolution of Ca and Mn compounds may take place in soil under flooded conditions contributing to P release in studied soils. However, the modest r^2 for these relationships between DRP concentration changes and Ca and/or Mn concentration changes indicate that there are other factors affecting the maximum absolute and relative changes of DRP concentration in surface flood water of studied soils. Soil solution properties that we could not take into consideration such as dissolved organic matter concentration might also have a significant influence on surface flood water DRP concentration changes in these soils. For example, ligand exchange of P with soil organic matter produced during anaerobic period has the capability to enhance P release to soil solution (Zhang et al., 2010). As well, dissolved organic matter (DOM) formed under reduced condition facilitates formation of turnery aqueous $DOM-Fe^{+3}-PO_4$

or DOM-Al^{+3}-PO$_4$ to increase dissolution of phosphate under reduced conditions (Hutchison and Hesterberg, 2004).

3.4.6. Changes in soil phosphorus buffer capacity, soil test phosphorus, and extractable elements in response to flooding

The P sorption capacities as determined by the single point P sorption index (P150) varied greatly among the soils prior to flooding and after 56 days of flooding (Figure 3.10). The interaction effect of soil*treatment*flooding was significant on the P sorption capacity (Appendix 3.E). Despite increased P release into the soil pore water and surface water during flooding, P sorption capacity of both unamended and manured Arborg and Osborne soils, unamended Newdale soil, and manured Almasippi, Reinland, Fyala, and Long Plain soils significantly increased after the flooding period. Phosphorus sorption capacity of all the other manured and unamended soils remained stable. Shober and Sims (2009) and Amer et al. (1991) also observed that both DRP concentrations in flood water and P sorption of soils increased during or after flooding. Even though Fe did not appear to be playing a role in P retention and release in these soils, increased P sorption with flooding has been commonly attributed to transformation of crystalline ferric hydroxide to amorphous ferrous or ferric hydroxide resulting in more surface sites (Holford and Patrick, 1981; Vadas and Sims, 1999). However, Al^{3+}, which is not redox active (Chacon et al., 2006), and reported to be responsible for P retention in these soils (Ige et al., 2005) could have more open reactive sites available for P sorption if Fe oxide coatings were removed due to reductive dissolution of Fe (Shober and Sims, 2009). However, it is reported that in reduced soils, the bonding energy associated with P

sorption is lower and therefore, desorption potential is higher compared to soils under aerobic conditions, where P is held more tightly even if P adsorption capacity is low (Patrick and Khalid, 1974). In addition, when soil solution P concentration is lower than EPC_0, desorption of P into soil solution would be favored. Thus, P retention in flooded soil is controlled by P concentration of the soil pore water and physicochemical characteristics of the soil/water interface. Therefore, the use of soil P sorption data alone to predict P retention and release from submerged upland or lowland soils, wetlands or sediments is not very accurate (Reddy et al., 1999).

According to the correlation analysis between P150 and soil properties, P sorption capacity of soils prior to flooding was controlled mainly by M3Mg ($r = 0.74$, $P < 0.01$ for unamended; $r = 0.75$, $P < 0.01$ for manured soils). The M3Al also correlated with P150 ($r = 0.62$, $P < 0.05$) only in manured soils (Table 3.5). As well, M3Mn in unflooded soil was negatively correlated with P retention in unamended soils ($r = -0.74$, $P < 0.01$). However, after flooding, the negative correlation of M3Mn and P150 disappeared for unamended soils. A significant correlation was observed between P150 of flooded unamended soils and M3Al concentration ($r = 0.61$, $P < 0.05$) in addition to the strong correlation with M3Mg (Table 3.5). There was no difference after flooding in correlations between P150 and soil properties for manured soil. There was no correlation observed between P150 and M3Fe before or after flooding suggesting that extractable Fe did not play a dominant role in P sorption by these alkaline to calcareous soils.

Since the solubility of Al is not affected by redox status of the soil, concentration of M3Al, which earlier showed a significant correlation with the P150, did not change

after flooding in most of the studied soils (Appendix 3.F; Table I). However, three manured and one unamended soils showed a decrease in M3Al concentration. Flooding significantly increased the M3Fe in eight unamended and nine manured soils. Other studies also reported increases in extractable Fe after flooding. For example, Shober and Sims (2009) reported that concentrations of oxalate extractable Fe increased from 6 to 20 times in slightly acidic soils while Amer et al., (1991) found two to three times increase in oxalate extractable Fe in calcareous soils. However, Mehlich-3 extractable Fe in Lakeland 2 and Sprague soils, which showed the least and delayed reduction during flooding, and Long Plain soils, remained stable after flooding (Appendix 3.F; Table II). Mehlich-3 extractable Mn concentrations significantly increased in five unamended and six manured soils after flooding. Increases in extractable Mn have been attributed to reductive dissolution of Mn compounds in soils, converting less soluble Mn compounds into easily soluble Mn compounds (Shenker et al., 2006; Willet, 1989). The three-way interaction was not significant for M3Ca where soil*treatment and soil*flooding interactions were significant. Mehlich-3 extractable Mg, which appeared to play the main role in P retention in these soils, increased in only one unamended and two manured soils while there was no significant change in M3Mg in other soils after flooding.

Table 3.5 Correlation coefficients (*r*) between single point P sorption index (P150) and soil properties in soils before and after flooding.

	Treatment	M3Ca	M3Mg	M3Fe	M3Mn	M3Al	Ols-P	WEP	M3P$_{MRP}$	M3P$_{ICP}$	SOM	pH
Before	Unamended	0.48	0.74**	-0.13	-0.74**	0.41	0.38	-0.06	0.34	0.13	0.22	0.13
flooding	Manured	0.34	0.75**	-0.15	-0.55	0.62*	0.45	-0.02	0.49	-0.02	0.31	-0.24
After	Unamended	0.45	0.85***	0.20	-0.22	0.61*	0.74**	0.15	0.52	0.29	0.34	-0.17
flooding	Manured	0.50	0.78**	0.26	-0.25	0.60*	0.65*	0.05	0.26	0.17	0.43	-0.20

*, **, *** significance at the 0.05, 0.01 and 0.001 probability levels
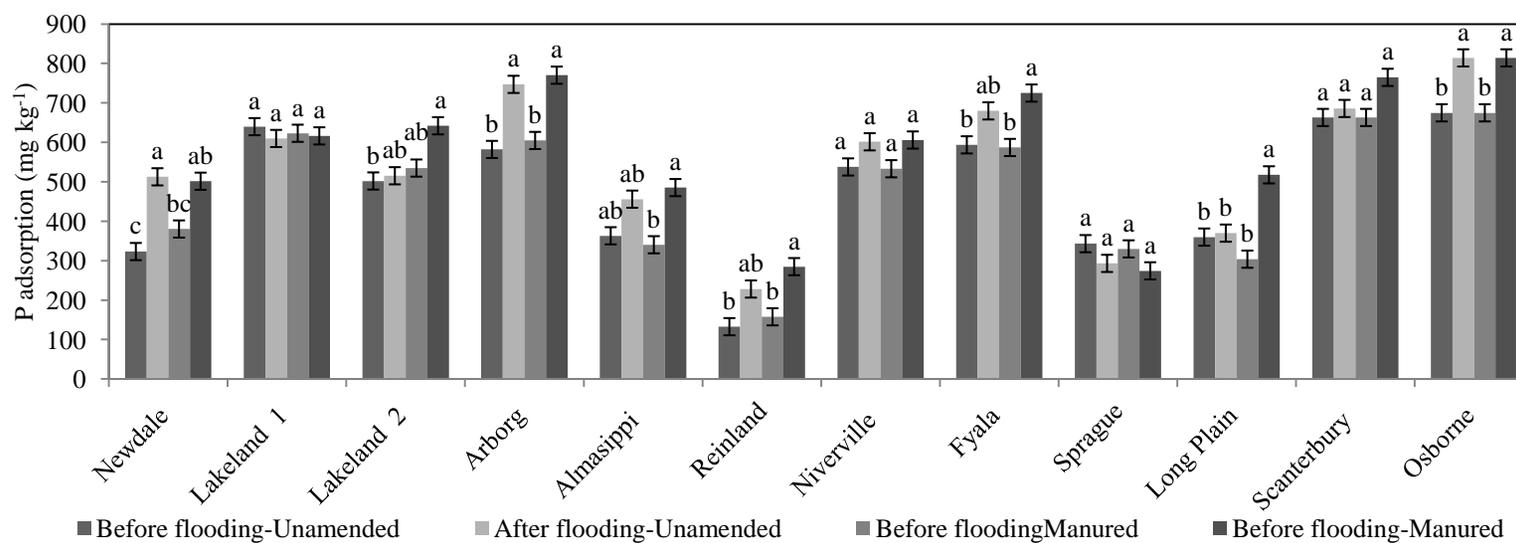
Figure 3.10   Effect of flooding on phosphorus sorption capacity (P150) of the unamended and manured soils. Means within a soil followed by the same letter are not significantly different.

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Olsen extractable P contents varied greatly from 12.6 to 77.1 mg kg^{-1} in the unamended soils and from 23.5 to 96.1 mg kg^{-1} in manured soils (Table 3.6). Mehlich-3 extractable P concentration measured by molybdate blue method (M3P$_{MRP}$) varied from 14.9 to 94.7 mg kg^{-1} in unamended soils and from 29.1to 122 mg kg^{-1} in manured soils. However, manure addition significantly increased Ols-P (Table 3.6) and M3P$_{MRP}$ (Appendix 3.G; Table I) only in soils with low initial P. Mehlich-3 extractable P measured by ICP-AES (M3P$_{ICP}$), which ranged from 27.8 to 141.5 mg kg^{-1} in unamended soils and from 48.7 to 166 mg kg^{-1} in manured soils (Table 3.7), was significantly greater than the Mehlich-3 extractable P concentration measured by molybdate blue method ($P < 0.0001$) since ICP-AES measures total P in the extract, including organic P and molybdate unreactive inorganic P forms. As well, M3P$_{ICP}$ was significantly greater in manured soils compared to unamended soils. Water extractable P concentration varied from 1.93 to 12.7 mg kg^{-1} in unamended soils and from 3.8 to 15.4 mg kg^{-1} in manured soils (Appendix 3.G; Table II).

Table 3.6 Effect of soil series, manure treatment, and flooding on Olsen extractable phosphorus (mg kg^{-1}).

Soil Series	Unamended		Manured	
	Before flooding	After flooding	Before flooding	After flooding
		mg kg^{-1}		
Newdale	23.4b[†]	29.1ab	33.8ab	35.9a
Lakeland 1	19.5b	26.6b	27.8ab	39.0a
Lakeland 2	65.5a	66.2a	79.5a	81.9a
Arborg	77.1a	92.8a	96.1a	99.9a
Almasippi	12.6c	13.9c	33.1a	22.0b
Reinland	13.7c	20.7b	23.5ab	33.8a
Niverville	31.5b	34.9ab	44.1ab	48.2a
Fyala	43.4b	57.3ab	52.7ab	71.3a
Sprague	23.5c	26.4bc	34.6ab	45.4a
Long Plain	16.7c	19.5bc	25.1ab	30.8a
Scanterbury	22.7b	31.8ab	30.6ab	37.2a
Osborne	37.1a	37.9a	44.1a	49.9a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	0.0002
Soil * Treatment			11	0.0001
Flooding			1	<0.0001
Soil * Flooding			11	<0.0001
Treatment * Flooding			1	0.15
Soil * Treatment * Flooding			11	0.05
CV[‡] (%)				11

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡]CV - coefficient of variation

The interaction of soil*treatment*flooding was significant on Ols-P (Table 3.6), M3P$_{MRP}$, WEP (Appendix 3.G; Table I and II, respectively) and M3P$_{ICP}$ (Table 3.7). Even though DRP release increased with the reduction of soil, STP (Ols-P, M3P$_{MRP}$, WEP) in most of the soils remained unchanged after flooding. However, unamended Reinland soils showed a significant increase in Ols-P concentrations, while manured Almasippi soil showed a significant decrease in Ols-P after flooding.   Mehilich-3 extractable P concentration measured by molybdate blue method increased significantly

after flooding only in unamended Lakeland 1 soil and decreased significantly in manured Lakeland 1 soil (Appendix 3.G; table I). However, WEP, which is the form of easily available P, did not significantly change in most of the soils except unamended and manured Newdale soils and manured Scanterbury soil (Appendix 3.G; table II). Nevertheless, $M3P_{ICP}$, which takes into account of organic P and molybdate unreactive inorganic P forms in the extract as well, showed that in six unamended soils and four manured soils $M3P_{ICP}$ increased significantly with flooding. Manured Scanterbury and Almasippi soils showed a significant decrease in $M3P_{ICP}$ concentration after flooding while in other soils, the change in $M3P_{ICP}$ was not statistically significant (Table 3.7). The difference between $M3P_{ICP}$ and $M3P_{MRP}$ in response to flooding reflects the flooding effect on easily soluble organic P fraction of soil. Racz (1979), who studied effect of flooding on P extractability of Manitoba soils, also reported that flooding and resulting anaerobic conditions increased the NH_4Cl and NH_4F extractable P content due to hydrolysis of pyro- and long chain phosphates in soil and increased mineralization of organic P.   The number of unamended soils that showed increased $M3P_{ICP}$ after flooding was higher than the number of manured soils.   This might be because of easily soluble P added along with manure might have already dissolved and released into soil pore or surface flood water.

Table 3.7 Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable phosphorus measured by ICP (mg kg^{-1}).

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	44.5b	44.1b	60.8a	58.7a
Lakeland 1	30.6c	43.9b	48.9b	69.9a
Lakeland 2	141.5b	145.6b	166.0a	175.6a
Arborg	137.2b	144.5b	165.4a	172.0a
Almasippi	27.8c	28.4c	61.0a	42.8b
Reinland	43.0c	50.6b	64.7a	70.9a
Niverville	69.3b	73.4b	101.6a	95.7a
Fyala	100.7c	120.0b	124.1b	145.8a
Sprague	45.2d	52.1c	69.6b	81.6a
Long Plain	45.0d	52.5c	66.9b	83.6a
Scanterbury	35.7c	40.8b	48.7a	40.8b
Osborne	50.2b	55.6b	67.8a	63.3a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	<0.0001
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	<0.0001
Soil * Treatment *Flooding			11	<0.0001
CV[‡] (%)				4

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡]CV - coefficient of variation

3.4.7. Predicting changes in dissolved reactive phosphorus in surface flood water of flooded soils

Previous studies have shown that some soils have the potential to release greater quantities of P into surface flood and soil pore water under flooded and anaerobic conditions than other soils. Therefore, there is a need to identify soils that are prone to release large quantities of P and to predict the magnitudes of P release from flooded and

anaerobic soils for efficient P management. To develop models to predict relative and absolute changes of DRP in surface flood water, initial PLS analysis was conducted using 30 initial soil properties (STP, DPS, Mehlich-3 extractable Ca, Mg, Fe, Al, and Mn, P fractions obtained from modified Hedley method and other soil properties) measured prior to flooding in unamended and manured soils as predictor variables. For further PLS analysis, initial soil properties were categorized into three groups as (a) soil P measures which included both STP methods and DPS methods, (b) P fractions obtained from the modified Hedley fractionation method, and (c) other soil properties which included chemical and physical soil properties. The relative change in surface flood water DRP concentrations (ΔDRP_{ratio}) and absolute change in surface flood water DRP concentrations (ΔDRP_{abs}) were used as the response variables. Even though the PLS analysis was conducted separately for unamended and manured soils as well as combining both treatments together, only the results obtained for the analysis combining two treatments will be discussed in this section.

Table 3.8 Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 30 predictors in the preliminary model for estimation of absolute change in DRP in surface flood water (ΔDRP_{abs}).

Soil property	All		Unamended		Manured	
	B	VIP[†]	B	VIP	B	VIP
DPS2	**0.138**	**1.73**	**0.108**	**1.50**	**0.127**	**2.04**
DPS3	**0.152**	**1.64**	**0.097**	**1.17**	**0.127**	**2.03**
WEP	**0.126**	**1.62**	**0.101**	**1.57**	**0.107**	**1.71**
DPS1	**0.112**	**1.57**	**0.088**	**1.30**	**0.113**	**1.82**
DPS6	**0.109**	**1.57**	**0.092**	**1.36**	**0.111**	**1.79**
M3P$_{ICP}$	**0.104**	**1.56**	**0.103**	**1.59**	**0.101**	**1.63**
DPS5	**0.066**	**1.38**	**0.082**	**1.42**	**0.077**	**1.24**
M3P$_{MRP}$	**0.069**	**1.33**	**0.093**	**1.53**	**0.069**	**1.11**
Ols-P	**0.049**	**1.29**	**0.073**	**1.42**	**0.069**	**1.11**
DPS4	**0.035**	**1.21**	**0.053**	**1.19**	**0.065**	**1.04**
HCl-Pi	**0.122**	**1.16**	**0.113**	**1.20**	**0.087**	**1.40**
NaHCO$_3$-Pi	-0.046	0.79	**0.027**	**0.94**	-0.006	0.09
Labile	-0.060	0.75	0.030	0.68	*-0.012*	0.20
NaOH-Pi	-0.032	0.72	**-0.003**	**0.91**	-0.004	0.06
H$_2$O-Pi	-0.067	0.69	0.024	0.33	-0.012	0.20
M3Al	-0.071	0.68	-0.058	0.68	-0.047	0.76
Residual P	0.017	0.65	**0.045**	**0.93**	0.022	0.36
M3Ca	0.061	0.65	**0.063**	**0.91**	0.026	0.42
Clay	-0.050	0.64	-0.038	0.63	-0.047	0.75
Silt	0.036	0.62	**0.054**	**0.93**	0.028	0.44
P150	-0.037	0.61	-0.024	0.56	-0.043	0.69
CEC	0.039	0.60	*0.030*	*0.82*	0.016	0.25
Sand	0.023	0.52	0.008	0.69	0.025	0.40
M3Mg	-0.017	0.49	0.006	0.65	-0.018	0.29
M3Mn	-0.045	0.42	-0.017	0.39	-0.015	0.24
NaOH-Pt	-0.015	0.36	0.004	0.71	-0.008	0.12
pH	-0.026	0.34	0.005	0.26	-0.001	0.02
M3Fe	-0.028	0.32	-0.009	0.19	0.005	0.08
HCl-Po	-0.004	0.29	0.013	0.53	-0.008	0.12
SOM	0.012	0.21	-0.002	0.02	-0.010	0.16

[†]Significant VIP values exceeding 0.8 are in bold

Absolute DRP concentration change in surface flood water in combined treatments can be predicted by two factor models (Table 3.8). Only 11 of the 30 predictor variables contributed significantly (VIP > 0.8) to absolute change in DRP concentration in surface water during flooding (Table 3.8). According to the PLS analysis, absolute change in DRP concentration in surface water was strongly related to soil test P measures and different DPS measures suggesting that the magnitude of increase in flood water DRP concentration during flooding depends largely on the initial concentration of P in the soil. The DPS2 measurement followed by DPS3 showed the highest VIP values indicating their importance in influencing the DRP concentration in surface flood water during flooding. Among the STP methods, WEP, the only environmental STP method used, showed the strongest relationship with absolute change in DRP concentration. Olsen extractable P, which is the routine agronomic STP method used in Manitoba and DPS4 showed the weakest relationships with the absolute change in DRP concentration. From the soil P fractions, only HCl-Pi contributed significantly (VIP > 0.8) to the absolute change in DRP concentration in surface water during flooding indicating that Ca- and Mg-bound P is a major source of P released into surface water upon flooding. However, no other chemical or physical soil property showed a significant effect on absolute change in surface flood water DRP concentration. Together, the 11 soil properties accounted for 85% of response variability (root mean PRESS = 0.57). The weak relationship of absolute change in DRP concentration with SOM indicated that the initial concentration of organic P in the soil does not affect ΔDRP_{abs}. Even though changes in dissolved Ca and Mn concentration were significantly related to the changes in DRP concentration in surface water, they were not significantly related (VIP < 0.8) to absolute change in DRP

concentration in flood water. As well, M3Mg and M3Ca concentrations, which were strongly related to P150, did not significantly relate with absolute changes in DRP concentration. Similarly, P150 values measured prior to flooding were not significantly related with P release during flooding. These suggest that variables that are responsible for P release during flooding are very difficult to identify prior to flooding.

Further analysis showed that a single variable model with only DPS2 ($r^2 = 0.79$, root mean PRESS = 0.56) effectively described the response variable. However the two variable model with DPS2 and WEP ($r^2 = 0.81$, root mean PRESS = 0.57) did not perform significantly better than the single variable model with DPS2. Notably, all the factors that significantly contributed to the response variable at the preliminary PLS analysis could be used as predictors addressing varying amounts of response variability (Table 3.9). However, Ols-P, which is the general agronomic soil test P in Manitoba, had a poor relationship with the absolute changes in DRP concentration. The relationships between predictive values, obtained by cross validation, and observed values for the models were significant ($P < 0.05$), with r^2 values ranging from 0.28 to 0.80 (Table 3.10). However, the two models with DPS2 and WEP together or DPS2 alone provided the best fit relative to the 1:1 relationship, indicating their high accuracy. Water extractable P, DPS3, M3P$_{ICP}$, DPS1, and DPS6 as predictors also provided good predictive powers and fitted well with the 1:1 linear relationship. However, relationships between predictive values and observed values for the models with Ols-P, DPS4 and HCl-Pi as predictors showed the least predictive power and did not fit well with the 1:1 relationship.

Table 3.9 Partial least squares analysis (PLS) for absolute change in dissolved reactive phosphorus in surface flood water during flooding.

Predictor variable	Fitted model equation[†]	$r^{2\ddagger}$	Root mean PRESS[§]
DPS2 + WEP	$\Delta DRP_{abs} = -1.07 + 0.237\ DPS2 + 0.136\ WEP$	0.81	0.54
DPS2	$\Delta DRP_{abs} = -1.15 + 0.437\ DPS2$	0.79	0.56
WEP	$\Delta DRP_{abs} = -0.63 + 0.251\ WEP$	0.70	0.64
M3P$_{ICP}$	$\Delta DRP_{abs} = -0.52 + 0.022\ M3P_{ICP}$	0.66	0.66
DPS1	$\Delta DRP_{abs} = -0.96 + 0.539\ DPS1$	0.66	0.72
DPS3	$\Delta DRP_{abs} = -0.72 + 0.242\ DPS3$	0.66	0.75
DPS6	$\Delta DRP_{abs} = -1.22 + 0.260\ DPS6$	0.66	0.73
DPS5	$\Delta DRP_{abs} = -0.75 + 0.299\ DPS5$	0.51	0.83
M3P$_{MRP}$	$\Delta DRP_{abs} = -0.13 + 0.025\ M3P_{MRP}$	0.47	0.80
Ols-P	$\Delta DRP_{abs} = -0.14 + 0.035\ Ols\text{-}P$	0.42	0.86
DPS4	$\Delta DRP_{abs} = -0.45 + 0.336\ DPS4$	0.36	0.94
HCl-Pi	$\Delta DRP_{abs} = -1.28 + 0.009\ HCl\text{-}Pi$	0.32	0.95

[†] ΔDRP_{abs} = Absolute change in dissolved reactive P concentration during flooding; Ols-P - Olsen extractable P; WEP = water extractable P; M3P$_{MRP}$ = Mehlich-3 extractable P measured by molybdate blue method; M3P$_{ICP}$ = Mehlich-3 extractable P measured by ICP-AES; DPS1 = Ols-P / (2 * P150) + Ols-P * 100; DPS2 = M3P$_{MRP}$/ (2 * P150) + M3P$_{MRP}$ * 100; DPS3 = M3P$_{ICP}$ / (2 * P150) + M3P$_{ICP}$ * 100; DPS4 = Ols-P / α (M3Ca + M3Mg) + Ols-P * 100; DPS5 = M3P$_{MRP}$ / α (M3Ca + M3Mg) + M3P$_{MRP}$ * 100; DPS6 = M3P$_{ICP}$ / α (M3Ca + M3Mg) + M3P$_{ICP}$ * 100; HCl-Pi = 1 M extractable P
[‡]Equivalent to variability explained by the fitted model
[§]Root mean predicted residual sums of squares

Table 3.10 Relationship between predicted and observed absolute change in dissolved reactive phosphorus concentrations in surface flood water.

Predictor variable/s	Relationship between predicted and observed values	r^2	P
DPS2 + WEP	Predicted = 0.22 + 0.809 Observed	0.80	<0.0001
DPS2	Predicted = 0.24 + 0.794 Observed	0.78	<0.0001
WEP	Predicted = 0.36 + 0.698 Observed	0.68	<0.0001
DPS3	Predicted = 0.40 + 0.663 Observed	0.65	<0.0001
M3P$_{ICP}$	Predicted = 0.39 + 0.638 Observed	0.64	<0.0001
DPS1	Predicted = 0.41 + 0.659 Observed	0.64	<0.0001
DPS6	Predicted = 0.40 + 0.660 Observed	0.64	<0.0001
DPS5	Predicted = 0.59 + 0.506 Observed	0.48	<0.0001
M3P$_{MRP}$	Predicted = 0.64 + 0.473 Observed	0.44	0.0002
Ols-P	Predicted = 0.69 + 0.423 Observed	0.39	0.0006
DPS4	Predicted = 0.76 + 0.364 Observed	0.33	0.0018
HCl-Pi	Predicted = 0.83 + 0.319 Observed	0.28	0.0042

[†]Ols-P - Olsen extractable P; WEP = water extractable P; M3P = Mehlich-3 extractable P measured by molybdate blue method; M3P$_{ICP}$ = Mehlich-3 extractable P measured by ICP-AES; DPS1 = Ols-P / (2 * P150) + Ols-P * 100; DPS2 = M3P$_{MRP}$/ (2 * P150) + M3P$_{MRP}$ * 100; DPS3 = M3P$_{ICP}$ / (2 * P150) + M3P$_{ICP}$ * 100; DPS4 = Ols-P / α (M3Ca + M3Mg) + Ols-P * 100; DPS5 = M3P$_{MRP}$ / α (M3Ca + M3Mg) + M3P$_{MRP}$ * 100; DPS6 = M3P$_{ICP}$ / α (M3Ca + M3Mg) + M3P$_{ICP}$ * 100; HCl-Pi = 1 M extractable P

Partial least squares analysis indicated that one factor models can be used to predict relative change in DRP concentration in surface flood water of soils. Thirteen initial soil properties significantly contributed (VIP > 0.8) to relative change in surface water DRP concentrations (Table 3.11). The relative change in surface water DRP concentrations was strongly related to DPS, P fractions as well as other soil properties. However, relative change in DRP was not related to agronomic or environmental STP methods. The DPS3, clay %, and P150 (mg kg^{-1}) were the most important variables, with values for VIP > 1.6. From the DPS methods, DPS3 showed the strongest relationship with the relative change in DRP concentration while DPS1, DPS2, and DPS6 were also positively related. The inverse relationship with clay % was expected since the soils with high clay contents showed stable or relatively low increase in surface water DRP concentrations. The percentage of sand (Sand %) of the soils was strongly positively related to the relative change in DRP concentration since sand % in soils decrease P retention in soils (Ige et al., 2005). Single point P sorption capacity, M3Mg, and M3Al, which are dominant soil properties affecting P retention in studied soils were negatively related with the relative change in surface water DRP concentration. Cation exchange capacity, which has previously been reported to positively relate with DRP release in soils (Amery and Smolders, 2012), however, was negatively related with the relative changes in DRP concentrations. The relative change in DRP concentrations in surface flood water in all soils after flooding showed significant positive relationships with the HCl-Pi, which consists of mostly Ca and/or Mg bound P fraction of soils. Mandal (1963) suggested that large volume of carbon dioxide in flooded soil solution may convert insoluble tri-calcium phosphate to more soluble mono- and di-calcium phosphate, increasing the DRP

release from soils. Total and inorganic P fractions extracted by 0.1 M NaOH, which

consists largely of Fe and/or Al bound P in soils, were negatively related to the relative

change in surface water DRP concentrations. This observation may further confirm the

minor role Fe plays in releasing P from flooded alkaline to calcareous soils.

Table 3.11 Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 30 predictors in the preliminary model for estimation of relative change in DRP in surface flood water (ΔDRP_{ratio}).

Soil property	All		Unamended		Manured	
	B	VIP[†]	B	VIP	B	VIP
DPS3	**0.115**	**1.93**	**0.116**	**1.62**	**0.114**	**1.89**
Clay	**-0.100**	**1.68**	**-0.137**	**1.51**	**-0.097**	**1.60**
P150	**-0.099**	**1.66**	**-0.108**	**1.33**	**-0.101**	**1.67**
Sand	**0.094**	**1.58**	**0.121**	**1.33**	**0.095**	**1.56**
DPS1	**0.093**	**1.55**	**0.061**	**1.22**	**0.097**	**1.61**
DPS2	**0.084**	**1.40**	**0.079**	**1.33**	**0.084**	**1.38**
DPS6	**0.081**	**1.36**	**0.070**	**1.26**	**0.077**	**1.27**
M3Mg	**-0.077**	**1.29**	**-0.100**	**1.06**	**-0.080**	**1.33**
HCl-Pi	**0.076**	**1.28**	**0.192**	**1.89**	0.048	0.80
M3Al	**-0.068**	**1.13**	**-0.129**	**1.29**	-0.056	0.93
CEC	**-0.062**	**1.04**	-0.041	0.62	**-0.071**	**1.16**
NaOH-Pt	**-0.056**	**0.93**	-0.041	0.50	**-0.069**	**1.14**
NaOH-i	**-0.053**	**0.88**	-0.081	0.74	**-0.061**	**1.01**
WEP	0.047	0.79	**0.065**	**0.98**	0.032	0.52
SOM	-0.047	0.78	-0.029	0.66	-0.048	0.79
Silt	-0.045	0.75	-0.042	0.44	-0.052	0.86
Residual P	-0.042	0.71	-0.018	0.17	**-0.061**	**1.00**
HCl-Po	-0.040	0.67	-0.011	0.28	**-0.052**	**0.86**
M3P$_{ICP}$	0.039	0.66	**0.058**	**0.95**	0.022	0.36
DPS4	0.035	0.58	-0.015	0.63	0.034	0.55
DPS5	0.034	0.57	0.020	0.79	0.021	0.34
M3Ca	-0.029	0.49	0.033	0.33	-0.050	0.82
M3Fe	0.024	0.40	-0.063	0.65	0.041	0.67
pH	0.022	0.36	0.069	0.60	0.028	0.47
H$_2$O-Pi	0.021	0.35	**0.170**	**1.59**	-0.014	0.23
Ols-P	0.012	0.21	0.005	0.50	-0.001	0.01
Labile	0.011	0.19	**0.118**	**1.13**	-0.017	0.28
M3Mn	0.011	0.18	0.021	0.28	0.007	0.12
M3P$_{MRP}$	0.011	0.18	0.030	0.67	-0.012	0.20
NaHCO$_3$-Pi	-0.006	0.09	0.021	0.24	-0.020	0.34

[†]Significant VIP values exceeding 0.8 are in bold

Further analysis showed that together, the above mentioned 13 variables accounted for 66% of the variability in the relative change in DRP concentration. Cross validation results based on 13 significant variables showed that a 9 variable model gave the minimum root mean PRESS (root mean PRESS = 0.64) and addressed the highest amount of response variation ($r^2 = 0.75$). However, the nine variable model was not significantly better than the two variable model with DPS3 and clay % which accounted for 74% of the variation in relative change in DRP concentration in surface flood water (root mean PRESS = 0.65) (Table 3.12). Further statistical analysis showed that the one factor model with only DPS3 described 59% of the variability in the relative DRP change in surface water while HCl-Pi alone predicted only 26% of the variation in relative DRP concentration change. Clay content of the soils, which negatively affects relative DRP change, predicted 45% of the variability. The two variable model had the best predictive power as evidenced by the relationship between predicted values, obtained by cross validation, and observed relative changes in DRP concentrations during flooding (Figure 3.11). As well, the model fitted well with the 1:1 linear relationship indicating its high predictive power. Use of DPS3 alone as the predictive power also showed a good relationship between predicted and observed values and fitted well with the 1:1 linear relationship. However, other predictive models had comparatively lower predictive powers and they did not conform to the 1:1 relationship.

Table 3.12 Predictive models for relative change in dissolved reactive phosphorus concentration in surface flood water of flooded soils.

Fitted model equation for predicting[†]	$r^{2‡}$	Root mean PRESS[§]
ΔDRP_{ratio} = 4.54 + 0.481 DPS3 - 0.067 Clay %	0.74	0.65
ΔDRP_{ratio} = 0.209 + 0.68 DPS3	0.59	0.76
ΔDRP_{ratio} = 9.48 - 0.095 Clay %	0.45	0.86
ΔDRP_{ratio} = 12.25 - 0.014 P150	0.44	0.90
ΔDRP_{ratio} = 3.29 + 0.068 Sand %	0.40	0.87
ΔDRP_{ratio} = -1.119 + 0.024 HCl-Pi	0.26	0.90

[†] ΔDRP_{ratio} = Relative change in dissolved reactive P concentration during flooding; DPS3 = $M3P_{ICP}$ / (2 * P150) + $M3P_{ICP}$ * 100; P150 = Single point P sorption capacity; HCl-Pi = 1 M extractable P
[‡]Equivalent to variability explained by the fitted model
[§]Root mean predicted residual sums of squares

Our results have important implications for drainage design planning and management of flooded soils since these predictive models can estimate the DRP release from flooded soils under anaerobic conditions. The wide range of soil properties, including different P concentrations in soils used in the study, allow the model to be applied in a range of soils with different soil properties. However, the data were obtained under laboratory conditions where there were limited environmental variables. The models, therefore, may not reflect the P release from a natural system with a large number of variables, for example, removal of dissolved P through surface runoff, crops, and plants. As well, we conducted the experiment under room temperature, which is close to typical summer temperatures: thus, the model may not mirror the DRP release during spring flooding when temperatures are much lower. Therefore, the models should be used with caution, as well as, the predictive models should be validated under natural field conditions. Despite the shortcomings, the results provided important insights into improve our understanding on P dynamics in calcareous and alkaline soils under flooded conditions.
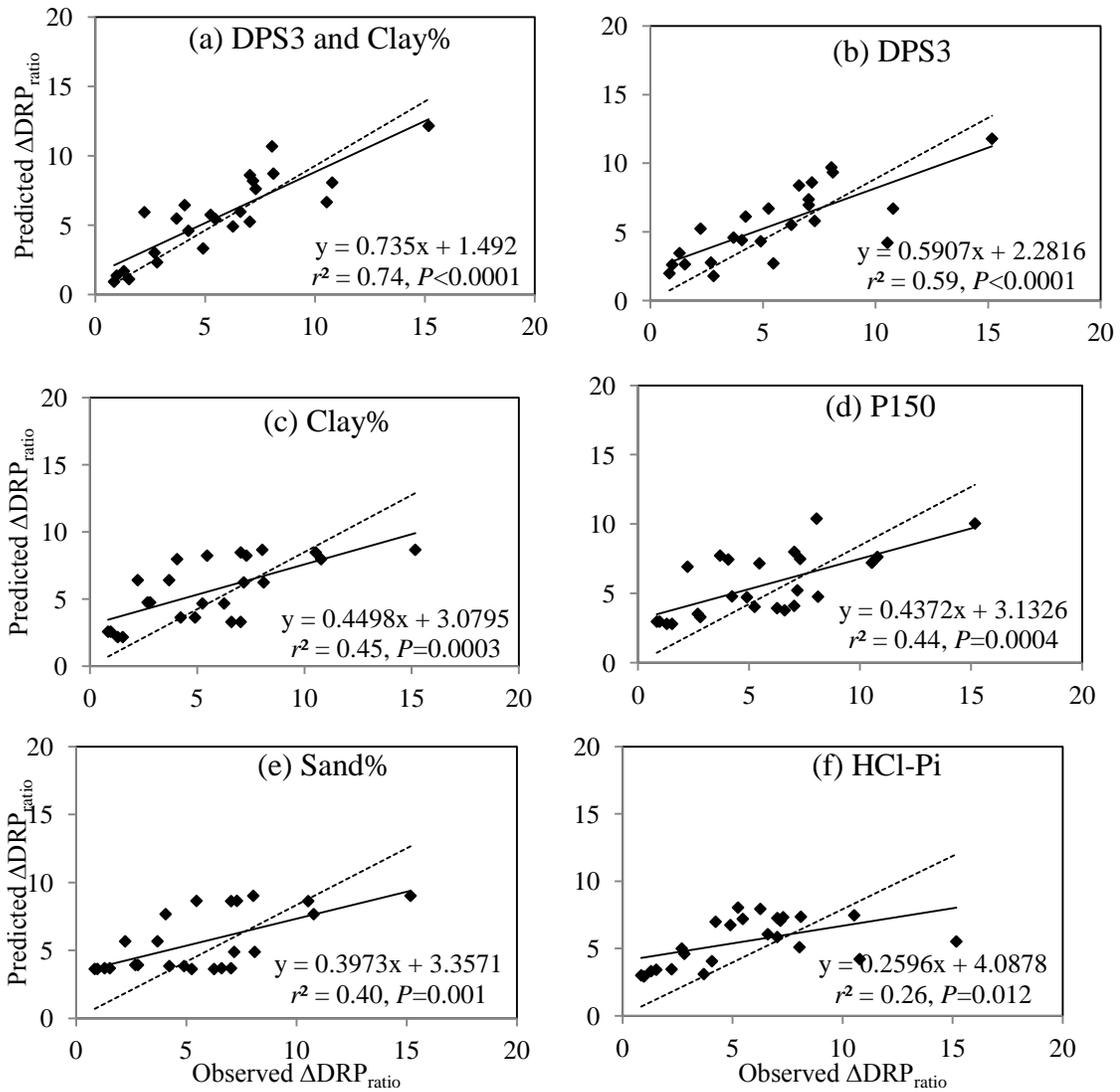
Figure 3.11 Relationship between predicted and observed relative changes in dissolved reactive phosphorus concentration in surface flood water of flooded soils. The dotted line presents the 1:1 relationship.

3.5. Conclusions

Release of P into surface water and pore water under anaerobic conditions was highly variable among the studied soils depending on the soil properties. Ten out of twelve soils showed an increase in P release into surface water during flooding and development of anaerobic conditions while P released into soil pore water increased in all soils. Scanterbury and Osborne heavy clay soils showed low and relatively stable DRP concentrations in surface water for unamended soils, whereas DRP concentration in surface water decreased over the flooding period in these soils when manured. Manure addition resulted in a slight increase in DRP concentration in surface flood and soil pore water, but the pattern of P release into waters was similar for both unamended and manured treatments of each soil with the exception of Scanterbury and Osborne soils. Therefore, results suggest that most of the studied soils pose an increased threat in varying degrees in releasing P to surrounding water bodies under flooded and anaerobic conditions. Relationships between changes in dissolved Ca and Mn and changes in DRP concentrations suggest that Ca and Mn dissolution plays a significant role in P release into surface flood water under flooded conditions. However, observed relationships were not very strong, indicating the need to investigate the influence of other properties, which are capable of affecting P retention and release under flooded conditions.

Despite increased P release into surface flood and soil pore water under anaerobic conditions, P sorption capacity as well as Olsen and Mehlich-3 extractable P of most unamended soils remained unchanged after flooding. In manured soils, P sorption capacity increased in some soils but remained relatively unchanged in the other soils.

More importantly, results suggest that the use of P sorption capacity or maximum P sorption capacity of a soil alone is not a good predictor of a soil's ability to release or retain P under flooding and consequent anaerobic conditions. Furthermore, P released from soils to surface flood and soil pore water under flooded conditions does not always result in a decrease in soil available P.

Among the soil P fractions, Ca-bound P appeared to consistently contribute to the relative increase in surface water DRP concentrations from flooded unamended and manured soils to surface flood water. Clay content of the soils had a negative effect on the relative change in DRP concentration in surface flood water. Initial soil test P and degree of P saturation were highly related with the absolute change in DRP concentration in surface water.

Through this study, we were able to identify effective tools for predicting the absolute and relative changes in dissolved P concentration in surface flood water during flooding and development of anaerobic conditions. These tools were based on a few soil properties that can be measured easily using standard laboratory procedures. The models had reasonable predictive powers and had the capability to address a maximum of 81% of the variation in changes in DRP concentration in surface flood water after reduction of soil. Therefore, these models may be effective in assessing the environmental risk of P release from flooded and anaerobic soils. However, the models should be field-validated prior to use under natural field situations.

3.6. References

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4. OVERALL SYNTHESIS

Study of P release from soil to floodwater is of great importance in our efforts to minimize eutrophication of surface water bodies. The main purpose of this research was to investigate the dynamics of P release from alkaline to calcareous soils in Manitoba to ponded surface water under anaerobic conditions. A field ponding study was conducted to identify the release of P from manured, fertilized and unamended soils under waterlogged, anaerobic conditions in a field of relatively flat landscape with slowly permeable, heavy clay soils typical for the Red River Valley region of Manitoba. Another study was conducted under laboratory conditions to investigate the variation of P release from manured and unamended Manitoba soils with varying soil properties under flooded, anaerobic conditions.

Results of the field ponding study and laboratory incubation study showed that P released from flooded soils varied greatly from soil to soil, and the increase in P loadings to surface flood water and soil pore water under anaerobic conditions could be substantial in some soils. The results of the field ponding study showed that anaerobic conditions in Scanterbury heavy clay soil did not enhance P release to surface flood water or soil pore water. Relatively stable DRP concentrations in surface flood water over Scanterbury soil were also observed in the laboratory incubation study. In the laboratory incubation study, P release from Osborne soil, another heavy clay soil, was similar to that of Scanterbury soil, and did not show an increase in DRP concentration of surface flood water after the flooded soil became anaerobic. However, all ten of the other soils in the incubation study

showed significant and substantial increases in dissolved P concentrations in both surface flood and soil pore water under reduced conditions.

Partial least squares analysis also showed that the relative increase of DRP, the proportionate increase of P release to surface water with prolonged flooding, was significantly and negatively related to percent clay content and P sorption capacity, and positively related to degree of P saturation. However, Ige et al. (2005) observed that there is no direct relationship between clay content and P retention in aerobic calcareous Manitoba soils. Exchangeable Ca and Mg, which are responsible for P retention in these soils, might be associated with clay particles in the soils thereby controlling the P release from flooded soils. Although Mehlich-3 extractable Ca and Mg were measured, exchangeable Ca and Mg were not. Therefore, in future studies, it would be advisable to take exchangeable Ca and Mg concentrations into account. Another way in which clay content may affect P release and retention in flooded soils, is its capability to buffer soil pH. However, the pH changes during flooding of the heavy clay soils were similar to those observed in other soils. Therefore, the mechanism(s) by which clay content controls P release from flooded alkaline to calcareous soils is not clear and is worthy of further study.

Unlike previously reported literature indicating a strong relationship between DRP release to flood water and Fe solubilization, DRP release to flood water in both studies did not seem to be influenced by Fe solubilization. In the laboratory study, we observed a significant relationship between changes in DRP concentration and changes in dissolved Ca concentration suggesting that Ca plays a vital role in DRP release to surface flood

water from these soils when flooded. However, it is well known that $CaCO_3$ system controls the P solubility in alkaline to calcareous soils even under aerobic situations. Therefore, $CaCO_3$ dynamics in soil over the flooding period would also be a factor that should be taken into consideration. Manganese dissolution also appeared to significantly contribute to P release into soil solution and surface flood water in the laboratory study. However, the effect of Mn on P release from flooded soils is not well documented, especially for alkaline to calcareous soils. Therefore, there is a necessity for further study of the effect of Mn. Nevertheless, according to the regression analyses for the laboratory incubation study, dissolution of Ca and Mn accounted for a small part of P released from flooded Manitoba soils thus, raising the necessity for further studies to investigate other factors and fundamental processes that affect P dynamics during flooding. For example, other processes such as dissolution of organic matter may also play an important role in governing P release from flooded soils.

The absolute magnitude of DRP increase was mainly governed by initial soil test P in the soils while the relative change in DRP was governed by degree of P saturation, P sorption capacity, and percent clay content. Even though the changes in dissolved Ca and Mn were related to the changes in DRP concentration suggesting that dissolution of Ca and Mn has a major effect on P input to the surface flood water, there was no effect from initial Ca and Mn contents in soils on the maximum increase in DRP concentration during flooding. That is, initial soil properties that we measured in aerobic soils prior to flooding did not necessarily reflect the mechanism of P release under flooded conditions.

Partial least squares provided effective models to account for the increase in dissolved reactive P concentration in surface flood water after flooding and consequent anaerobic conditions. One factor models with a few variables adequately described the response variable. The magnitude of DRP increase was predicted using any soil test P method or degree of P saturation method. However, the best options would be the use of DPS2, which used $M3P_{MRP}$ as the intensity factor with P150 plus $M3P_{MRP}$ as the capacity factor and/or WEP. Olsen extractable P, which is the routine agronomic STP method in Manitoba, was a poor predictor of the magnitude of DRP increase in surface flood water. The relative increase in DRP could be adequately predicted with a reasonable accuracy using DPS3, which used $M3P_{ICP}$ as the intensity factor with P150 plus $M3P_{ICP}$ as the capacity factor and clay % in soils together.

According to the models, soils with high STP resulted in a greater absolute release of P under flooded conditions; indicating that farmers need to keep STP to a minimum. As well, accurate predicting of P release from soil under anaerobic condition may help minimize the surface water eutrophication by identifying soils that are prone to release large fluxes of P into surface water during flooding.

The field ponding study and the laboratory incubation study demonstrated that fertilizer and manure addition enhanced the DRP concentration in surface flood and soil pore water in most of the soils. Therefore, proper rate and proper time of fertilizer and manure application would be helpful to minimize the addition of P into water bodies.

These results have important implications for the design and management of artificial drainage systems, restored wetlands, or constructed wetlands, etc in order to

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minimize P loadings into surface water bodies. For example, soils that are susceptible to large releases of P when anaerobic should be drained as quickly as possible, while drainage systems may be managed in a more flexible manner in soils such as Scanterbury and Osborne that are not as susceptible to this process. As well as, prolonged water retention in drainage ditches might enhance P release from ditch sediments due to development of anaerobic conditions to enhance P loading to surface water bodies.

Currently, restored and constructed wetlands are considered as low-cost alternatives for wastewater treatment for agricultural runoff. However, as suggested by our study, selecting and preparing these sites is critical since in most of the soils, P release was enhanced when flooded soils became anaerobic. Even though these wetlands provide additional buffers to minimize sediment and nitrogen transport, they might have the opposite effect for P, increasing P loadings. Therefore, when proposing sites, it is important to evaluate the ability of soils to sequester P and the P release potential under flooded and anaerobic condition. Sites with soils that are susceptible to releasing large amounts of P during anaerobic conditions may require removal of P-rich surface layers prior to flooding.

The field ponding study was conducted over one season with one soil and the laboratory incubation study with 12 soils. The predictive tools should be validated using more soils with varying soil properties, especially including more heavy clay soils. Also the models should be validated under different temperatures such as low temperatures to represent the spring conditions which result in flooding due to snowmelting. We conducted the laboratory incubation study at room temperature (22 °C) which is closer to

summer temperature than the spring temperature. Studies have observed that release of P during spring temperatures is lower than the P release during summer temperatures due to comparatively high reduction of soil at high temperatures (Sallade and Sims, 1997b; Stevens, 2008). Therefore, further research investigating P release from flooded soils maintaining soils at a low temperature would provide valuable information for Manitoba conditions, since flooding in Manitoba often occurs during spring snowmelt.

These findings are also based on a laboratory study and a small scale field study with simulated flooding using a constructed set up, that does not exactly represent the natural flooding conditions. For example, for both studies, disturbed soils were used which would not possess the natural soils' structure, bulk density and other physical properties. Intact cores would be a good option for future studies as proposed by Dunne et al. (2005), since they preserve the original soil structure and bulk density to a greater extent. As well, intact cores can be used even under field conditions. However, it is also important to conduct laboratory experiments and small scale field experiments with disturbed soils since they facilitate experimental replication, treatment manipulation, and experimental control.

After flooding, surface flood and soil pore water samples were collected and transported under normal laboratory and field conditions thus allowing changes in redox status, which alters the chemical composition. The use of anion and cation resin strips as an in-situ method would facilitate extraction and determination of dissolved P and ion concentrations at the existing redox status at the surface flood water (Qian and Schoenau, 2002; Tiessen and Moir, 1993). The use of de-oxygenated diffusive gradient thin films

(DGT) technique, as proposed by Zhang et al. (1998) and Harper et al. (1998), would help collect the soil solution samples at the existing redox condition. As well, this method can be used to determine both pore water dissolved P concentration and the "ability of the solid phase to resupply P locally" into the pore water.

Another limitation of the study was the preparation of previously flooded soils prior to analysis, which involved air drying, and grinding which altered the soils' redox status as well as P extractability and sorption capacity relative to their condition during flooding. Allowing flooded soils to re-oxidize could result in rapid transformation of soil solution Fe^{2+} to Fe^{3+} and precipitation of $Fe(OH)_3$ within a short time of period. Newly formed $Fe(OH)_3$ has a great P adsorption capacities and can reduce the P extractability and solubility (Brand-Klibanski et al., 2007; Moore et al., 2000). Thus, to avoid this, soil sampling and sample preparation should be conducted and maintained under anaerobic conditions until analysis. For example, the sampling method and sample handling proposed by Moore et al. (2000) would be an appropriate alternative. Further, EPC_0 would be a better alternative to maximum P adsorption (Smax) or single point P sorption capacity, (P150 in our study) since it accurately describes the P sorption capacity in the environment. In addition, to avoid the precipitation of P during P sorption studies due to external addition of high P concentration, Brand-Klibanski et al. (2007) suggested the use of small initial P concentrations in the range of 0-10 mg L^{-1}.

In summary, these studies demonstrated that dynamics of P release from soil to surface flood and soil pore water are greatly different among soils depending on soil properties. Magnitude of P release to surface flood water under anaerobic conditions

could be substantial in some soils. As well, the laboratory study identified models with initial soil properties to predict the changes in P concentration during flooding. This knowledge would be useful to design beneficial management practices to minimize eutrophication of surface water bodies by controlling P loading. Even though this information represents a significant step towards identifying responses of different soils to flooding and development of anaerobic conditions in soils, future research should be conducted integrating hydrology, climate, soil chemical, biological, and physical properties, processes and their interactions, as well as soil management practices.

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APPENDICES

Appendix 2.A; Plot lay out of the field ponding study
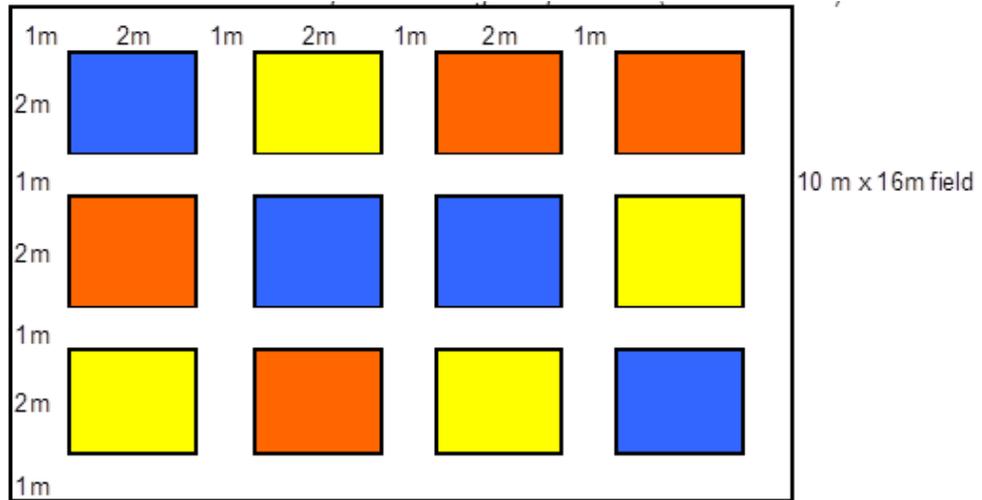
Appendix 2.B; Variation of redox potential (Eh) and pH in flooded Scanterbury heavy clay soils

Days after flooding	Eh (mV)				pH			
		Unamended	Fertilized	Manured		Unamended	Fertilized	Manured
1	271.5a[†‡]	279.0	263.2	272.3	6.97a[‡]	6.98	7.12	6.82
5	219.1b	225.4	222.3	209.7	6.79abcd	6.72	7.02	6.62
7	187.1b	216.5	180.5	164.3	6.91abc	6.90	7.14	6.69
11	88.0c	93.6	100.3	70.0	6.95ab	7.13	7.00	6.71
14	72.9cd	79.7	81.4	57.8	6.97a	6.95	7.15	6.82
19	62.0cde	65.9	58.5	61.7	6.85abc	6.83	7.05	6.68
22	50.4cdef	44.8	51.9	54.4	6.67cde	6.66	6.81	6.54
25	39.8def	43.5	45.5	30.4	6.69cde	6.71	6.80	6.55
28	30.6ef	34.5	38.4	18.9	6.68cde	6.64	6.86	6.54
32	28.6ef	28.8	38.4	18.8	6.49e	6.52	6.59	6.38
34	26.1ef	29.1	35.9	13.2	6.74bcd	6.72	6.88	6.61
39	23.3f	26.6	31.4	11.8	6.72bcd	6.81	6.85	6.51
42	23.3f	29.2	26.7	13.9	6.60de	6.58	6.76	6.45

ANOVA	df	$P > F$			$P > F$			
Treatment	2	0.110			0.087			
Time	12	<0.0001			<0.0001			
Treatment*Time	24	0.316			0.696			
CV[§] %		11			2			

[†]Means followed by the same lower case letter within a column are not significantly different
[‡]Mean values are averaged across the treatments
[§]CV - coefficient of variation

Appendix 2.C; Table I. Dissolved Fe, Mn, Ca and Mg concentrations[‡] in surface ponded water of Scanterbury clay soil.

	Fe	Mn	Ca	Mg
Treatment		mg L^{-1}		
Unamended		0.00245ab[†]		
Fertilized		0.00178b		
Manured		0.00339a		
Days after flooding (time)				
1		0.00300bc	6.02 c	0.79 d
5		0.00681ab	13.8 bc	3.65 cd
7		0.00321abc	14.2 bc	3.85 cd
11		0.00294bc	15.6 bc	4.86 bcd
14		0.00123bc	18.4 abc	5.49 bcd
19		0.00182bc	20.1 abc	6.58 abcd
22		0.00361abc	21.8 abc	7.45 abcd
25		0.00082c	21.0 abc	8.11 abcd
28		0.01746a	35.4 a	14.2 a
32		0.00204bc	25.2 ab	8.77 abcd
34		0.00393abc	25.6 ab	9.71 abc
39		0.00077c	28.6 ab	11.8 abc
42		0.00085c	28.5 ab	13.2 ab

Treatment *time	Unamended	Fertilized	Manured
1	0.06 a	0.04 a	0.03 ab
5	0.14 a	0.09 a	0.03 ab
7	0.05 ab	0.03 a	0.02 ab
11	0.04 ab	0.02 a	0.04 ab
14	0.01 bc	0.02 a	0.01 b
19	0.02 ab	0.03 a	0.04 ab
22	0.07 a	0.07 a	0.06 ab
25	0.01 c	0.01 a	0.01 b
28	0.13 a	0.15 a	0.12 a
32	0.01 a	0.04 a	0.02 ab
34	0.03 c	0.03 a	0.02 ab
39	0.00 d	0.00 b	0.00 c
42	0.00 d	0.00 b	0.00 c

ANOVA	df		P > F		
Treatment	2	0.1421	0.0038	0.4540	0.6167
Time	2	<0.0001	<0.0001	0.0004	0.0008
Treatment* time	24	0.0008	0.1690	0.9598	0.9983
CV[§] (%)		69	61	48	61

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]Arithmetic means for Ca and Mg and geometric least square means for Fe and Mn

[§]CV - coefficient of variation

Appendix 2.C; Table II. Variation of dissolved Ca concentration over the flooding period in pore water of Scanterbury clay soil. Mean values are averaged across 5 and 10 cm depths (arithmetic means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
	mg L^{-1}		
1	23.0a[†]	32.8c	22.3c
5	27.9a	36.9c	22.5c
7	26.3a	37.5c	26.6c
11	25.8a	41.0abc	32.3bc
14	27.7a	39.1bc	29.5c
19	31.5a	38.4c	42.2abc
22	33.8a	39.3c	44.5abc
25	34.0a	39.1c	46.6abc
28	38.9a	63.6ab	40.2abc
32	46.4a	64.3a	36.9bc
34	44.8a	50.7abc	58.6a
39	45.2a	52.9abc	57.0ab
42	45.8a	54.2abc	57.5ab

ANOVA	df	*P* > F
Treatment	2	0.537
Depth	1	0.084
Treatment*Depth	2	0.891
Time	12	<0.0001
Treatment*Time	24	0.0003
Depth*Time	12	0.855
Treatment*Depth*Time	24	1.000
CV[‡] (%)		31

[†]Mean values followed by the same lowercase letter within a column are not significantly different
[‡]CV - coefficient of variation

Appendix 2.C; Table III. Variation of dissolved Mg concentration over the flooding period in pore water of Scanterbury clay soil.   Mean values are averaged across 5 and 10 cm depths (arithmetic means).

Days after flooding		Unamended	Fertilized	Manured
			mg L^{-1}	
1		6.56b†	8.55d	6.79d
5		8.56ab	11.1cd	7.06d
7		8.34ab	11.2cd	8.93cd
11		8.63ab	13.6cd	11.8cd
14		10.6ab	12.9cd	10.5cd
19		12.5ab	13.5cd	16.9abcd
22		13.8ab	13.9cd	18.6abcd
25		15.4ab	14.8bcd	20.4abc
28		16.2ab	26.1a	14.1bcd
32		18.3ab	26.0ab	14.2bcd
34		17.8ab	19.3abcd	25.4ab
39		19.2a	21.2abc	26.1a
42		19.6a	22.0abc	26.0ab
Depth				
10 cm	16.3a			
5 cm	14.3b			

ANOVA	df	$P > $F
Treatment	2	0.673
Depth	1	0.032
Treatment*Depth	2	0.999
Time	12	<0.0001
Treatment*Time	24	0.0002
Depth*Time	12	0.809
Treatment*Depth*Time	24	1.000
CV‡ (%)		39

†Mean values followed by the same lowercase letter within a column are not significantly different
‡CV - coefficient of variation

Appendix 2.C; Table IV. Variation of dissolved Fe concentration over the flooding period in pore water of Scanterbury clay soil. Mean values are averaged across 5 and 10 cm depths (geometric least square means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
	mg L^{-1}		
1	0.07bc[†]	0.07a	0.07b
5	0.07abc	0.07a	0.09b
7	0.08abc	0.08a	0.10b
11	0.04c	0.16a	0.16ab
14	0.05c	0.10a	0.20ab
19	0.13abc	0.18a	0.31ab
22	0.20abc	0.22a	0.33ab
25	0.13abc	0.15a	0.36ab
28	0.50a	0.34a	0.17ab
32	0.36ab	0.28a	0.26ab
34	0.18abc	0.27a	0.83a
39	0.18abc	0.19a	0.82a
42	0.24abc	0.23a	0.95a

ANOVA		df	$P >$ F
Treatment		2	0.319
Depth		1	0.460
Treatment*Depth		2	0.111
Time		12	0.0001
Treatment*Time		24	0.0005
Depth*Time		12	0.057
Treatment*Depth*Time		24	0.803
CV[‡] (%)			99

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]CV - coefficient of variation

Appendix 2.C; Table V. Variation of dissolved Mn concentration over the flooding period in pore water of Scanterbury clay soil. Mean values are averaged across 5 and 10 cm depths (geometric least square means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
	mg L^{-1}		
1	0.008d†	0.006c	0.009d
5	0.081abc	0.064b	0.096c
7	0.059bc	0.081b	0.154abc
11	0.039cd	0.128ab	0.226abc
14	0.106abc	0.143ab	0.297abc
19	0.169abc	0.185ab	0.385abc
22	0.205abc	0.205ab	0.469abc
25	0.242ab	0.237ab	0.591ab
28	0.244ab	0.562a	0.152bc
32	0.330ab	0.556a	0.348abc
34	0.360ab	0.340ab	0.867a
39	0.394a	0.389ab	0.944a
42	0.421a	0.372ab	0.854ab

ANOVA	df	$P > F$
Treatment	2	0.299
Depth	1	0.492
Treatment*Depth	2	0.341
Time	12	<0.0001
Treatment*Time	24	<0.0001
Depth*Time	12	0.008
Treatment*Depth*Time	24	0.629
CV‡ (%)		75

†Mean values followed by the same lowercase letter within a column are not significantly different

‡CV - coefficient of variation

Appendix 2.C; Table VI. Variation of dissolved Mn concentration in pore water of Scanterbury clay soil over the flooding period. Mean values are averaged across treatments (geometric least square means).

Days after flooding	Depth	
	10 cm	**5 cm**
	mg L^{-1}	
1	0.007d†	0.008c
5	0.073c	0.087b
7	0.096bc	0.085b
11	0.156abc	0.069b
14	0.201abc	0.135ab
19	0.254abc	0.207ab
22	0.309abc	0.236ab
25	0.368ab	0.285ab
28	0.168abc	0.453a
32	0.348ab	0.459a
34	0.525a	0.427a
39	0.574a	0.480a
42	0.570a	0.458a

ANOVA	df	$P > F$
Treatment	2	0.299
Depth	1	0.492
Treatment*Depth	2	0.341
Time	12	<0.0001
Treatment*Time	24	<0.0001
Depth*Time	12	0.008
Treatment*Depth*Time	24	0.629
CV‡ (%)		75

†Mean values followed by the same lowercase letter within a column are not significantly different

‡CV - coefficient of variation

Appendix 2.D; Table I. Variation of Mehlich-3 extractable P in Scanterbury heavy clay soil during flooding period in field ponding study (geometric least square means).

Days after flooding	Treatment		
	Unamended	**Fertilized**	**Manured**
		mg kg^{-1}	
1	16.9aA[†‡]	35.0abA	30.4aA
5	21.8aB	46.7aA	32.6aAB
7	18.9aA	19.6cA	31.4aA
11	20.2aA	19.3cA	27.8aA
14	18.7aA	23.5bcA	29.2aA
19	14.1aA	23.7bcA	27.0aA
22	16.6aA	21.7bcA	24.4aA
25	16.5aA	23.6bcA	23.3aA
28	21.8aA	36.5abA	34.6aA
32	13.9aA	22.1bcA	25.1aA
34	15.3aA	18.6cA	23.9aA
39	17.4aA	25.2bcA	28.7aA
42	18.1aB	47.7aA	30.5aAB

ANOVA		df	$P > F$
Treatment		2	0.022
Flooding condition		1	1.000
Treatment*Flooding condition		2	1.000
Time		12	<0.0001
Treatment*Time		24	<0.0001
Flooding condition*Time		12	1.000
Treatment*Flooding*Time		24	1.000
CV§ (%)			25

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]Mean values followed by the same uppercase letter within a row are not significantly different

[§]CV - coefficient of variation

Appendix 2.D; Table II. Variation of Olsen extractable P analyzed in air-dried Scanterbury soil during flooding period in field ponding study (geometric least square means).

	Ols-P (mg kg^{-1})	
Treatment		
Unamended	15.4b	
Fertilized	22.9a	
Manured	20.8a	
Days after flooding	Flooding condition	
	Flooded	Unflooded
	mg kg^{-1}	
1	19.0a†	22.3abc
5	19.2a	27.2a
7	18.5a	17.9bc
11	18.6a	17.9bc
14	17.1a	18.9bc
19	18.4a	18.1bc
22	19.9a	17.6bc
25	17.9a	17.8bc
28	19.3a	24.8ab
32	19.4a	17.2c
34	18.6a	18.1bc
39	19.6a	22.8abc
42	18.9a	23.6abc
ANOVA	df	$P >$ F
Treatment	2	0.005
Flooding condition	1	0.174
Treatment*Flooding condition	2	0.685
Time	12	0.000
Treatment*Time	24	0.656
Flooding condition*Time	12	0.005
Treatment*Flooding*Time	24	0.676
CV‡ (%)		23

†Mean values followed by the same lowercase letter within a column are not significantly different

‡CV - coefficient of variation

Appendix 2.D; Table III. Variation of Olsen extractable P analyzed in wet Scanterbury heavy clay soil during flooding period in field ponding study (geometric least square means).

Days after flooding	Treatment			Flooding condition[§]	
	Unamended	**Fertilized**	**Manured**	**Flooded**	**Unflooded**
	mg kg^{-1}			mg kg^{-1}	
1	13.0aA[†‡]	22.6aA	16.2bA	13.1bA[‡]	21.6bcdA
5	17.1aA	32.2aA	22.4abA	14.4abB	37.1aA
7	14.2aA	27.9aA	18.8bA	17.7abA	21.7abcdA
11	12.5aB	19.7aAB	43.0aA	23.8aA	20.3bcdA
14	16.2aA	21.4aA	20.6bA	15.9abA	23.3abcdA
19	16.5aA	28.3aA	23.6abA	15.6abB	31.9abcA
22	14.3aA	23.5aA	21.1bA	16.6abA	22.3abcdA
25	14.6aA	20.6aA	19.8bA	17.4abA	18.8dA
28	14.6aB	31.6aA	30.5abA	17.3abB	33.7abA
32	13.6aA	24.2aA	20.2bA	17.5abA	20.2bcdA
34	13.9aA	20.7aA	17.5bA	15.2abA	19.3cdA
39	13.2aA	20.3aA	19.0bA	17.1abA	17.3dA
42	12.4aB	26.4aA	15.1bAB	16.0abA	18.2dA

ANOVA				df	$P > $F
Treatment				2	0.0005
Flooding condition				1	<0.0001
Treatment*Flooding condition				2	0.0070
Time				12	0.0002
Treatment*Time				24	0.0004
Flooding condition*Time				12	<0.0001
Treatment*Flooding*Time				24	0.6700
CV[¶] (%)					36

[†]Mean values followed by the same lowercase letter within a column are not significantly different

[‡]Mean values followed by the same uppercase letter within a row are not significantly different

[§]Mean values are averaged across treatments

[¶]CV - coefficient of variation

Appendix 2.E;   Variation of Mehlich-3 extractable Al, Fe, Mn, Ca and Mg concentrations over the flooding period of Scanterbury heavy clay soil (arithmetic means).

		Al	Fe	Mn	Ca	Mg	M3P$_{ICP}$
				mg kg^{-1}			
Treatment							
Unamended							22.3 b
Fertilized							32.3 a
Manured							30.3 a
Days after flooding							
1		864.4	292.7bc[†]	53.3c	6274.6b	1919.3c	34.7 a
7		792.4	268.0c	54.1c	7670.2a	2127.5bc	24.2 b
14		1001.5	301.4bc	56.4bc	7943.7a	2428.7a	28.3 ab
22		889.5	294.0bc	59.1bc	6873.0ab	2171.6abc	27.4 ab
28		910.7	302.2bc	61.3bc	7019.8ab	2208.3ab	26.5 b
34		959.8	335.4ab	68.2ab	7667.7a	2289.5ab	25.8 b
42		905.6	359.5a	73.4a	7795.2a	2363.7ab	29.6 ab
ANOVA	df			*P* > F			
Treatment	2	0.310	0.141	0.988	0.266	0.921	<0.0001
Time	6	0.261	0.002	0.0002	0.008	0.0003	0.003
Treatment*Time	12	0.831	0.176	0.741	0.198	0.796	0.503
CV[‡] (%)		12	9	15	10	3	20

[†]Mean values followed by the same lowercase letter within a column are not significantly different
[‡]CV - coefficient of variation
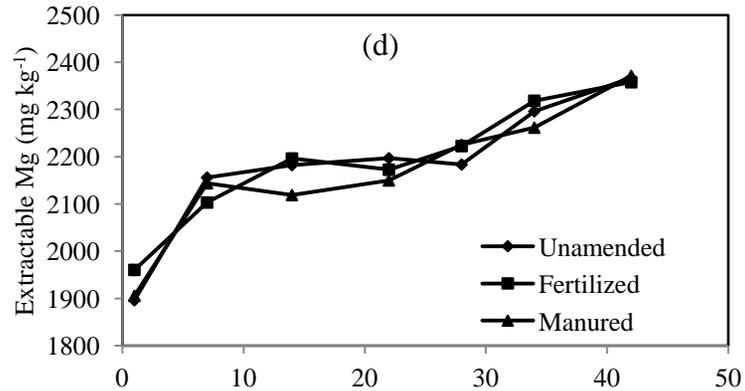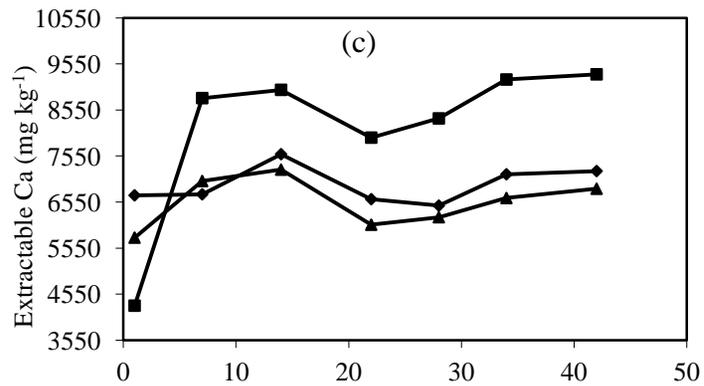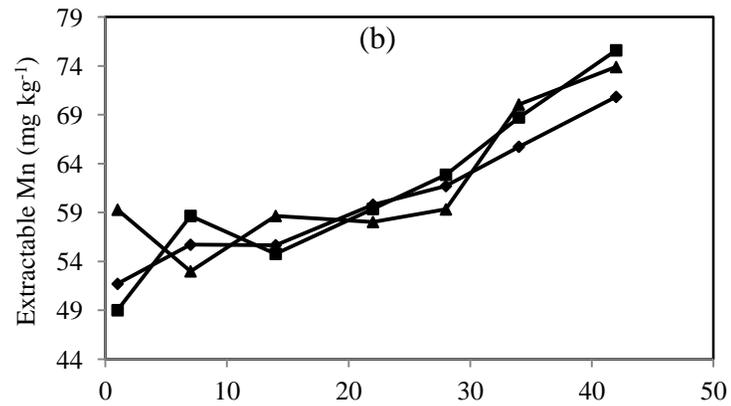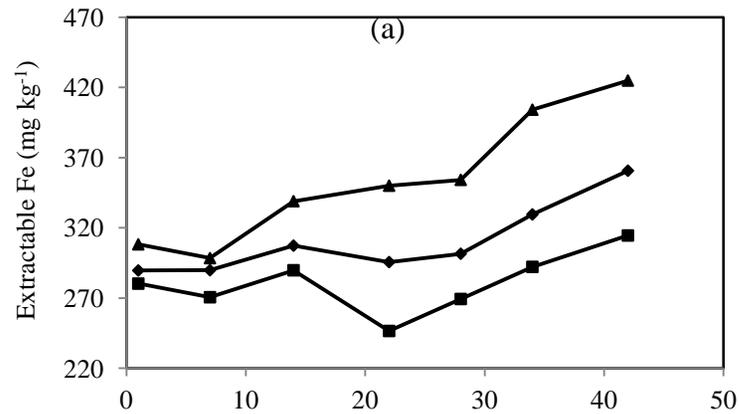
Appendix 2.F; Variation of Mehlich-3 extractable (a) Fe, (b) Mn, (c) Ca, and (d) Mg concentrations over the flooding period of Scanterbury heavy clay soil.

Appendix 2.G;
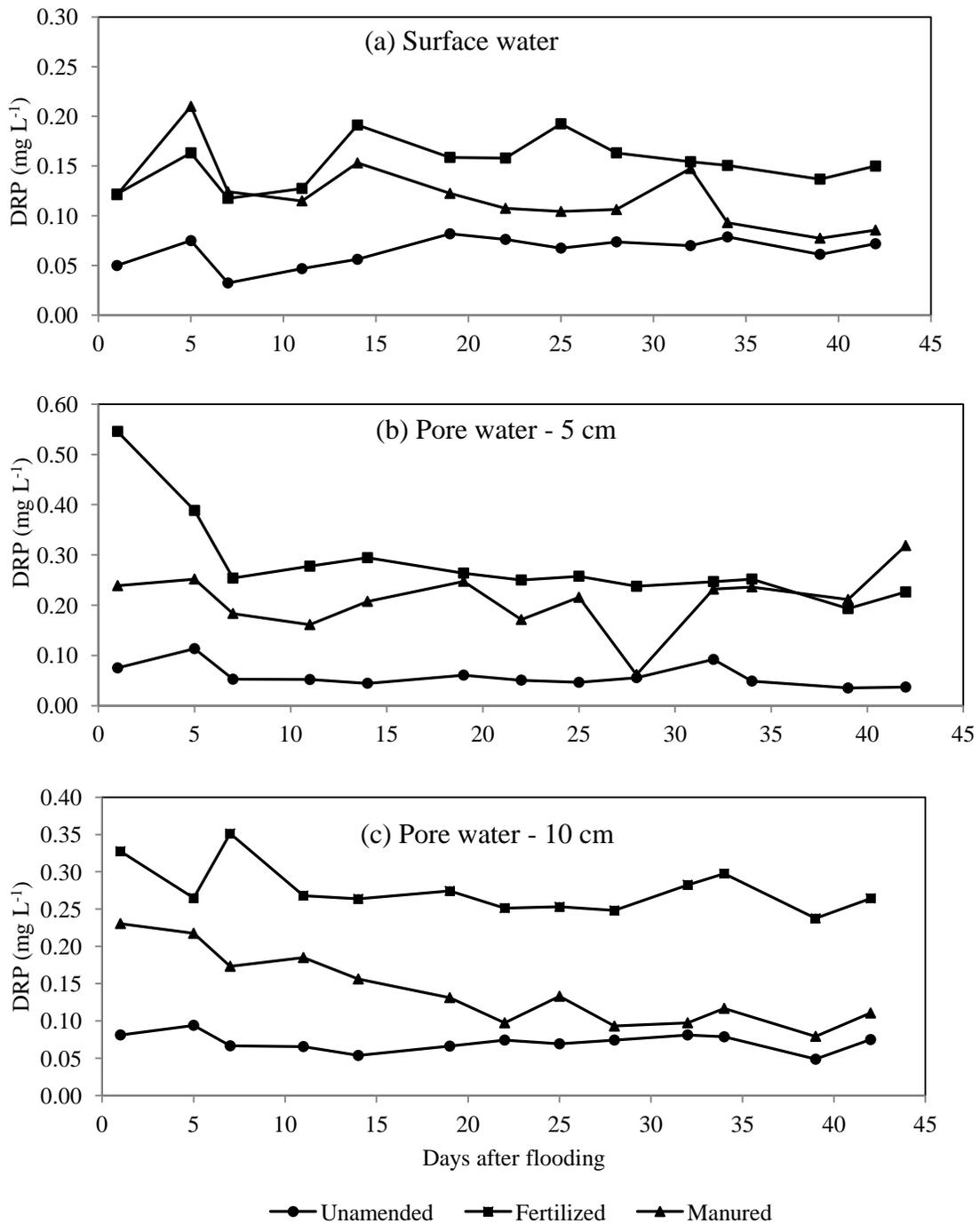
Figure I. Variation of dissolved reactive P concentration (DRP) at (a) surface flood water, (b) soil pore water at 5 cm depth, and (c) soil pore water at 10 cm depth, in unamended, fertilized and manured soils over the flooding period of Scanterbury heavy clay soil (geometric least square means).
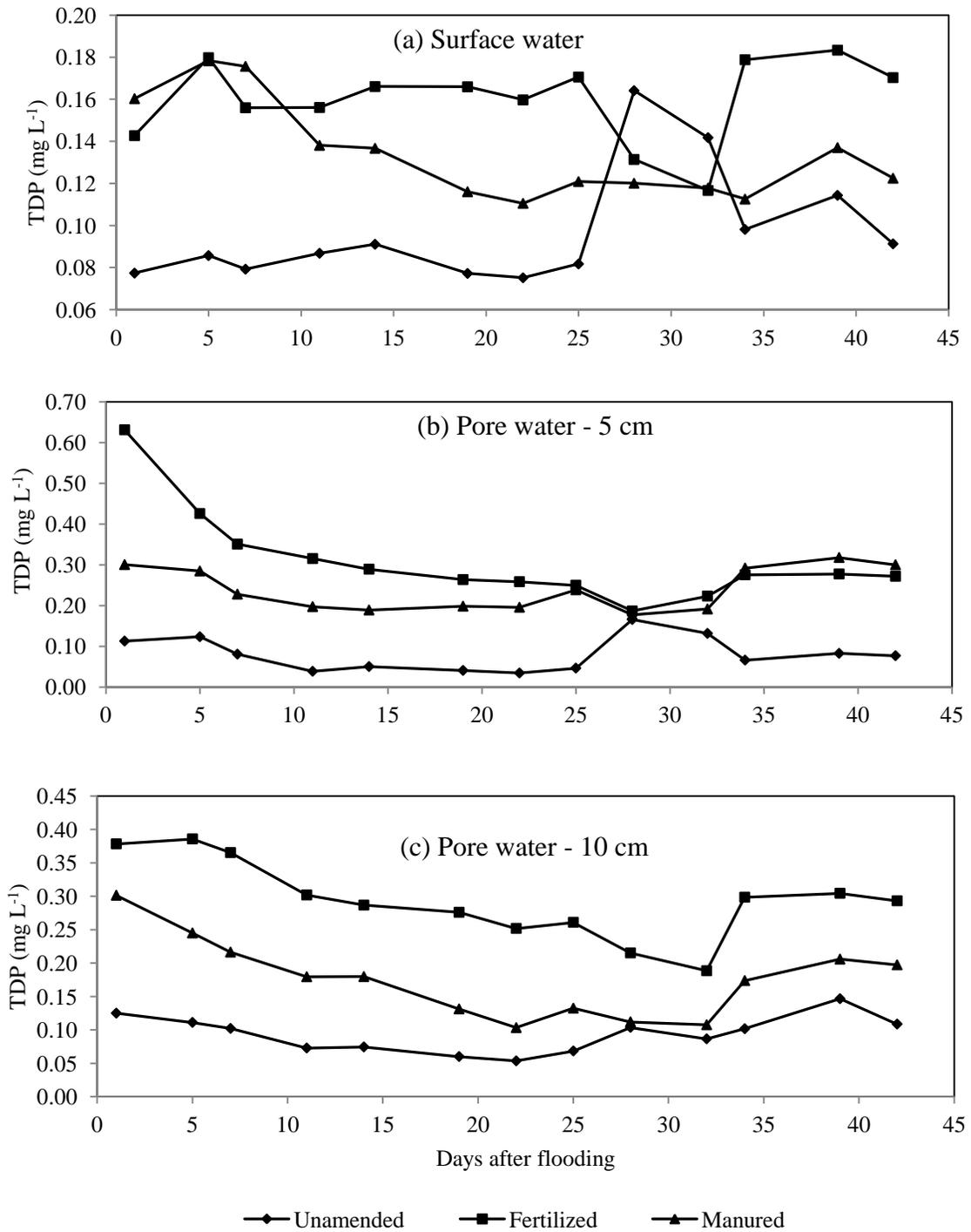
Figure II. **Variation of total dissolved P concentration (TDP) at (a) ponded surface water, (b) soil pore water at 5 cm depth, and (c) soil pore water at 10 cm depth, in unamended, fertilized and manured soils over the flooded period of Scanterbury heavy clay soil (geometric least square means).**
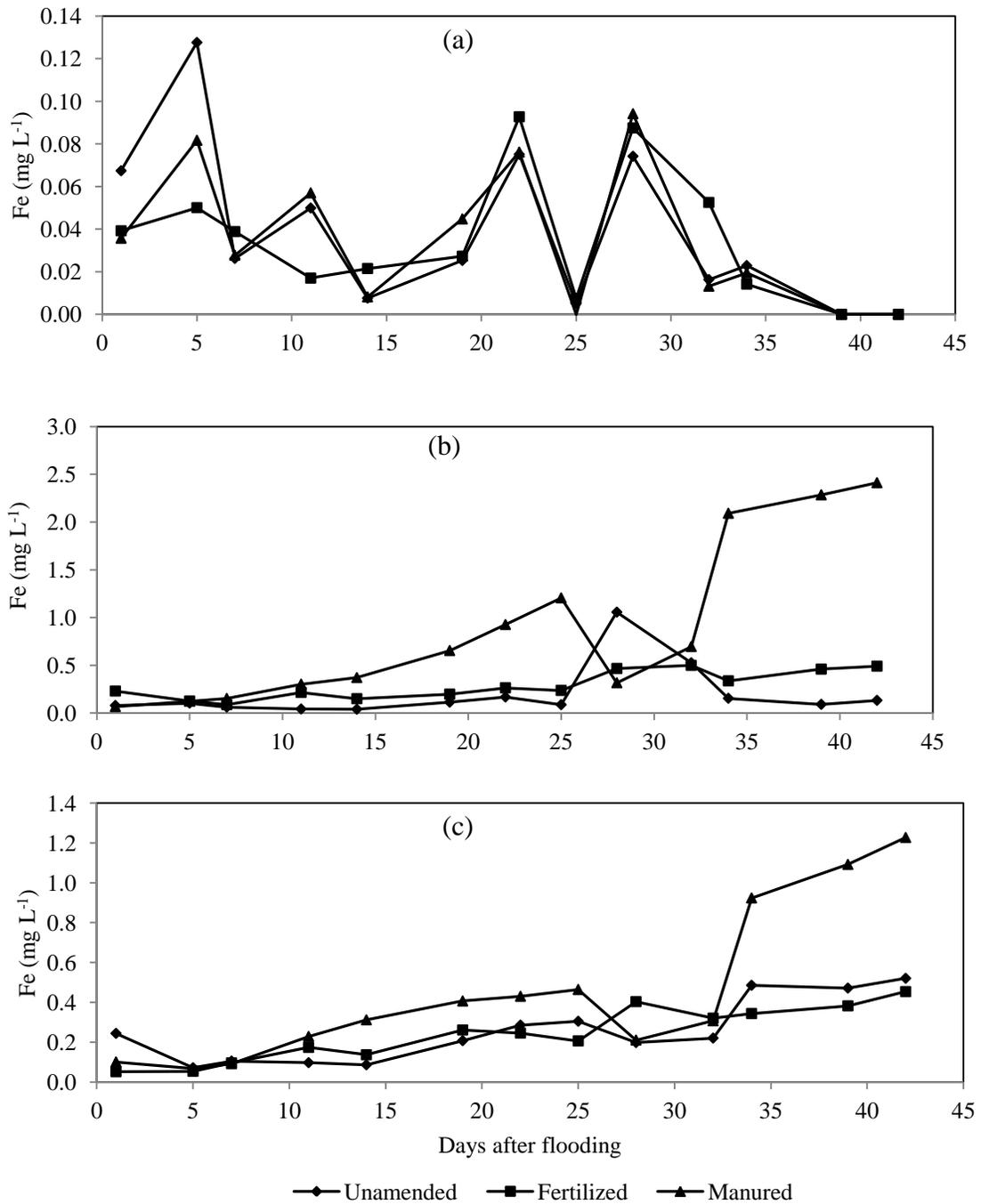
Figure III. Variation of dissolved Fe concentration over the flooding period in (a) surface water, (b) pore water at 5 cm, and (c) pore water at 10 cm depth, in unamended, fertilized and manured Scanterbury heavy clay soil (geometric least square means).
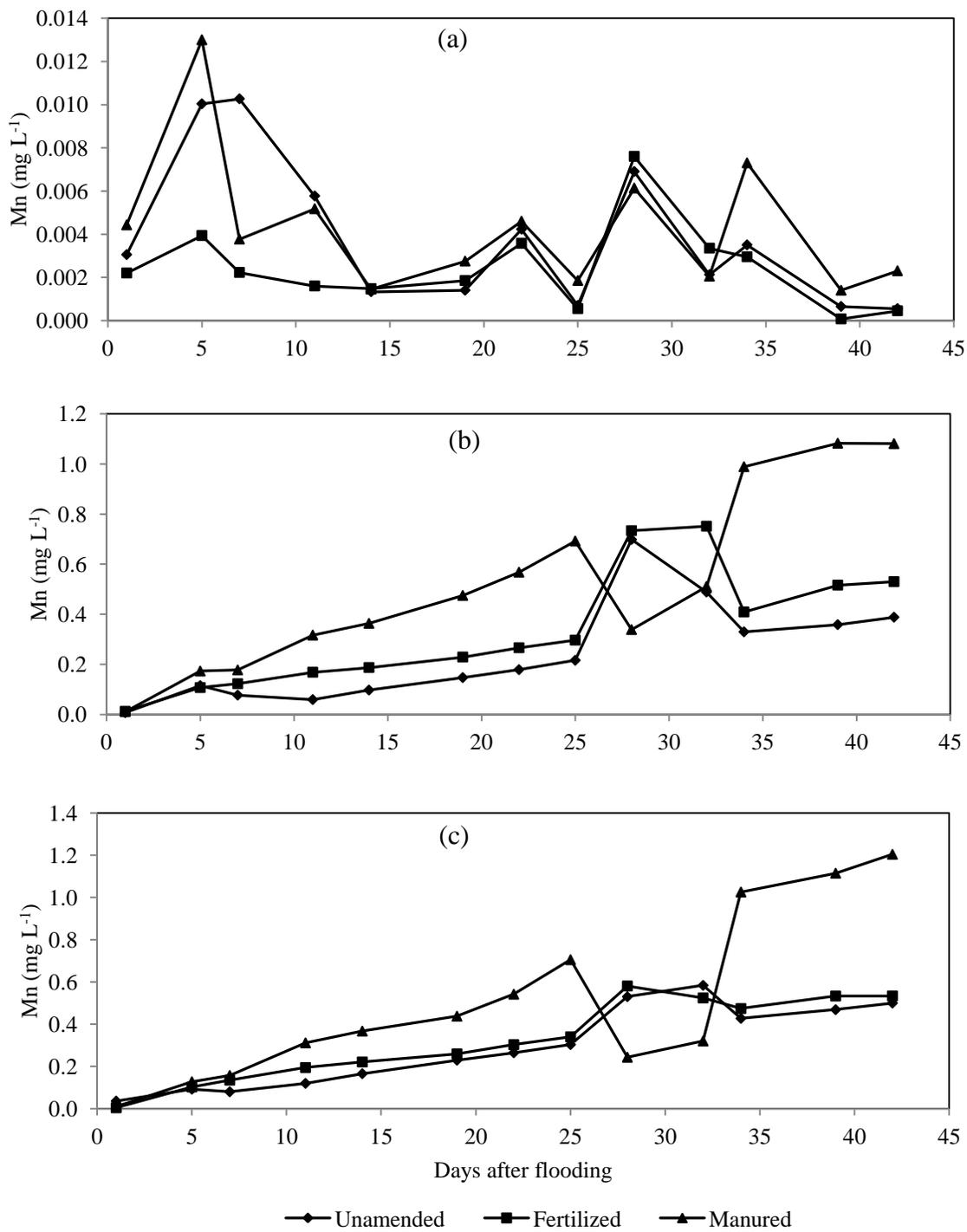
Figure IV. Variation of dissolved Mn concentration over the flooded period in (a) surface water, (b) pore water at 5 cm, and (c) pore water at 10 cm depth, in unamended, fertilized and manured Scanterbury heavy clay soil (geometric least square means).
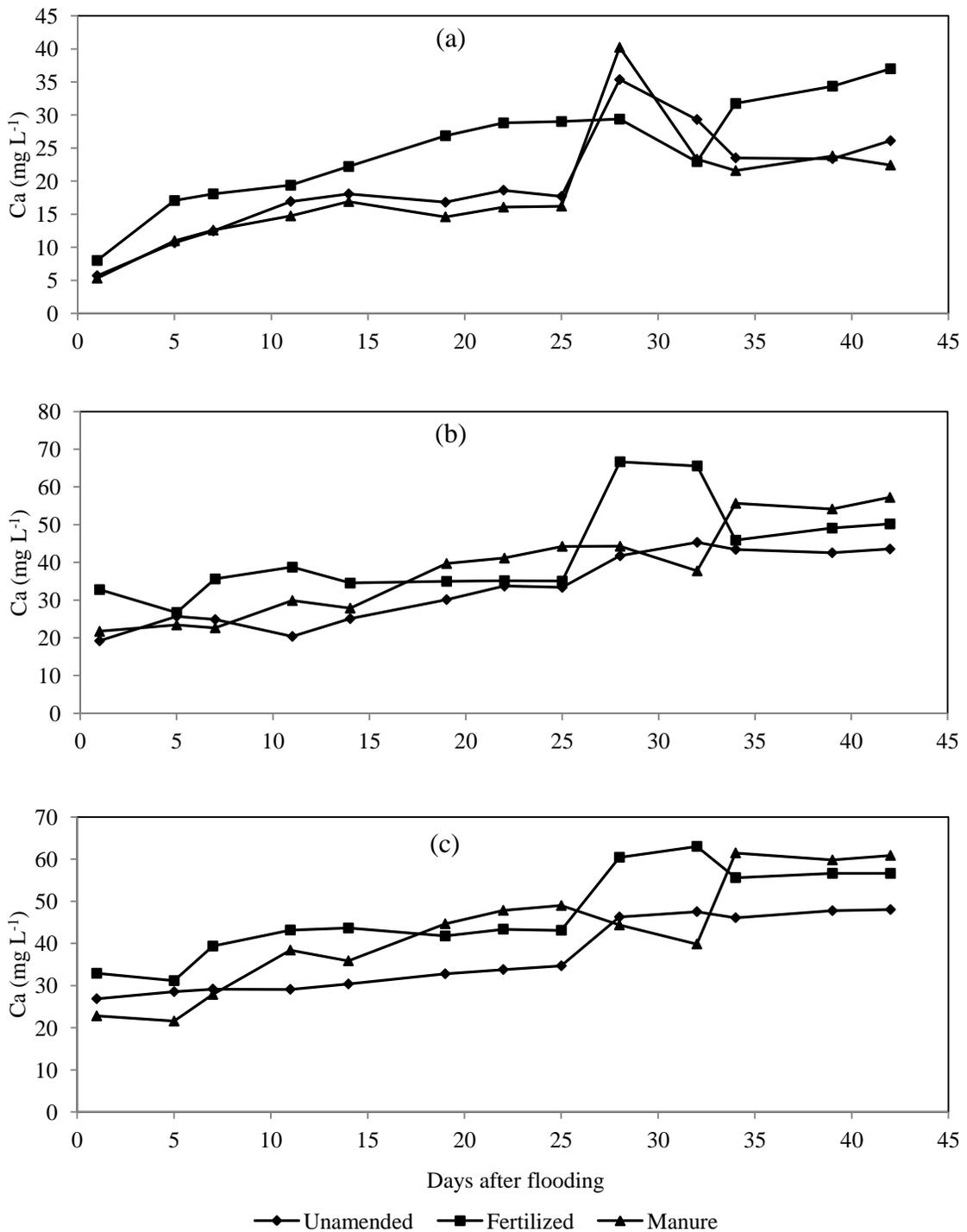
Figure V. Variation of dissolved Ca concentration over the flooding period in (a) surface water, (b) pore water at 5 cm, and (c) pore water at 10 cm depth, in unamended, fertilized and manured Scanterbury heavy clay soil (arithmetic means).
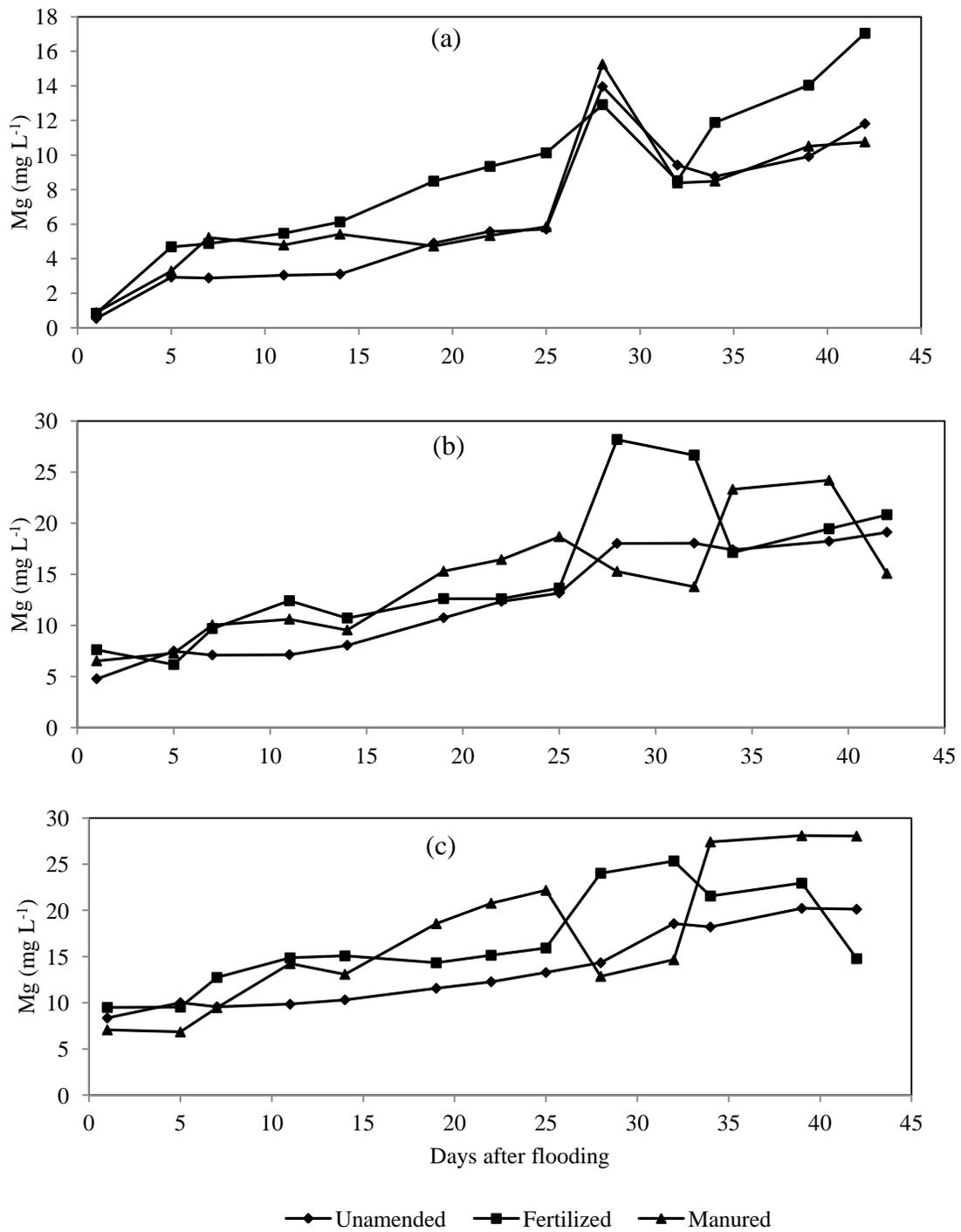
Figure VI. Variation of dissolved Mg concentration over the flooding period in (a) surface water, (b) pore water at 5 cm, and (c) pore water at 10 cm depth, in unamended, fertilized and manured Scanterbury heavy clay soil (arithmetic means).

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Appendix 3.A; Table I. Changes in soil pore water pH over the flooding period (arithmetic means).

Soil series and treatment		1	7	14	21	28	35	42	49	56
		Days after flooding (Time)								
Newdale	Unamended	7.25aA	7.26aA	7.22aA	6.99aA	7.03aA	7.08aA	7.05aA	7.05aA	7.24aA
	Manured	7.16aA	7.44aA	7.24aA	7.09aA	7.41aA	7.46aA	7.22aA	7.44aA	7.35aA
Lakeland 1	Unamended	7.89aA	7.42bA	7.07cA	6.92cA	6.93cA	7.08cB	7.06cA	7.05cB	7.11bcA
	Manured	7.56abA	7.54abcA	7.20bcA	7.07cA	7.33abcA	7.57abA	7.32bcA	7.72aA	7.10cA
Lakeland 2	Unamended	7.37aA	7.47aA	7.41aA	7.40aA	7.56aA	7.56aA	7.35aA	7.24aA	7.30aA
	Manured	7.31bA	7.57abA	7.49abA	7.48abA	7.75abA	7.82aA	7.42bA	7.61abA	7.31bA
Arborg	Unamended	7.92aA	7.73aA	7.31bA	7.07bA	7.02bA	7.19bA	7.05bA	7.11bA	7.07bA
	Manured		7.78aA	7.53abA	7.20bcA	7.09cA	7.03cA	6.94cA	7.07cA	7.07bcA
Almasippi	Unamended	8.06aA	8.06aA	7.83abA	7.52bcA	7.44cA	7.58bcA	7.64abcA	7.47bcA	7.52bcA
	Manured	7.92aA	7.92aA	7.71abA	7.36bB	7.37bA	7.49baA	7.38bA	7.32bB	7.41baA
Reinland	Unamended	7.74aA	7.84aA	7.78aA	7.69abA	7.55abA	7.86aA	7.68abA	7.31bB	7.34bA
	Manured	7.65aA	7.73aA	7.62aA	7.53aA	7.70aA	7.75aA	7.76aA	7.78aA	7.51aA
Niverville	Unamended	7.96aA	7.33bA	6.97bcA	6.78cA	6.76cA	6.91bcA	6.87cA	6.90bcA	6.90bcA
	Manured	7.61aA	7.36abA	6.75cA	6.69cA	6.68cA	6.78cA	6.70cA	6.99bcA	7.05bcA
Fyala	Unamended	7.53aA	7.68aA	7.52aA	7.33aA	7.53aA	7.65aA	7.41aA	7.57aA	7.30aA
	Manured	7.44aA	7.61aA	7.51aA	7.33aA	7.48aA	7.61aA	7.43aA	7.38aA	7.18aA
Sprague	Unamended	7.17aA	7.40aA	7.34aA	7.26aA	7.38aA	7.53aA	7.58aA	7.37aA	7.42aA
	Manured	7.24aA	7.34aA	7.28aA	7.24aA	7.54aA	7.59aA	7.43aA	7.28aA	7.37aA
Long Plain	Unamended	7.85aA	7.79abA	7.68abA	7.55abcA	7.45abcA	7.54abcA	7.49abcA	7.21cA	7.36bcA
	Manured	7.79aA	7.62aA	7.61aA	7.23bA	7.38abA	7.50abA	7.29abA	7.28abA	7.37abA
Scanterbury	Unamended	7.19abA	7.39aA	7.20abA	6.92abcA	6.81bcA	6.84bcA	6.81bcA	6.68cB	6.72cB
	Manured	7.27aA	7.04abA	6.74bA	6.68bA	6.72bA	6.83abA	6.73bA	6.92abA	7.24aA
Osborne	Unamended	7.78aA	7.61aA	7.21bA	7.00bA	6.96bA	7.11bA	7.07bA	6.77bA	6.87bA
	Manured	7.60aA	7.31abA	6.87cA	6.67cA	6.67cA	6.69cA	6.72cA	6.79cA	7.08bcA

ANOVA	df	P > F		df	P > F
Soil	11	<0.0001	Soil *Time	88	<0.0001
Treatment	1	0.64	Treatment * Time	8	<0.0001
Time	8	<0.0001	Soil * Treatment * Time	88	<0.0001
Soil * Treatment	11	<0.0001	CV (%)		2

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.A; Table II. Changes in surface flood water pH over the flooding period (arithmetic means)

Soil series and treatment		1	7	14	21	28	35	42	49	56
				Days after flooding (Time)						
Newdale	Unamended	7.52abcA	7.51 abcA	7.45cA	7.65 abcA	7.77 abcA	8.03aA	8.01abA	7.58 abcA	7.85 abcA
	Manured	7.32cA	7.51 abcA	7.57 abcA	7.77 abcA	7.90abA	7.97aA	7.71 abcA	7.48bcA	7.87abA
Lakeland 1	Unamended	7.53bA	7.76abA	7.92abA	7.84abA	8.10aA	7.86abA	7.63abA	7.68abA	7.99abA
	Manured	7.64 abcA	7.46bcA	7.33cA	7.57bcA	7.77 abcA	7.91abA	7.91abA	7.91abA	8.09aA
Lakeland 2	Unamended	7.70bA	7.87abA	8.06abA	8.10abA	8.19abA	8.27aA	8.24aA	8.30aA	8.38aA
	Manured	7.60bA	7.84abA	7.77abA	7.88abA	7.94abA	8.03abA	7.95abA	7.94abA	8.17aA
Arborg	Unamended	7.72bA	8.10abA	8.12abA	8.16abA	8.19abA	8.10abA	8.12abA	7.97abA	8.29aA
	Manured	7.62cA	8.09abA	8.20abA	8.22aA	8.21aA	8.20aA	8.00 abcA	7.70bcA	8.21aA
Almasippi	Unamended	7.86bA	8.07abA	8.17abA	8.22abA	8.29abA	8.33abA	8.40abA	8.30abA	8.37aA
	Manured	7.92bA	8.11bA	8.25bA	8.26bA	8.29bA	8.34bA	8.31bA	8.41bA	8.45aA
Reinland	Unamended	7.84abA	7.72bA	8.03abA	8.08abA	8.21abA	8.19abA	8.26aA	8.24aA	8.32aA
	Manured	7.56bA	7.88abA	8.04abA	8.16aA	8.34aA	8.20aA	8.14aA	8.20aA	8.26aA
Niverville	Unamended	7.71aA	8.01aA	8.00aA	7.89aA	7.97aA	7.90aA	8.02aA	7.96aA	8.19aA
	Manured	7.62abA	7.68abA	7.48bA	7.63abA	7.58abA	7.77abA	7.78abA	7.66abA	8.01aA
Fyala	Unamended	7.69bA	7.92abA	8.01abA	7.94abA	7.95abA	8.09abA	8.06abA	8.20abA	8.25aA
	Manured	7.74aA	7.98aA	8.03aA	7.98aA	8.12aA	8.21aA	8.09aA	8.16aA	8.24aA
Sprague	Unamended	7.37cA	7.69bcA	7.75bcA	7.87bcA	7.99abA	8.12abA	8.12abA	8.23aA	8.40aA
	Manured	7.38cA	7.73bcA	7.77bcA	7.84bcA	8.01abA	8.09abA	7.96abA	7.93abA	8.30aA
Long Plain	Unamended	7.62bA	7.99abA	8.05abA	8.01abA	8.10abA	8.13abA	8.11abA	8.18aA	8.29aA
	Manured	7.59bA	7.93abA	7.90abA	7.97abA	8.11aA	8.08abA	8.10abAA	8.00abA	8.25aA
Scanterbury	Unamended	7.22cdA	7.52abA	7.00dA	7.50 abcA	7.63 abcA	7.69 abcA	7.70 abcA	7.74abA	7.98aA
	Manured	7.29abA	7.31aA	6.83bA	7.12abA	7.04abB	7.17abB	7.06abB	7.08abB	7.46aB
Osborne	Unamended	7.66bA	7.93abA	8.07abA	8.04abA	8.09abA	8.09abA	8.07abA	8.10abA	8.22aA
	Manured	7.54aA	7.47aA	7.63aA	7.60aA	7.57aA	7.63aAA	7.53aB	7.37aB	7.75aA

ANOVA	df	P > F				df	P > F
Soil	11	<0.0001		Soil *Time		88	<0.0001
Treatment	1	0.052		Treatment * Time		8	0.0029
Time	8	<0.0001		Soil * Treatment * Time		88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)			2

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.A; Table III. Changes in soil redox potential[†] over the flooding period

Soil series and treatment		Days after flooding (Time)								
		1	7	14	21	28	35	42	49	56
						mV				
Newdale	Unamended	336	224	109	54	-21	-18	-6	1	-18
	Manured	393	185	166	12	-55	-69	-49	-88	-90
Lakeland 1	Unamended	247	-7	-98	-88	-86	-87	-72	-88	-84
	Manured	267	132	23	-32	-36	-65	-53	-86	-88
Lakeland 2	Unamended	256	214	179	166	158	215	185	80	-19
	Manured	271	225	195	151	226	169	116	25	-43
Arborg	Unamended	278	119	-31	-59	-37	-24	-33	-41	-47
	Manured	262	206	179	20	-26	-65	-85	-61	-52
Almasippi	Unamended	308	201	105	-42	-60	-77	-131	-92	-93
	Manured	305	185	142	-41	-74	-64	-56	-65	-69
Reinland	Unamended	312	196	179	-21	-84	-85	-76	-73	-66
	Manured	424	200	148	-22	-87	-106	-86	-102	-95
Niverville	Unamended	280	116	33	6	-7	-16	-22	-29	-16
	Manured	249	44	-63	-50	-56	-52	-48	-53	-49
Fyala	Unamended	247	221	216	68	15	-33	-49	-51	-49
	Manured	270	99	123	93	-26	-124	-57	-119	-122
Sprague	Unamended	284	204	168	213	237	226	208	25	-51
	Manured	315	200	246	237	242	234	139	-5	-64
Long Plain	Unamended	351	224	96	58	-7	-36	-29	-64	-66
	Manured	287	197	205	34	-47	-66	-53	-47	-48
Scanterbury	Unamended	285	79	57	3	-15	-10	-26	-16	-14
	Manured	264	174	53	48	50	1	-37	-20	-26
Osborne	Unamended	281	151	121	105	85	64	43	27	22
	Manured	249	145	46	35	35	23	2	-2	-3

[†]Eh was measured only in one replicate

Appendix 3.B; Table I. Variation of dissolved reactive phosphorus concentration in soil pore water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)									Degree of change[§]
		1	7	14	21	28	35	42	49	56	
						mg L^{-1}					
Newdale	Unamended	0.44bB	0.50bB	0.56abB	0.38bB	0.38bB	0.67abB	0.79aB	0.81aB	0.69aB	1.8
	Manured	1.26abA	1.42abA	1.67aA	1.32abA	0.79cA	1.25abA	1.07bcA	0.88cA	0.93cA	1.3
Lakeland 1	Unamended	0.17dB	0.25cA	0.32cB	0.52bB	0.62bB	0.77abB	0.79abB	1.03aB	1.14aB	6.5
	Manured	0.59dA	1.01cA	1.05cA	1.28cA	1.45abcA	1.75abA	1.32bcA	1.65bcA	2.29aA	3.9
Lakeland 2	Unamended	1.51dA	2.16cA	2.53cA	2.79bcA	2.90bcA	3.15bcA	3.14bcA	4.09abA	5.79aA	5.8
	Manured	2.00eA	2.77cdA	3.45cdA	3.69cA	3.61cA	4.04bcA	4.57bcA	5.85bA	8.80aA	4.4
Arborg	Unamended	1.23eA	1.55cdA	1.70cdA	2.00cA	2.61bcA	3.32abA	3.73aA	4.38aA	4.71aA	3.8
	Manured	1.74fA	2.34deA	2.65deA	2.79cdA	3.15cdA	3.93bcA	4.65abA	5.77aA	6.29aA	3.6
Almasippi	Unamended	0.11eB	0.22cdB	0.26bcdB	0.40aB	0.48aB	0.47aB	0.18dB	0.38abB	0.31abcB	4.3
	Manured	0.43dA	0.79bcA	1.07bA	1.39abA	1.64aA	1.57aA	1.06bcA	1.25abA	1.26abA	3.9
Reinland	Unamended	0.43dA	0.53cdB	0.61cdB	0.67cB	0.64cdB	0.61cdB	0.61cdB	1.07bB	1.66aB	3.9
	Manured	1.46cA	1.89cA	2.21bcA	1.84cA	2.24bcA	3.62aA	3.19abA	3.92aA	4.25aA	2.9
Niverville	Unamended	0.40gB	0.61fB	0.86eB	1.22dB	1.58cdB	3.34aB	2.17bcB	2.49abB	2.74abB	6.8
	Manured	0.83dA	1.60cA	2.45bA	3.92aA	4.77aA	5.19aA	5.14aA	4.93aA	5.07aA	6.2
Fyala	Unamended	0.58gB	0.98fB	1.18efB	1.47deB	1.92cB	2.82bcB	3.45abB	4.55aA	5.45aA	9.4
	Manured	0.84eA	1.39dA	1.75cdA	2.08cA	2.47cA	3.41bA	4.30bA	5.99aA	6.96aA	8.3
Sprague	Unamended	0.13fB	0.25eB	0.28deB	0.37dB	0.37deB	0.43cdB	0.44cdB	0.70bB	1.20aB	9.0
	Manured	0.65fA	1.03eA	1.21deA	1.26deA	1.47deA	1.74dA	2.40cA	4.08bA	6.16aA	9.9
Long Plain	Unamended	0.19eB	0.29dB	0.34cdB	0.36cdB	0.48cB	0.83bB	1.05bB	1.47aB	1.79aB	9.1
	Manured	0.88dA	1.04cdA	1.25cdA	1.47cA	2.64bA	3.65aA	3.69aA	3.84aA	4.26aA	4.9
Scanterbury	Unamended	0.13dA	0.16cdA	0.15dA	0.23cA	0.23cA	0.27bcA	0.30bcA	0.44aA	0.50aA	3.7
	Manured	0.31fA	0.40efA	0.47deA	0.78abcA	0.92abA	0.92abA	0.67bcdA	0.54cdeA	0.43efA	3.0
Osborne	Unamended	0.16dB	0.24bcB	0.24cB	0.30abcB	0.28bcB	0.28bcB	0.29bcB	0.39abB	0.42aB	2.6
	Manured	0.36dA	0.56cA	0.67cA	1.08bA	1.42abA	1.62aA	1.41abA	1.37abA	1.36abA	4.5

ANOVA	df	$P > F$				df	$P > F$
Soil	11	<0.0001		Soil *Time		88	<0.0001
Treatment	1	<0.0005		Treatment * Time		8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time		88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)		13	

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡]Mean values followed by the same uppercase letter within a column are not significantly different
[§]Degree of change = Maximuc DRP concentration / DRP concentration at day 1 of flooding

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Appendix 3.B; Table II. Variation of dissolved reactive phosphorus concentration in surface flood water over the flooding period (geometric means).

Soil series and treatment		1	7	14	21	28	35	42	49	56	Degree of change[§]
						mg L^{-1}					
Newdale	Unamended	0.13b[†]B	0.25aB	0.29aB	0.34aA	0.34aA	0.44aA	0.28aA	0.25abB	0.24abA	3.7
	Manured	0.32bA	0.71aA	0.69aA	0.64abA	0.64abA	0.49abA	0.37abA	0.54abA	0.41abA	2.2
Lakeland 1	Unamended	0.11abB	0.10bB	0.14abB	0.20abB	0.20abB	0.18abB	0.18abB	0.21abB	0.29aB	2.8
	Manured	0.34bA	0.52abA	0.63abA	0.76aA	0.85aA	0.91aA	0.90aA	0.92aA	0.92aA	2.7
Lakeland 2	Unamended	0.36cA	1.18abA	1.74abA	2.00abA	2.30abA	2.76aA	2.33abA	2.31abA	2.60aA	7.2
	Manured	0.53cA	1.75bA	2.78abA	3.89aA	4.52aA	4.64aA	3.83aA	3.59abA	3.89aA	8.1
Arborg	Unamended	0.34dB	0.80cA	1.05cA	1.20cA	1.34abcA	1.47abcA	1.53abcA	1.85abA	2.39aA	7.0
	Manured	0.45cA	1.24bA	1.60abA	1.81abA	2.17abA	2.31abA	2.38abA	2.71aA	2.98aA	6.6
Almasippi	Unamended	0.03cB	0.08bB	0.10abB	0.15abB	0.14abB	0.17aB	0.15abB	0.17aB	0.18aB	5.5
	Manured	0.10cA	0.33bcA	0.54abA	0.67aA	0.69aA	0.70aA	0.62abA	0.60abA	0.66abA	7.3
Reinland	Unamended	0.07cB	0.21bB	0.26bB	0.32abB	0.36abB	0.37abB	0.28abB	0.41abB	0.54aB	8.0
	Manured	0.24dA	0.64cA	0.88bcA	1.18bcA	1.51bA	1.79bA	1.89abA	1.82bA	3.65aA	15.2
Niverville	Unamended	0.20cB	0.30bcB	0.40bB	0.52abB	0.64abB	0.70abB	0.72abB	0.84aB	0.97aB	4.9
	Manured	0.53cA	1.02bA	1.57abA	2.25aA	2.52aA	2.55aA	2.17aA	2.50aA	2.21aA	4.2
Fyala	Unamended	0.34cA	0.61bA	0.90bB	1.19abA	1.69abA	2.19aA	2.14aA	1.89aA	1.99aA	6.3
	Manured	0.58cA	1.24bA	1.87abA	1.98abA	2.09abA	2.50abA	2.74aA	2.84aA	3.03aA	5.2
Sprague	Unamended	0.08cB	0.15cB	0.15cB	0.21bcB	0.21bcB	0.24abB	0.26abB	0.29abB	0.33aB	4.1
	Manured	0.18dA	0.52bcA	0.61bcA	0.74bA	0.83bA	0.99abA	1.03abA	1.46aA	1.95aA	10.8
Long Plain	Unamended	0.06dB	0.16cB	0.20cB	0.25bcB	0.28bcB	0.48abB	0.36abB	0.49abB	0.63aB	10.5
	Manured	0.28cA	0.58bA	1.01abA	1.43aA	1.78aA	2.01aA	1.84aA	1.97aA	1.95aA	7.0
Scanterbury	Unamended	0.18aA	0.10bB	0.15abB	0.12abB	0.11abB	0.18abA	0.11abA	0.14abA	0.16abA	0.8
	Manured	0.34aA	0.31abA	0.35aA	0.29abA	0.27abA	0.34aA	0.13cA	0.21bcA	0.21bcA	0.6
Osborne	Unamended	0.13aB	0.18aB	0.17aB	0.19aA	0.19aA	0.19aA	0.16aA	0.18aA	0.20aA	1.5
	Manured	0.33abA	0.39abA	0.44aA	0.39abA	0.35abA	0.23abcA	0.19bcA	0.15cA	0.13cA	1.3

ANOVA	df	P > F					df	P > F
Soil	11	<0.0001		Soil *Time			88	<0.0001
Treatment	1	<0.0001		Treatment * Time			8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time			88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)				19

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different
[§]Degree of change = Maximuc DRP concentration / DRP concentration at day 1 of flooding

Appendix 3.C; Table I. Variation of dissolved Ca concentration in soil pore water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}				
Newdale	Unamended	65.7abB	67.3abB	38.8bB	28.3bB	43.1bA	66.6abA	67.8abA	50.7bA	157.9aA
	Manured	177.2aA	173.3aA	136.4abA	69.0bcA	42.4dA	59.8bcdA	39.0dA	35.1dA	138.9abA
Lakeland 1	Unamended	41.0cdA	33.7dA	32.4dA	42.1bcdA	47.4bcdA	100.6abA	157.5aA	94.7abcA	178.3aA
	Manured	232.4aA	52.8cA	44.3cA	60.1cA	46.1cA	158.3abA	91.2bcA	48.8cA	183.3abA
Lakeland 2	Unamended	747.7abA	724.6aA	518.4abcA	343.9abcA	323.8abcA	308.8abcA	233.2cA	291.7abcA	354.3abcA
	Manured	833.6aA	753.0abA	658.9abcA	329.1bcdA	321.1bcdA	263.3dA	280.3cdA	220.1dA	392.4abcdA
Arborg	Unamended	35.8eB	68.4bcdeA	55.8cdeA	39.5deA	46.9deA	112.5abcA	138.7abA	73.7bcdeA	202.1aA
	Manured	245.2aA	129.7abcdeA	87.3bcdeA	72.9cdeA	72.9cdeA	176.0abcA	192.5abA	56.3eA	266.5aA
Almasippi	Unamended	54.3bB	84.7abA	71.8abA	62.0abA	61.0abA	89.4abA	60.4abA	58.5bA	140.3aA
	Manured	90.1aA	97.4aA	85.2aA	92.2aA	90.2aA	110.7aA	116.0aA	103.8aA	167.4aA
Reinland	Unamended	70.9bA	88.4bA	58.5bA	53.6bA	71.1bA	99.8abA	87.0bA	69.5bA	219.8aA
	Manured	127.2abcA	181.1abA	90.9bcA	104.9bcA	58.2cA	186.9abA	101.1bcA	161.1abA	274.8aA
Niverville	Unamended	50.9bcB	37.8cA	44.8bcA	42.7bcA	42.2cA	80.3abcA	102.8abA	44.5bcA	187.3aA
	Manured	175.4abA	61.0eA	70.1cdeA	76.3bcdA	67.7deA	158.2abcdA	165.1abcA	96.4abcdeA	220.4aA
Fyala	Unamended	259.8aA	186.1abA	134.6abcA	107.3abcA	63.9cA	226.2abA	165.6abA	99.3bcA	325.9aA
	Manured	417.5aA	323.9abA	189.0abcA	158.8bcA	37.8eA	187.3abcA	208.9abcA	112.5cdA	335.2abA
Sprague	Unamended	616.7aA	484.5abA	400.9abcA	259.6abcA	197.6cdA	169.8cdA	119.0deA	79.9eA	208.9bcdA
	Manured	589.4aA	413.2abA	314.2abcA	183.2bcdA	103.0dA	161.6cdA	121.3dA	78.0dA	300.5abcA
Long Plain	Unamended	73.8abcA	104.5abA	56.4bcA	42.7cA	83.3abcA	113.4abA	130.6abA	145.8aA	165.2aA
	Manured	85.1cA	146.4abcA	91.0cA	98.2bcA	137.2abcA	191.6aabcA	235.2abA	115.0bcA	290.6aA
Scanterbury	Unamended	51.1abcB	26.6bcA	25.2cA	23.4cA	57.0abA	51.2abcA	37.7bcA	59.5abA	118.6aA
	Manured	163.4aA	39.8bA	46.5bA	41.1bA	48.2bA	74.6abA	71.6abA	38.9bA	169.8aA
Osborne	Unamended	50.2abcB	25.6cdeA	16.3deA	13.2eA	63.9abA	45.6abcA	49.6abcA	39.0bcdA	96.3aA
	Manured	166.5aA	33.9cdA	32.0cdA	25.1dA	51.0bcdA	91.2abA	64.5bcA	28.9cdA	120.1abA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001	Soil *Time					88	<0.0001
Treatment	1	0.092	Treatment * Time					8	0.0004
Time	8	0.155	Soil * Treatment * Time					88	0.013
Soil * Treatment	11	<0.0001	CV (%)						167

†Mean values followed by the same lowercase letter within a row are not significantly different

‡ Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table II. Variation of dissolved Ca concentration in surface flood water over the flooding period (arithmetic means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}				
Newdale	Unamended	1.53c[†]A[‡]	14.1bcA	17.5bcA	22.0bcA	35.3abA	41.3abA	49.4aA	36.6abA	45.2abA
	Manured	2.89cA	20.1bcA	25.1abcA	19.7bcA	40.9abA	45.6abA	44.5abA	36.4abA	55.0aA
Lakeland 1	Unamended	8.83dA	18.3cdA	18.1cdA	18.6bcdA	27.7bcdA	36.1bcdA	50.4abcA	49.3abcA	73.5aA
	Manured	9.82dA	29.6cdA	34.1cdA	34.1cdA	36.4cdA	50.8bcA	32.1cdA	78.6abA	97.9aA
Lakeland 2	Unamended	6.56fA	36.5efA	65.1deA	68.2deA	73.8deA	107.9bcA	96.1bcdA	117.1abA	149.3aA
	Manured	7.18hA	26.9ghA	72.5efA	57.8efgG	67.1efA	87.7deA	99.4cdA	128.1bcA	161.3aA
Arborg	Unamended	8.60dB	22.8cdA	39.2bcdA	39.0bcdA	66.4bA	69.0bA	68.2bA	105.6aA	125.7aA
	Manured	23.7cA	43.7bcA	52.8bcA	43.1bcA	59.4bA	65.8bA	61.2bA	110.5bA	127.1bA
Almasippi	Unamended	5.16deA	16.1cdeA	31.6abcdeA	33.3abcdA	26.5bcdeA	36.6abcdA	44.7abcA	56.2abA	59.3aA
	Manured	5.06deA	19.5cdeA	38.4bcA	48.8bA	0.09eA	64.3abA	57.3abA	79.1aA	83.3aA
Reinland	Unamended	3.34dA	18.5cdA	22.8cdA	24.1cdA	39.4cB	48.5bcA	48.7bcA	47.5bcA	81.8aB
	Manured	4.45dA	19.6cdA	24.3cdA	35.6cdA	77.2bA	72.6bA	79.6bA	101.5abA	130.2aA
Niverville	Unamended	6.74eA	20.1cdeA	24.9bcdeA	23.8bcdeA	32.4bcdeA	43.0bcdA	44.2bcA	48.8bcA	83.2aA
	Manured	11.2dA	23.9bcdA	36.0bcdA	38.0bcdA	52.4bcA	57.1bcA	75.2abcA	78.7abA	94.6aA
Fyala	Unamended	7.66iA	37.9fiA	77.4deA	65.3efA	82.0deA	126.5bcA	89.1deA	109.7bcdA	161.6aA
	Manured	9.12fA	39.6fA	85.0deA	74.9deA	81.2deA	82.6deA	98.4cdA	138.4bA	171.0aA
Sprague	Unamended	3.27eA	12.5deA	30.2bcdeA	38.1bcdA	48.0bcA	62.4abA	48.8bcA	57.2abcA	97.4aA
	Manured	3.50eA	15.4deA	29.7bcdA	28.8bcdeA	58.9bcA	59.2abcA	49.6bcA	87.3abA	106.7aA
Long Plain	Unamended	5.56fA	12.0efA	23.7cdefA	21.9defA	41.8bcdeA	43.4bcdeB	47.9bcdB	70.2abB	81.7aB
	Manured	7.28fA	15.2efA	25.9defA	33.2defA	55.2bcdA	76.1abcA	77.9abcA	104.3abA	123.0aA
Scanterbury	Unamended	2.49cA	9.35bcA	21.5bcA	13.4bcA	32.1bcA	35.9abA	32.9bcA	41.0abA	58.9aA
	Manured	12.4cA	24.1cA	21.0cA	18.7cA	33.3bcA	31.8bcA	33.8bcA	59.3abA	82.8aA
Osborne	Unamended	3.40bA	15.3abA	16.3abA	13.4abA	27.8abA	28.6abA	34.9abA	25.9abA	41.2aA
	Manured	9.46bA	19.9bA	31.6bA	17.2bA	30.1bA	40.7abA	25.2bA	37.3bA	70.5aA

ANOVA	df	P > F							df	P > F
Soil	11	<0.0001		Soil *Time					88	<0.0001
Treatment	1	<0.0001		Treatment * Time					8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time					88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)						17

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table III. Variation of dissolved Mg concentration in soil pore water over the flooding period (arithmetic means).

Soil series and treatment		1	7	14	21	28	35	42	49	56
		Time (Days after flooding)								
		mg L^{-1}								
Newdale	Unamended	29.5f†A	51.4efB	52.9defB	60.3cdefB	82.8abcdefA	105.9abcdeA	123.5abA	135.4abA	159.7aA
	Manured	73.9dA	111.9abcdA	117.9bcdA	107.5cdA	119.8bcdA	144.0abcA	153.2abcA	165.5abA	191.3aA
Lakeland 1	Unamended	37.8eB	62.9deB	90.3cdeB	103.5bcdB	130.6abcB	145.2abcA	146.6abA	151.7abA	162.7aA
	Manured	127.2aA	121.2abA	164.2aA	162.6aA	208.7aA	199.4abcA	191.0abcA	178.2cA	202.4bcA
Lakeland 2	Unamended	283.6aA	326.7aA	183.0abB	150.1bcA	141.6cA	158.4cA	126.4cA	142.3cA	137.5bA
	Manured	339.0aA	326.7aA	283.3aA	227.5bA	213.0bA	213.8bA	189.5bA	196.8bA	201.6bA
Arborg	Unamended	66.2cB	78.1bcB	84.4bcA	106.8abcA	154.6aA	127.8abA	140.7aA	148.3aA	154.7aA
	Manured	183.5aA	167.9aA	139.9aA	149.1aA	163.6aA	162.1aA	168.1aA	171.3aA	188.4aA
Almasippi	Unamended	79.8cB	128.4abB	125.0bcA	131.0abB	163.7abB	153.9abA	150.9abA	160.6abA	180.9aA
	Manured	146.0cA	200.2abA	176.6bcA	197.5abcA	237.8aA	201.8abA	203.0abA	220.3abA	224.7abA
Reinland	Unamended	23.1A	43.2aB	35.2aA	36.2aB	45.7aB	49.2aB	52.6aB	63.3aB	71.7aA
	Manured	50.8bA	101.6aA	82.9abA	93.9abA	110.9aA	119.1aA	114.6aA	124.2aA	122.0aA
Niverville	Unamended	45.2bB	78.5aA	94.1aA	86.2aA	101.3aA	108.7aA	102.5aA	104.1aA	117.5aA
	Manured	118.1aA	126.7aA	132.0aA	123.1aA	153.2aA	151.6aA	138.9aA	146.1aA	149.7aA
Fyala	Unamended	113.4cdB	106.2cd B	98.8dB	112.1cdA	124.3bcdA	149.7abcdA	154.7bcA	174.0abA	197.1aA
	Manured	174.1abcA	173.9abcA	158.4bcA	158.4bcA	127.5cA	169.5abcA	184.5abA	200.8abA	216.0aA
Sprague	Unamended	215.9aA	193.8abA	180.5abcA	144.6bcdA	132.0cdA	120.4cdA	102.7dA	96.5dA	113.0dA
	Manured	228.7aA	195.5abA	173.7abcA	148.5bcdA	137.5cdA	122.9cA	118.7cA	128.3cdA	145.5bcdA
Long Plain	Unamended	26.1aB	50.0aA	44.6aA	47.7aA	58.3aA	63.2aA	60.6aA	66.1aA	69.7aB
	Manured	38.6bA	92.1aA	107.3aA	95.3aA	110.4aA	111.6aA	104.5aA	107.1aA	115.4aA
Scanterbury	Unamended	22.0aB	21.5aB	28.9aB	34.3aB	52.4aB	57.8aB	56.3aB	63.2aB	72.4aB
	Manured	85.2bA	85.0abA	98.3abA	104.5abA	124.3abA	130.1abA	129.8abA	134.3abA	148.7aA
Osborne	Unamended	35.5aB	40.9aB	50.1aB	50.5aB	184.2bB	62.9aB	59.2aB	64.5aB	65.2aB
	Manured	110.5aA	109.5aA	113.1aA	114.3aA	104.7aA	137.6aA	133.4aA	136.6aA	145.0aA

ANOVA	df	$P > F$							df	$P > F$
Soil	11	<0.0001		Soil *Time					88	<0.0001
Treatment	1	<0.0001		Treatment * Time					8	0.146
Time	8	<0.0001		Soil * Treatment * Time					88	<0.0001
Soil * Treatment	11	0.0006		CV (%)						20

†Mean values followed by the same lowercase letter within a row are not significantly different

‡ Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table IV. Variation of dissolved Mg concentration in surface flood water over the flooding period (arithmetic means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}					
Newdale	Unamended	0.51f†A	5.53fA	11.4efA	17.5deB	25.3cdB	33.3bcB	35.8bcB	45.3abA	50.8aA
	Manured	0.95dA	8.34dA	20.5cA	26.8cA	41.2bA	49.7abA	56.1aA	57.4aA	57.9aA
Lakeland 1	Unamended	3.47eB	14.8dA	30.5cB	37.2cB	53.5bB	54.0abB	60.7abB	68.7aB	67.1aB
	Manured	3.83fA	24.9eA	45.6dA	54.7cdA	67.9bA	74.3abA	77.5abA	83.5aA	84.9aA
Lakeland 2	Unamended	2.48fA	16.3eA	29.4dA	34.8cdA	43.5cA	56.2abA	59.9abA	66.9aA	66.8aA
	Manured	2.72fA	16.3eA	33.9dA	41.3cdA	49.2cA	61.2bA	66.5abA	71.3aA	75.45aA
Arborg	Unamended	4.33eA	15.0dB	29.6cB	35.8cA	32.6cB	49.9bB	49.6bB	58.9abB	64.0aB
	Manured	12.7eA	31.4dA	42.9cA	48.1cA	51.9bcA	64.2abA	63.4bA	74.1abA	77.2aA
Almasippi	Unamended	3.62gA	16.1fA	32.4deA	42.0cdA	30.4eB	51.2bcB	56.1abB	61.7bB	64.8aB
	Manured	3.46gA	18.9fA	39.4eA	54.5dA	0.04gA	69.6cA	73.8bcA	84.6abA	90.5aA
Reinland	Unamended	0.94dA	5.38cdA	9.3bcdA	11.4abcdB	14.5abcB	17.1abcB	17.1abcB	20.1abcB	24.3aB
	Manured	1.34eA	6.73deA	15.9cdA	22.5bcA	30.8abA	34.1abA	36.0aA	40.4aA	42.9aA
Niverville	Unamended	3.03eA	14.1dA	26.7cB	31.9bcB	37.1abcB	41.2abB	44.9aB	47.5aB	49.7aB
	Manured	5.45dA	22.3cA	43.2bA	52.9bA	52.7bA	63.7abA	62.9abA	67.8aA	66.7aA
Fyala	Unamended	2.88eA	14.9dA	32.1cA	37.5cB	37.1cA	61.4bA	61.2bA	72.1abA	77.1aA
	Manured	3.50fA	18.6eA	40.5dA	52.7cA	35.4dA	71.2abA	60.8bcA	76.8aA	72.7abA
Sprague	Unamended	1.06cA	7.00cA	18.5bA	25.6abA	33.0aA	34.5aA	36.1aA	36.5aA	38.0aA
	Manured	1.22fA	8.72fA	17.7efA	22.5deA	31.9bcdA	36.0abA	37.4abA	42.6abA	46.7aA
Long Plain	Unamended	1.20dA	6.48bcdA	12.0abcdA	14.1abcA	17.3abA	18.8abB	21.1aB	23.3aB	24.4aB
	Manured	1.69eA	8.86deA	17.9cdA	24.6bcA	28.9abcA	32.7abA	36.1abA	38.4aA	39.4aA
Scanterbury	Unamended	0.92dA	3.85dB	9.2cB	11.9bcB	17.4abcB	20.1abcB	22.9abB	25.9aB	27.9aB
	Manured	4.68eA	18.8dA	30.3cA	35.7cA	49.5bA	51.2abA	53.7abA	61.4abA	63.1aA
Osborne	Unamended	1.96dA	9.6cdB	18.0bcB	20.8abcB	19.1abcB	28.0abB	28.6abB	29.9abB	31.4aB
	Manured	5.63eA	23.8dA	41.6cA	45.8bcA	40.9cA	59.3aA	58.1abA	62.6aA	64.3aA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001		Soil *Time				88	<0.0001
Treatment	1	<0.0001		Treatment * Time				8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)					53

†Mean values followed by the same lowercase letter within a row are not significantly different
‡ Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table V. Variation of dissolved Fe concentration in soil pore water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
		mg L^{-1}								
Newdale	Unamended	0.008c[†]A[‡]	0.006cA	0.008cA	0.026bcA	0.101abA	0.134aA	0.197aA	0.147abA	0.172aA
	Manured	0.009bA	0.007cA	0.007bA	0.012bA	0.135aA	0.303aA	0.252aA	0.137aA	0.435aA
Lakeland 1	Unamended	0.015bcA	0.011bA	0.025bcA	0.064abA	0.112abA	0.167aA	0.210aA	0.204aA	0.273aA
	Manured	0.015cdA	0.012dA	0.059bcA	0.090abA	0.190abA	0.320aA	0.216abA	0.214abA	0.418aA
Lakeland 2	Unamended	0.033aA	0.054 aA	0.034 aA	0.032 aA	0.028aA	0.041 aA	0.037 aA	0.148aA	0.173 aA
	Manured	0.037cA	0.038cA	0.051bcA	0.033cA	0.037cA	0.048bcA	0.138abcA	0.299aA	0.230abA
Arborg	Unamended	0.004eA	0.008cdeA	0.017cdeA	0.036bcdA	0.766aB	0.077bcA	0.103bA	0.123bA	0.135bA
	Manured	0.008cdA	0.007cA	0.012cdA	0.028bcdA	0.084cA	0.098abA	0.191aA	0.177aA	0.196aA
Almasippi	Unamended	0.009deA	0.009e A	0.020cdeA	0.044bcdA	0.158abA	0.186abA	0.198abA	0.276abA	0.417aA
	Manured	0.011cA	0.011cA	0.013cA	0.070bA	0.235abA	0.233abA	0.356abA	0.181abA	0.494aA
Reinland	Unamended	0.013bcA	0.007cdA	0.007eA	0.008cA	0.022bcA	0.041abA	0.045abA	0.060abA	0.151aA
	Manured	0.011bA	0.010bA	0.009bA	0.027abA	0.100aA	0.087aA	0.112aA	0.119aA	0.130aA
Niverville	Unamended	0.006bA	0.006bA	0.022abB	0.024abB	0.049aA	0.049aA	0.058aA	0.089aA	0.102aA
	Manured	0.008cA	0.006cA	0.055bA	0.179abA	0.170abA	0.213abA	0.217abA	0.282aA	0.517aA
Fyala	Unamended	0.068bcA	0.072bcA	0.046cA	0.077bcA	0.054cA	0.447aA	0.537aA	0.625aA	0.688aA
	Manured	0.046cA	0.052cA	0.054cA	0.054cA	0.103bcA	0.344abA	0.603aA	0.591aA	0.521aA
Sprague	Unamended	0.011cA	0.014cA	0.016cbcA	0.014cA	0.015bcA	0.016cdA	0.020bcB	0.069bB	0.355aA
	Manured	0.019bA	0.019bA	0.021bA	0.024bA	0.021bA	0.042bA	0.226aA	0.365aA	0.569aA
Long Plain	Unamended	0.007cdA	0.007cdA	0.005dA	0.017bcA	0.033abcA	0.074abA	0.105aA	0.122aA	0.152aA
	Manured	0.016cdA	0.009dA	0.013dA	0.034bcdA	0.101abA	0.123abA	0.145abA	0.179aA	0.171aA
Scanterbury	Unamended	0.011bcA	0.007cA	0.008bcB	0.010bcB	0.036abB	0.054aB	0.080aB	0.126aA	0.115aB
	Manured	0.013cA	0.008cA	0.133bA	0.418abA	1.348aA	1.457aA	1.259aA	0.397abA	0.949aA
Osborne	Unamended	0.006cdA	0.004dA	0.007cdB	0.008cdB	0.224aB	0.026bcB	0.027bcB	0.022cbcB	0.027bcB
	Manured	0.006deA	0.004eA	0.145bcA	0.371abA	0.043cA	1.108aA	0.325abA	0.169bcA	0.203bcA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001		Soil *Time				88	<0.0001
Treatment	1	<0.0001		Treatment * Time				8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)					48

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table VI. Variation of dissolved Fe concentration in surface flood water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}				
Newdale	Unamended	0.011ab†A‡	0.013abA	0.013abA	0.005bcA	0.004bcA	0.001cB	0.001cB	0.010bA	0.049aA
	Manured	0.029abA	0.016abA	0.013abA	0.010bA	0.019abA	0.023abA	0.026abA	0.049abA	0.066aA
Lakeland 1	Unamended	0.010cdA	0.005dA	0.005dB	0.005dB	0.007dB	0.014bcdB	0.046abcA	0.073bA	0.114aA
	Manured	0.015bcA	0.011cA	0.029abcA	0.048abcA	0.059abA	0.078abA	0.067abA	0.087aA	0.113aA
Lakeland 2	Unamended	0.013aA	0.016aA	0.017aA	0.013aA	0.013aA	0.011aA	0.008aA	0.008aA	0.011aA
	Manured	0.021aA	0.010aA	0.029aA	0.011aA	0.011aA	0.010aA	0.011aA	0.012aA	0.018aA
Arborg	Unamended	0.007aA	0.004aA	0.005aA	0.004aA	0.003aA	0.002aA	0.002aA	0.003aA	0.004aA
	Manured	0.004abcA	0.004abcA	0.004abcA	0.003abcA	0.002abcA	0.001cA	0.002bcA	0.009aA	0.009aA
Almasippi	Unamended	0.004aA	0.006aA	0.004aA	0.003aA	0.007aA	0.003aA	0.004aA	0.005aB	0.005aB
	Manured	0.005cA	0.006bcA	0.007abcA	0.006cA	0.012abcA	0.007cA	0.006cA	0.034abA	0.037aA
Reinland	Unamended	0.006aA	0.007aA	0.007aA	0.005aA	0.005aA	0.003aA	0.003aB	0.002aB	0.002aB
	Manured	0.016aA	0.012aA	0.010aA	0.008aA	0.009aA	0.007aA	0.018aA	0.018aA	0.017aA
Niverville	Unamended	0.003aA	0.007aA	0.003aA	0.003aA	0.003aA	0.002aA	0.002aA	0.000bB	0.004aA
	Manured	0.013aA	0.009aA	0.013aA	0.010aA	0.009aA	0.010aA	0.010aA	0.013aA	0.018aA
Fyala	Unamended	0.033bcA	0.033bcA	0.032bcA	0.023cA	0.023cA	0.050abcA	0.100abcA	0.121abA	0.212aA
	ManuredA	0.056abA	0.031abA	0.030abA	0.028bA	0.045abA	0.069abA	0.111abA	0.159aA	0.138abA
Sprague	Unamended	0.009aA	0.012aA	0.010aA	0.007aA	0.008aA	0.007aA	0.006aA	0.006aA	0.008aA
	Manured	0.012aA	0.017aA	0.013aA	0.011aA	0.010aA	0.011aA	0.007aA	0.010aA	0.025aA
Long Plain	Unamended	0.004aA	0.004aA	0.005aA	0.004aA	0.005aA	0.003aA	0.005aA	0.002aA	0.003aA
	Manured	0.007aA	0.007aA	0.012aA	0.010aA	0.008aA	0.011aA	0.012aA	0.010aA	0.011aA
Scanterbury	Unamended	0.010abA	0.008abcA	0.015aA	0.006abcA	0.005abcB	0.002bcB	0.002cB	0.004abcB	0.002cB
	Manured	0.019bA	0.010bA	0.018bA	0.018bA	0.034abA	0.025abA	0.028abA	0.051abA	0.127aA
Osborne	Unamended	0.003aA	0.003aA	0.004aA	0.004aA	0.006aA	0.001bB	0.001bB	0.000bB	0.0003bB
	Manured	0.011aA	0.008aA	0.014aA	0.010aA	0.013aA	0.012aA	0.017aA	0.013aA	0.025aA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001		Soil *Time				88	<0.0001
Treatment	1	<0.0001		Treatment * Time				8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)					46

†Mean values followed by the same lowercase letter within a row are not significantly different

‡ Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

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Appendix 3.C; Table VII. Variation of dissolved Mn concentration in soil pore water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}					
Newdale	Unamended	0.0033d[†]A[‡]	0.0621bcA	0.0262cB	0.0720bcA	0.1288bcA	0.4793abA	0.3070abA	0.3030abA	2.3057aA
	Manured	0.0104dA	0.4152abA	0.3610abcA	0.0886bcdA	0.0217dA	0.0761bcdA	0.0651bcdA	0.0360cdA	0.9726aA
Lakeland 1	Unamended	0.0031cA	0.0198cA	0.0169cA	0.0492bcA	0.0194cA	0.2654abA	0.6059aA	0.2694abA	0.7547aA
	Manured	0.0085cA	0.0377bcA	0.0116cA	0.0676abcA	0.0085cA	0.3168abA	0.1969abA	0.0713abcA	0.6554aA
Lakeland 2	Unamended	0.0189bA	0.2687aA	0.4834aA	0.6274aA	0.4266aA	0.7940aA	0.6923aA	0.9073aA	0.5271aA
	Manured	0.0248bA	0.3322aA	0.6134aA	0.7072aA	0.3582aA	0.7355aA	0.9913aA	0.6099aA	0.5623aA
Arborg	Unamended	0.0012eA	0.0161dA	0.0448bcA	0.0410cdA	0.0206dA	0.3726abcA	0.4569abA	0.1027abcA	0.8548aA
	Manured	0.0098bA	0.0146bA	0.0372bA	0.0289bA	0.0140bA	0.3917aA	0.6755aA	0.1297abA	1.1476aA
Almasippi	Unamended	0.0094bA	0.1599aA	0.2419aA	0.1316aA	0.0823abA	0.1967aA	0.1217aA	0.0953abA	0.6524aA
	Manured	0.0164bA	0.4175aA	0.3224aA	0.4281aA	0.1178abA	0.3412aA	0.2356aA	0.2998aA	0.6644aA
Reinland	Unamended	0.0033dA	0.0810bcA	0.0475cA	0.0904bcA	0.2740bcA	0.5658abA	0.4618abcA	0.3532bcA	3.6781aA
	Manured	0.0077eA	0.3811abcA	0.0854cdA	0.2597bcdA	0.0426deA	1.7923aA	0.4047abcdA	0.6672abcA	2.9236aA
Niverville	Unamended	0.0021eA	0.0374bcdA	0.1226abcA	0.1361abcA	0.0197cdeA	0.1051bcA	0.3266abA	0.0704bcA	1.2253aA
	Manured	0.0058dA	0.0448bcdA	0.1250abcA	0.1217abcA	0.0244cdA	0.4662abA	0.8610aA	0.1762abcA	1.1921aA
Fyala	Unamended	0.0093bA	0.0674abA	0.0579abA	0.0640abA	0.0796abA	0.1813abA	0.1527aA	0.1289aA	0.3745aA
	Manured	0.0083cA	0.0883abA	0.1895aA	0.1453aA	0.0092bcA	0.2656aA	0.2571aA	0.2528aA	0.3152aA
Sprague	Unamended	0.0109cA	0.5359abA	0.8102aA	0.2667abA	0.0849abcA	0.2039abA	0.1096abcA	0.0674bcA	0.4717abA
	Manured	0.0284cA	0.7498abA	0.6849abA	0.3656abA	0.0148cA	0.2571abcA	0.1174bcA	0.1427abcdA	1.2315aA
Long Plain	Unamended	0.0019dA	0.0620abcA	0.0075cdA	0.0271cA	0.0443bcA	0.4539aA	0.3914abA	0.4342abA	0.5875aA
	Manured	0.0040cA	0.1972abA	0.0467bA	0.1398abA	0.2937abA	0.8642aA	1.0575aA	0.3029abA	0.9812aA
Scanterbury	Unamended	0.0010dA	0.0017cdA	0.0061cdA	0.0123bcA	0.1145aA	0.1413aA	0.1279abA	0.3137aA	1.1746aA
	Manured	0.0059cA	0.0078cA	0.0502bcA	0.0505bcA	0.0508bcA	0.3765abA	0.2390abA	0.0646bA	1.7346aA
Osborne	Unamended	0.0013dA	0.0081cdA	0.0077cdA	0.0047cdA	0.0356bcA	0.1367abA	0.1832abA	0.1194abA	0.6413aA
	Manured	0.0045cA	0.0039cA	0.0122cA	0.0140bcA	0.0376bcA	0.4530aA	0.3267abA	0.0357bcA	0.6018aA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001		Soil *Time				88	<0.0001
Treatment	1	<0.0001		Treatment * Time				8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	0.022		CV (%)					94

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table VIII. Variation of dissolved Mn concentration in surface flood water over the flooding period (geometric means).

Soil series and treatment		1	7	14	21	28	35	42	49	56
						mg L^{-1}				
Newdale	Unamended	0.0003b[†]A[‡]	0.000bA	0.0007bA	0.0009bA	0.0024bB	0.0051bB	0.1001aA	0.3481aA	0.8304aA
	Manured	0.0002cA	0.0036bcA	0.0077bcA	0.0302abA	0.2192abA	0.3463aA	0.3314abA	0.3278abA	0.7923aA
Lakeland 1	Unamended	0.0007cA	0.0007cB	0.0005cB	0.0035bcB	0.0082abcA	0.0437abA	0.1614aA	0.1000abA	0.2140aA
	Manured	0.0008bA	0.0196abA	0.0368aA	0.0810aA	0.0900aA	0.1220aA	0.1142aA	0.2921aA	0.2202aA
Lakeland 2	Unamended	0.0005aA	0.0006aA	0.0010aA	0.0009aA	0.0027aA	0.0015aA	0.0022aA	0.0020aA	0.0034aA
	Manured	0.0005bA	0.0013abA	0.0098abA	0.0041abA	0.0135abA	0.0102abA	0.0167abA	0.0485aA	0.0447aA
Arborg	Unamended	0.0007abA	0.0001bA	0.0004bA	0.0004bA	0.0005abA	0.0005bA	0.0013abA	0.0089abA	0.0223aA
	Manured	0.0003bcA	0.0002cA	0.0003bcA	0.0003bcA	0.0003bcA	0.0004bcA	0.0024abcA	0.0376aA	0.0706aA
Almasippi	Unamended	0.0002aA	0.0004aA	0.0006aA	0.0006aA	0.0015aA	0.0005aA	0.0016aA	0.0056aA	0.0085aA
	Manured	0.0003cA	0.0008bA	0.0013bcA	0.0051abcA	0.0101abcA	0.0111abcA	0.0165abA	0.1282aA	0.0580aA
Reinland	Unamended	0.0002aA	0.0004aA	0.0010aA	0.0007aA	0.0002aB	0.0005aB	0.0006aB	0.0006aB	0.0053aB
	Manured	0.0004cA	0.0005cA	0.0028cA	0.0098bcA	0.3433aA	0.2184abA	0.3094abA	0.5802aA	1.4708aA
Niverville	Unamended	0.0004aA	0.0009aA	0.0001aA	0.0003aA	0.0002aB	0.0005aB	0.0008aB	0.0005aB	0.0022aB
	Manured	0.0009cA	0.0020bcA	0.0057abcA	0.0072abcA	0.0102abcA	0.0204abcA	0.0594abA	0.1092aA	0.1022aA
Fyala	Unamended	0.0004cA	0.0011cA	0.0029bcA	0.0027bcA	0.0147abcA	0.0769abA	0.1317aA	0.0978abA	0.1767aA
	Manured	0.0007cA	0.0013bcA	0.0122abcA	0.0321abA	0.0721aA	0.0961aA	0.1426aA	0.1183aA	0.2097aA
Sprague	Unamended	0.0002aA	0.0005aA	0.0010aA	0.0005aA	0.0008aA	0.0015aA	0.0011aA	0.0012aA	0.0016aA
	Manured	0.0005aA	0.0006aA	0.0010aA	0.0006aA	0.0010aA	0.0014aA	0.0023aA	0.0217aA	0.0254aA
Long Plain	Unamended	0.0002aA	0.0002aA	0.0002aA	0.0002aA	0.0003aB	0.0005aB	0.0008aB	0.0002aB	0.0008aB
	Manured	0.0003dA	0.0005cdA	0.0022bcdA	0.0059abcdA	0.0175abcA	0.0611aA	0.0341abA	0.1056aA	0.1055aA
Scanterbury	Unamended	0.0007aA	0.0002aA	0.0009aA	0.0005aA	0.0002aB	0.0005aB	0.0008aB	0.0010aB	0.0011aB
	Manured	0.0006dA	0.0040bcdA	0.0112bcdA	0.0070bcdA	0.0466abA	0.0566abA	0.1108abA	0.4080aA	1.0305aA
Osborne	Unamended	0.0003aA	0.0002aA	0.0006aA	0.0006aA	0.0006aA	0.0002aA	0.0007aA	0.0003aB	0.0002aB
	Manured	0.0005cA	0.0042bcA	0.0040bcA	0.0015bcA	0.0057bcA	0.0059bcA	0.0087bcA	0.0473abA	0.4167aA

ANOVA	df	P > F						df	P > F
Soil	11	<0.0001		Soil *Time				88	<0.0001
Treatment	1	<0.0001		Treatment * Time				8	<0.0001
Time	8	<0.0001		Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)					117

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡] Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table IX. Variation of dissolved S concentration in soil pore water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}				
Newdale	Unamended	11.2ab[†]A[‡]	17.4aA	17.3aA	13.9aA	11.6aA	3.6cA	1.6cA	3.7cA	1.8cA
	Manured	27.7 aA	33.5aA	38.6aA	33.2aA	26.2aA	6.4bA	2.5bA	2.5bA	2.6bA
Lakeland 1	Unamended	36.4aA	20.7aA	6.0bB	1.8cA	2.1bcA	2.0bcA	2.2bcA	2.3bcA	2.4bcA
	Manured	46.0aA	47.5aA	31.2aA	4.0bA	4.2bA	3.7bA	3.8bA	3.0bA	3.8bA
Lakeland 2	Unamended	419.9aA	390.6aA	342.23aA	339.6aA	286.4aA	275.5aA	248.4aA	243.1aA	240.1aA
	Manured	402.3aA	409.6aA	398.2aA	309.0aA	320.2aA	294.6aA	267.6aA	244.9aA	202.2aA
Arborg	Unamended	13.7aB	14.2aB	9.69abB	5.77abB	4.24bcB	1.23dB	1.23dB	1.36dA	1.37cdA
	Manured	43.6aA	48.6aA	41.3aA	35.1aA	36.9aA	16.5aA	5.33bA	2.05bA	2.22bA
Almasippi	Unamended	72.7aA	113.2aA	98.2aA	82.7aA	66.4aA	20.2bA	2.11cA	1.94cA	1.94cA
	Manured	101.9aA	126.3aA	112.0aA	93.9aA	62.6abA	4.6bA	3.07bA	2.95bA	3.02bA
Reinland	Unamended	6.30abB	11.8aA	11.3aA	10.8aA	11.4aA	9.26aA	6.98abA	2.65bcA	1.42cA
	Manured	18.1aA	34.3aA	31.3aA	27.9aA	11.0abA	2.62bB	2.40bA	2.54bA	2.34bA
Niverville	Unamended	39.1aA	27.4aA	13.9aA	4.2bA	2.47bcA	1.51bcA	1.13cA	1.17cA	1.24cA
	Manured	48.8aA	49.7aA	27.9aA	2.85bA	2.82bA	2.63bA	2.72bA	2.73bA	2.65bA
Fyala	Unamended	79.7aA	69.9aA	64.0aA	59.8abA	9.32cA	45.8abA	20.4bcA	9.65cA	9.94cA
	Manured	115.1aA	95.3aA	83.2aA	80.7aA	2.21cB	54.8aA	18.0bA	10.1bA	9.76bA
Sprague	Unamended	32.1aA	29.2aA	28.6aA	24.7aA	27.1aA	25.1aA	23.5aA	23.0aA	21.8aA
	Manured	50.2aA	40.1aA	36.9aA	36.0aA	40.6aA	36.9aA	31.4aA	17.6abA	6.75B
Long Plain	Unamended	12.7abA	22.7aA	22.1aA	19.3aA	17.8abA	16.4abA	11.9abA	6.02bA	1.41cA
	Manured	22.8cA	35.6aA	39.8aA	27.5aA	19.5aA	6.25bA	2.19cB	2.06cA	2.07cA
Scanterbury	Unamended	9.15aA	7.95aB	8.32aA	5.80aA	1.18bA	0.64bA	0.66bA	0.70bB	0.81bA
	Manured	25.7aA	28.1aA	14.0aA	2.055bA	1.99bA	1.95bA	1.90bA	2.21bA	1.97bA
Osborne	Unamended	24.4abA	21.5abA	11.2bcA	6.71cdA	62.7aA	4.49cdA	3.33dA	3.14dA	1.69dA
	Manured	35.8aA	36.4aA	16.5aA	1.48bB	12.6aB	1.41bB	1.34bA	1.40bA	1.45bA

ANOVA	df	P > F							df	P > F
Soil	11	<0.0001			Soil *Time				88	<0.0001
Treatment	1	0.316			Treatment * Time				8	<0.0001
Time	8	<0.0001			Soil * Treatment * Time				88	<0.0001
Soil * Treatment	11	<0.0001			CV (%)					35

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different

Appendix 3.C; Table X. Variation of dissolved S concentration in surface flood water over the flooding period (geometric means).

Soil series and treatment		Time (Days after flooding)								
		1	7	14	21	28	35	42	49	56
						mg L^{-1}					
Newdale	Unamended	0.05c†B‡	0.50abcA	1.22aA	1.08abA	0.98abA	0.72abcA	0.55abcA	0.35bcA	0.30cA
	Manured	0.18bA	0.73aA	1.04aA	0.68aA	0.54abA	0.52abA	0.58abA	0.49abA	0.50abA
Lakeland 1	Unamended	0.81aA	1.00aB	0.86aA	0.48aA	0.46aA	0.47aA	0.52aA	0.65aA	0.76aA
	Manured	0.82cA	3.88aA	2.41abA	1.15bcA	1.13bcA	1.14bcA	1.21abcA	1.33abcA	1.36abcA
Lakeland 2	Unamended	1.09bA	6.20bA	12.9abA	18.3aA	25.0aA	33.0aB	34.6aB	38.9aB	41.7aA
	Manured	1.27bA	5.44aA	11.0aA	12.7aA	10.4aA	8.8aA	6.2aA	8.0aA	16.1aA
Arborg	Unamended	0.88cdA	2.18abcA	3.07abA	2.71abA	3.27aA	1.89abcA	1.45abcA	1.05bcA	0.77dA
	Manured	2.90bA	6.65aA	8.47aA	8.54aA	9.82aA	7.73aA	4.65abA	2.61bA	1.41bA
Almasippi	Unamended	0.46bA	2.36bA	5.64abA	8.12aA	3.10abB	5.41abA	5.06abA	7.48abB	8.37aB
	Manured	0.55bcA	2.72aA	4.25aA	3.39aA	0.36cA	1.73abA	1.54abA	1.66abA	1.61abA
Reinland	Unamended	0.09cA	0.31bA	0.74aA	1.20aA	1.84aA	2.19aA	2.21aA	1.90aA	1.57aA
	Manured	0.16bA	0.52aA	0.76aA	0.64aA	0.64aA	0.61aA	0.68aA	0.62aA	0.65aA
Niverville	Unamended	1.11aA	1.93aA	1.58aA	1.10aA	1.00aA	0.91aA	0.85aA	0.70aA	0.71aA
	Manured	1.71bA	4.56aA	4.05aA	2.35abA	1.42bA	1.32bA	1.22bA	1.21bA	1.26bA
Fyala	Unamended	0.45bA	1.73aA	2.72aA	2.38aA	2.90aA	2.17aA	2.32aA	2.66aA	2.74aA
	Manured	0.48bA	1.89aA	2.25aA	1.95aA	2.45aA	2.55aA	2.21aA	2.70aA	2.90aA
Sprague	Unamended	0.15dA	0.57cA	1.18bcA	1.94abA	2.51abA	3.39abA	3.95aA	4.57aA	5.23aA
	Manured	0.23cA	1.01bA	1.81abA	2.64abA	3.94aA	5.23aA	5.16aA	4.28aA	2.97abA
Long Plain	Unamended	0.10cA	0.41bA	0.99abA	1.44aA	1.96aB	1.96aB	1.89aB	1.55aB	1.34abA
	Manured	0.22aA	0.50aA	0.47aA	0.43aA	0.44aA	0.49aA	0.51aA	0.49aA	0.75aA
Scanterbury	Unamended	0.29bB	0.54abB	1.13aA	1.11aA	1.05aA	0.94abA	0.79abA	0.70abA	0.63abA
	Manured	1.37bcA	3.60aA	3.01abA	1.07cA	0.71cA	0.58cA	0.53cA	0.51cA	0.53cA
Osborne	Unamended	0.94aA	1.68aA	1.83aA	1.67aA	2.39aA	1.75aA	1.81aA	1.70aB	1.64aB
	Manured	1.84abA	3.42aA	1.67abA	0.80abA	0.85abA	0.56bA	0.56bA	0.41bA	0.36bA

ANOVA	df	P > F					df	P > F
Soil	11	<0.0001		Soil *Time			88	<0.0001
Treatment	1	0.022		Treatment * Time			8	0.193
Time	8	0.284		Soil * Treatment * Time			88	<0.0001
Soil * Treatment	11	<0.0001		CV (%)				162

†Mean values followed by the same lowercase letter within a row are not significantly different

‡Mean values followed by the same uppercase letter within a soil for treatments in each day are not significantly different
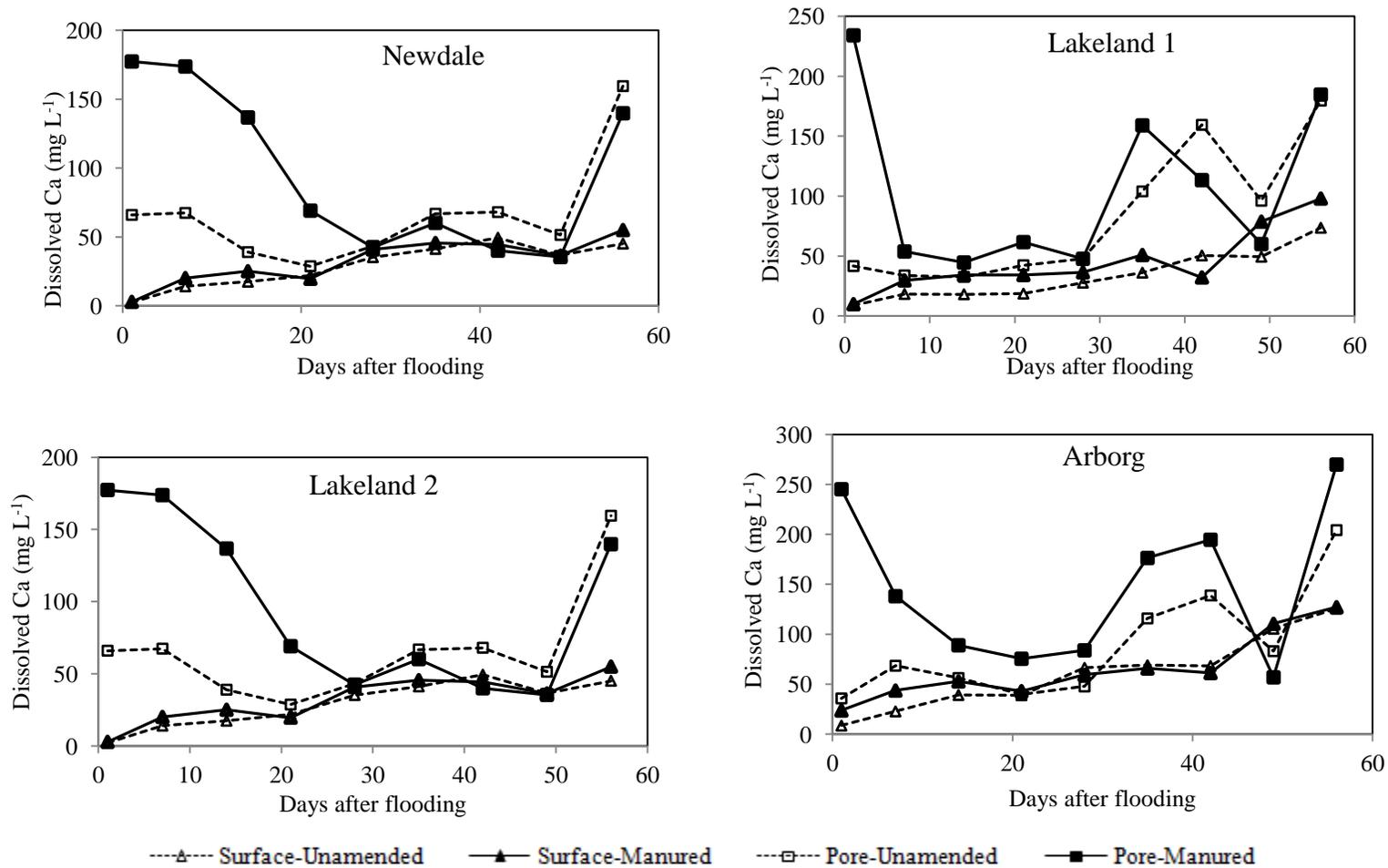
Appendix 3. D; Figure Ia. Variation of Ca (mg L^{-1}) concentration in surface and pore water over the flooding period in Newdale, Lakeland 1, Lakeland 2, and Arborg series.
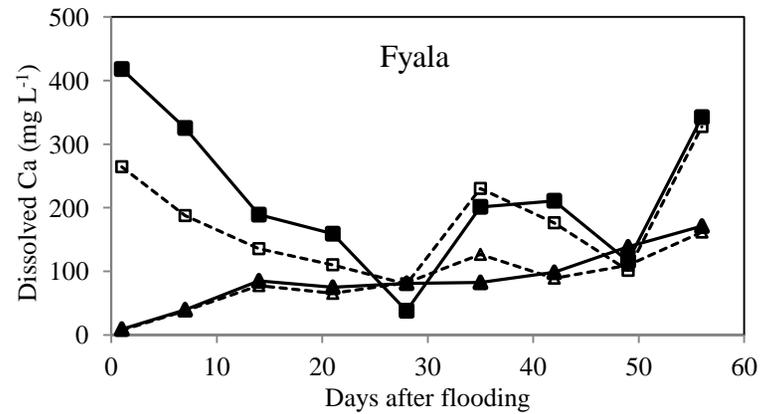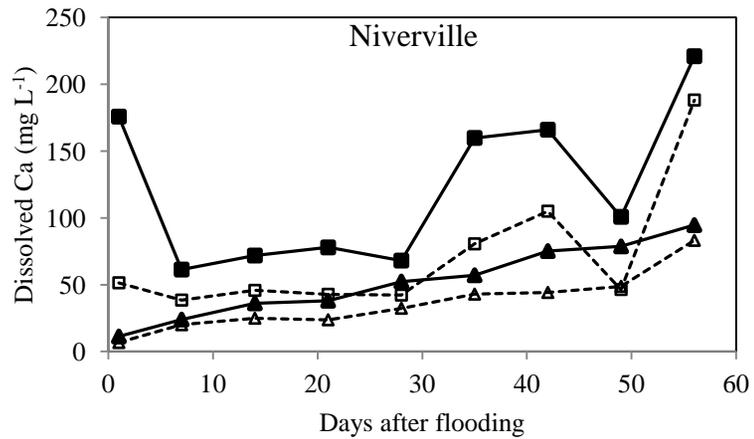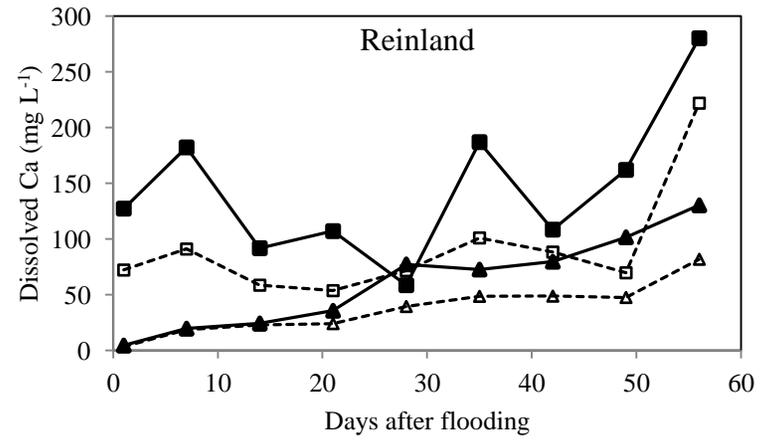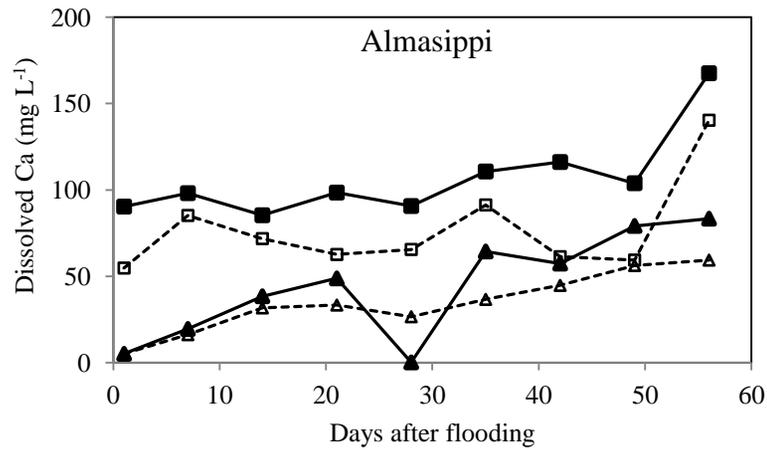
Appendix 3. D; Figure Ib. Variation of Ca (mg L^{-1}) concentration in surface and pore water over the flooding period in Almasippi, Reinland, Niverville, and Fyala series.
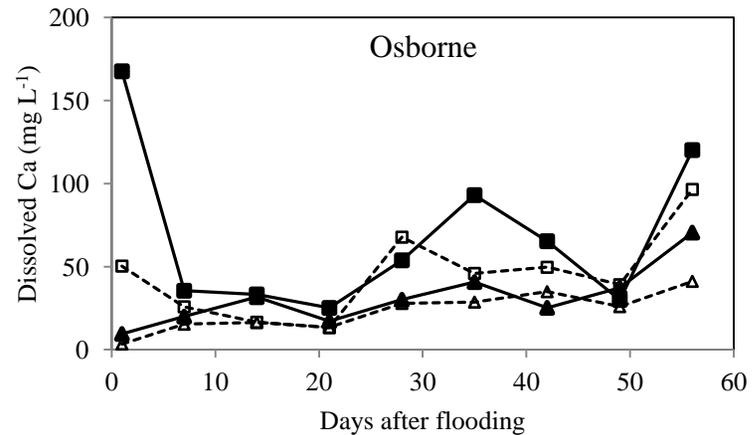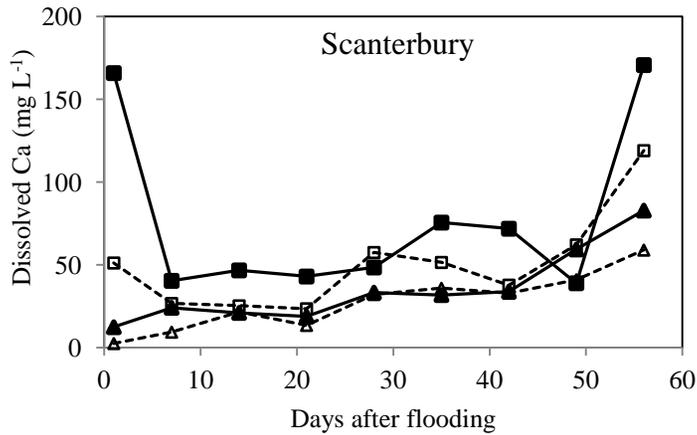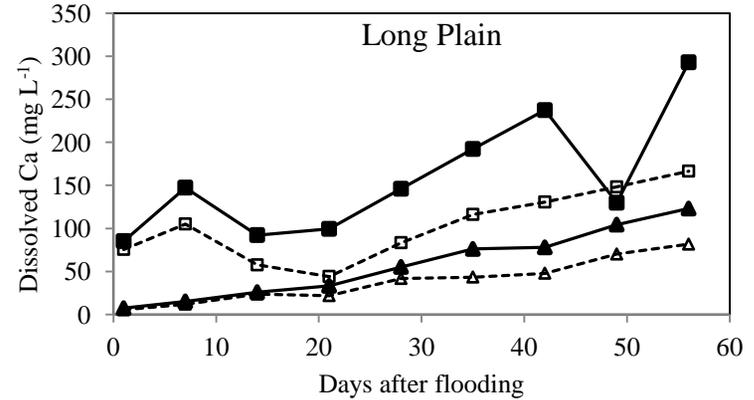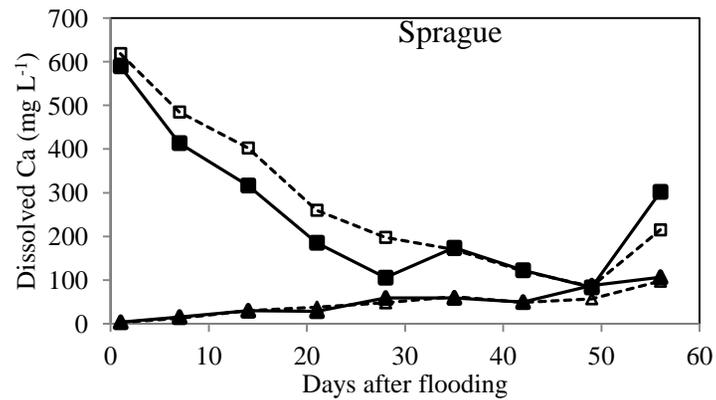
Appendix 3. D; Figure Ic. Variation of Ca (mg L^{-1}) concentration in surface and pore water over the flooding period in Sprague, Long Plain, Scanterbury, and Osborne series.
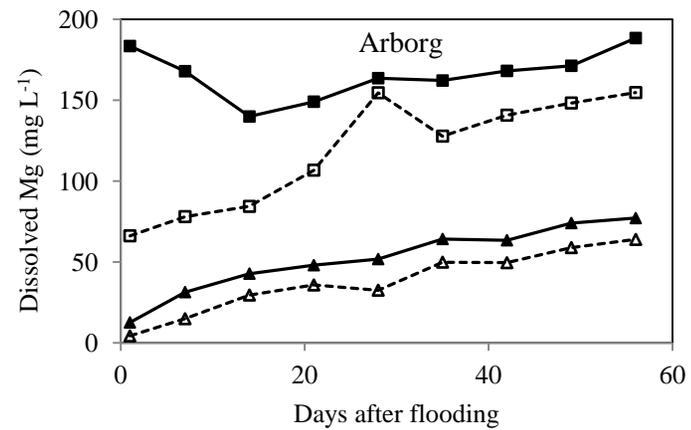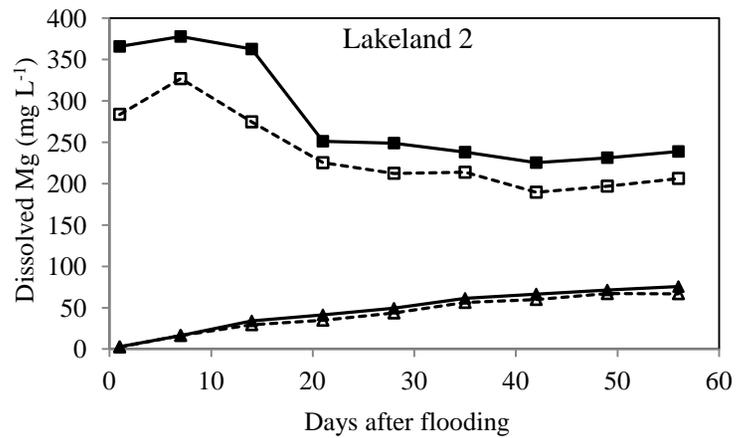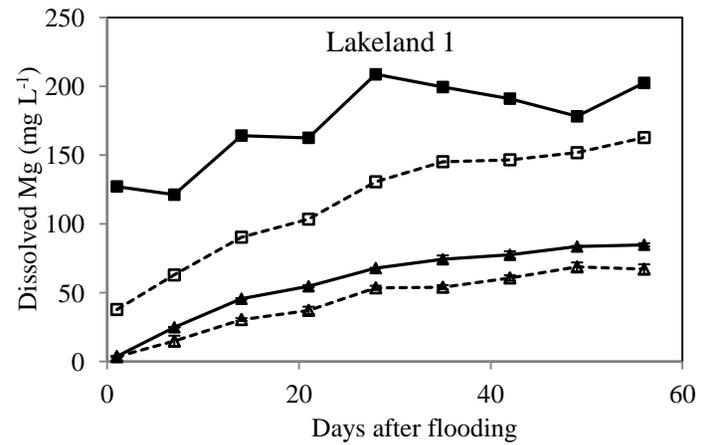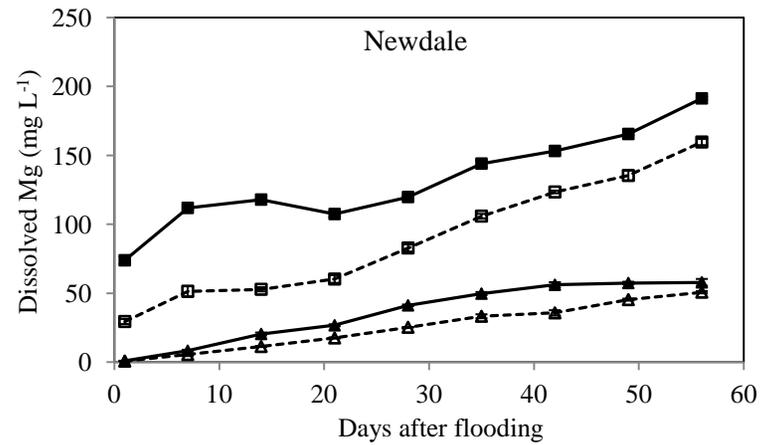
Appendix 3. D; Figure IIa. Variation of Mg (mg L^{-1}) concentration in surface and pore water over the flooding period in Newdale, Lakeland 1, Lakeland 2, and Arborg series.
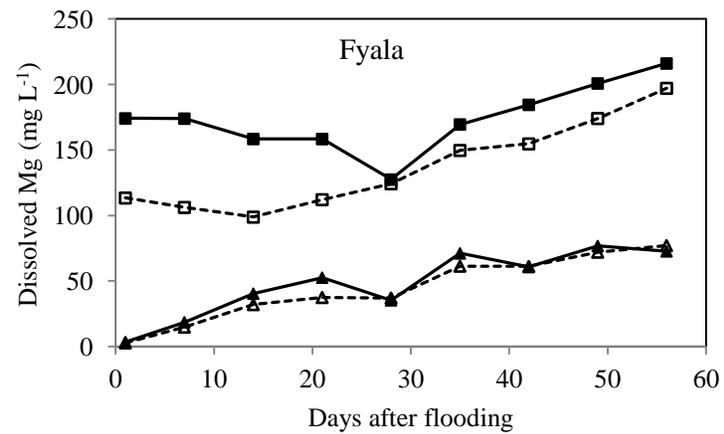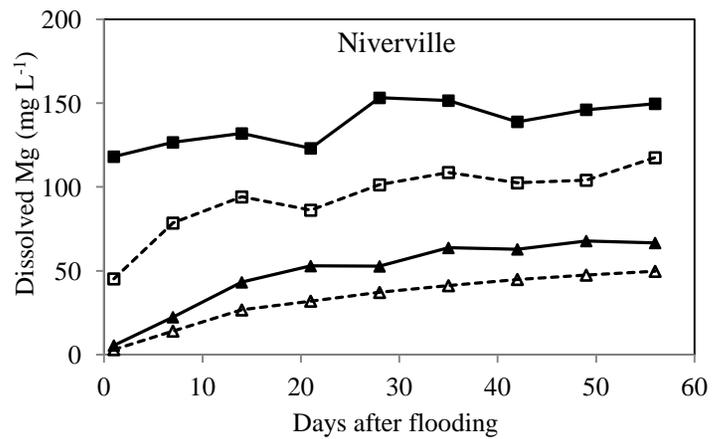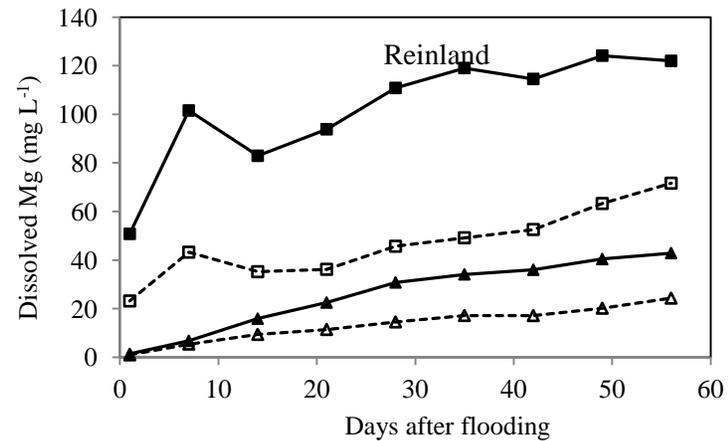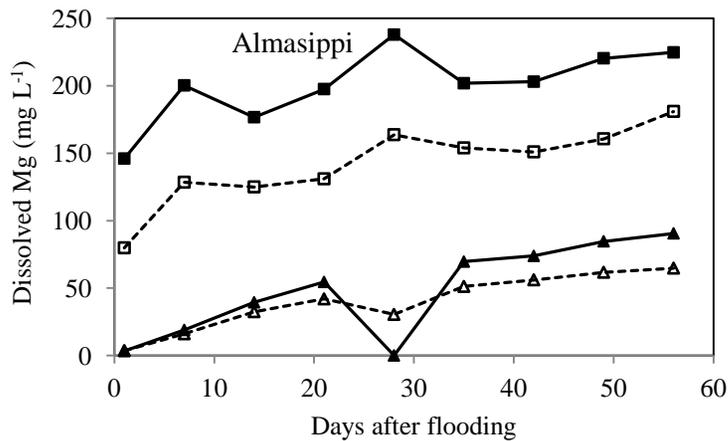
Appendix 3. D; Figure IIb. Variation of Mg (mg L^{-1}) concentration in surface and pore water over the flooding period in Almasippi, Reinland, Niverville, and Fyala series.
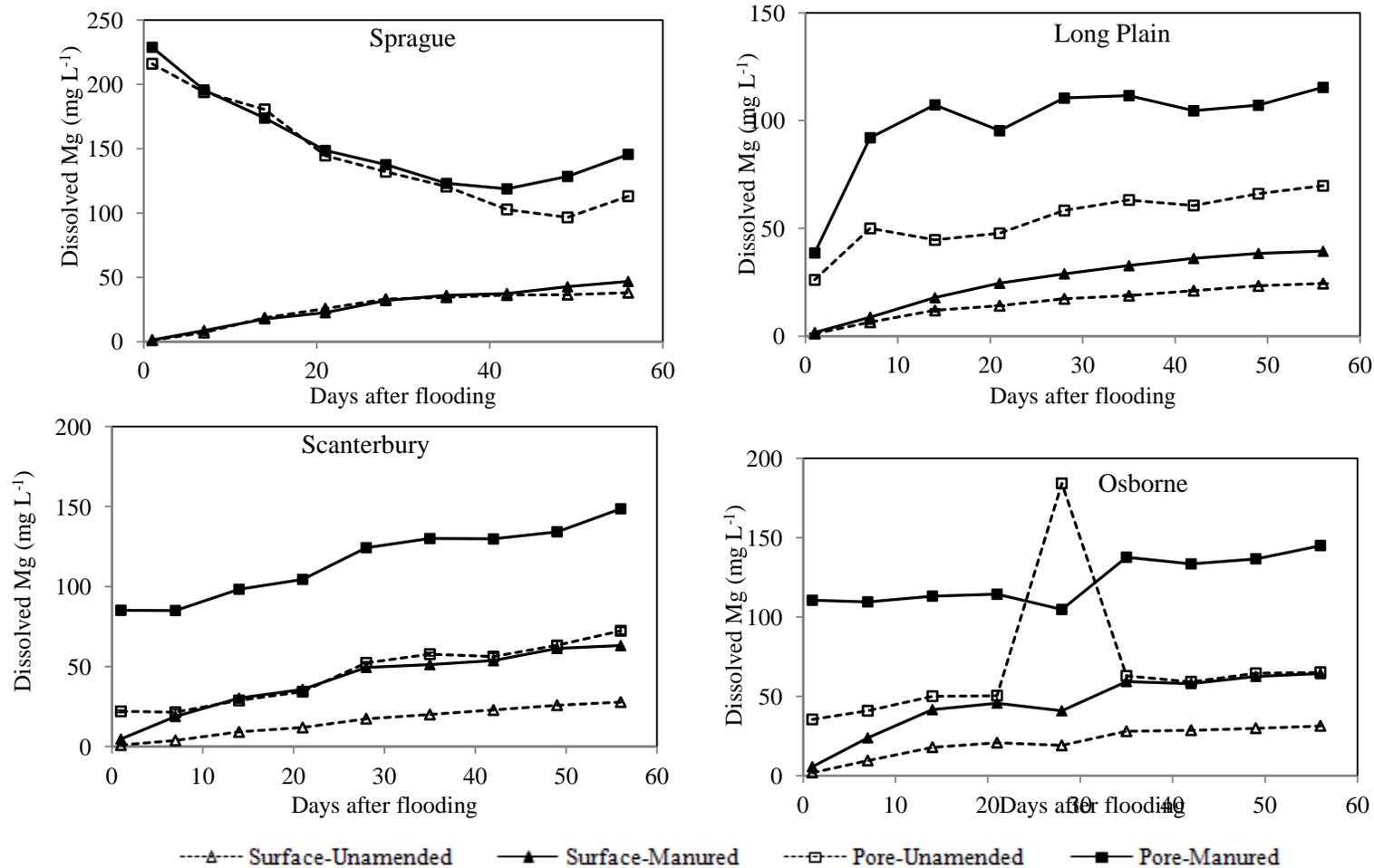
Appendix 3. D; Figure IIc. Variation of Mg (mg L^{-1}) concentration in surface and pore water over the flooding period in Sprague, Long Plain, Scanterbury, and Osborne series.
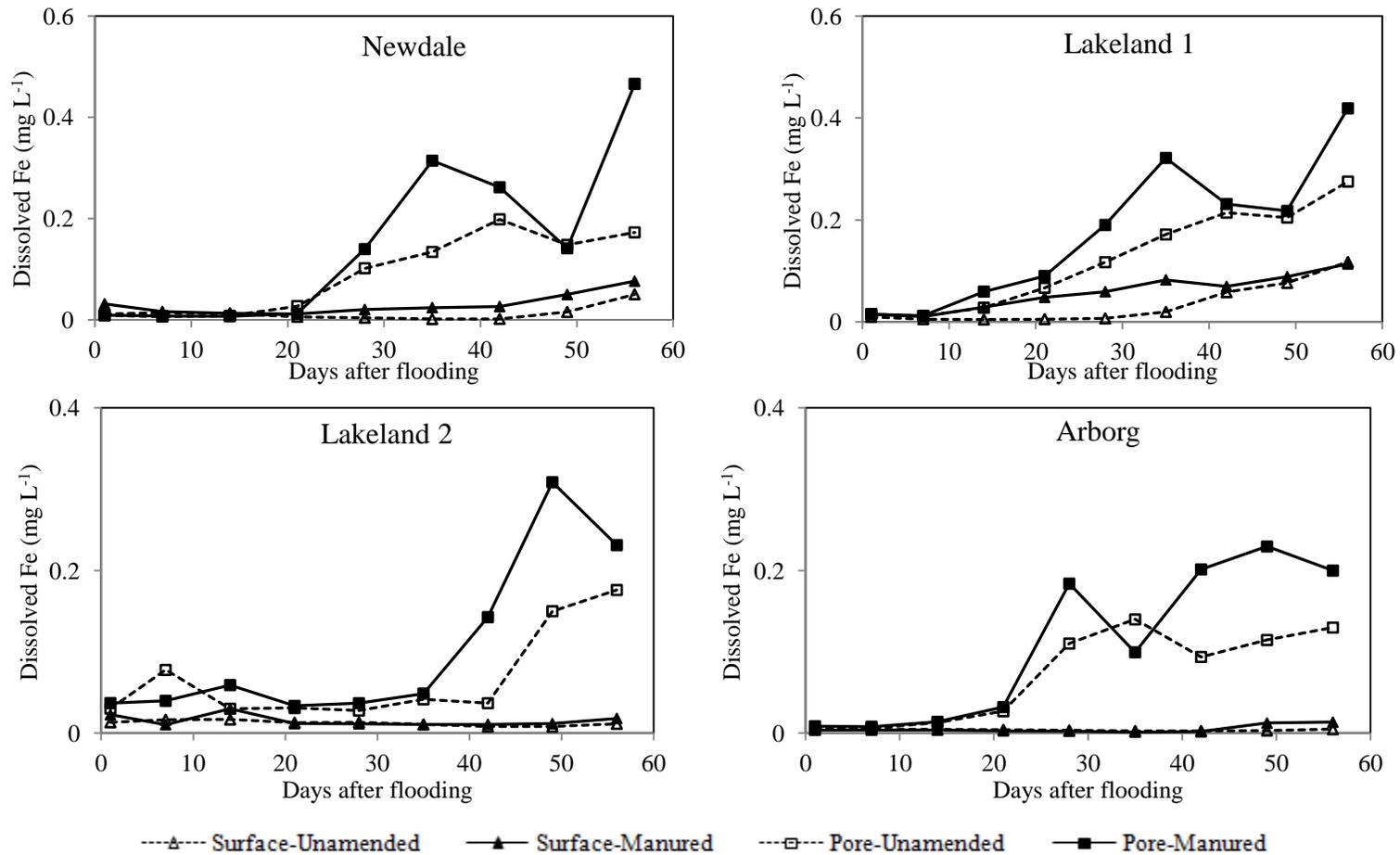
Appendix 3. D; Figure IIIa. Variation of Fe (mg L^{-1}) concentration in surface and pore water over the flooding period in Newdale, Lakeland 1, Lakeland 2, and Arborg series.
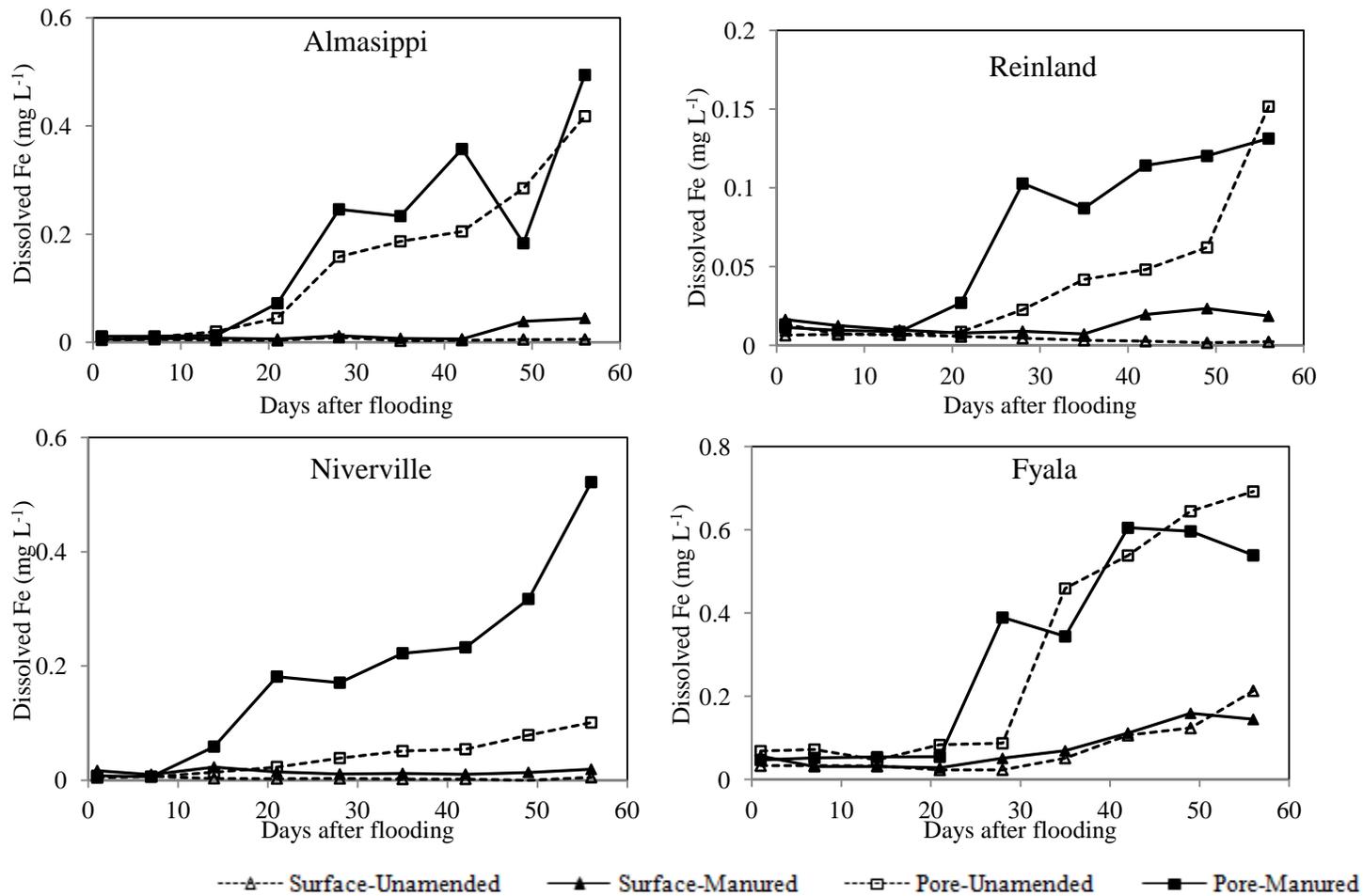
Appendix 3. D; Figure IIIb. Variation of Fe (mg L^{-1}) concentration in surface and pore water over the flooding period in Almasippi, Reinland, Niverville, and Fyala series.
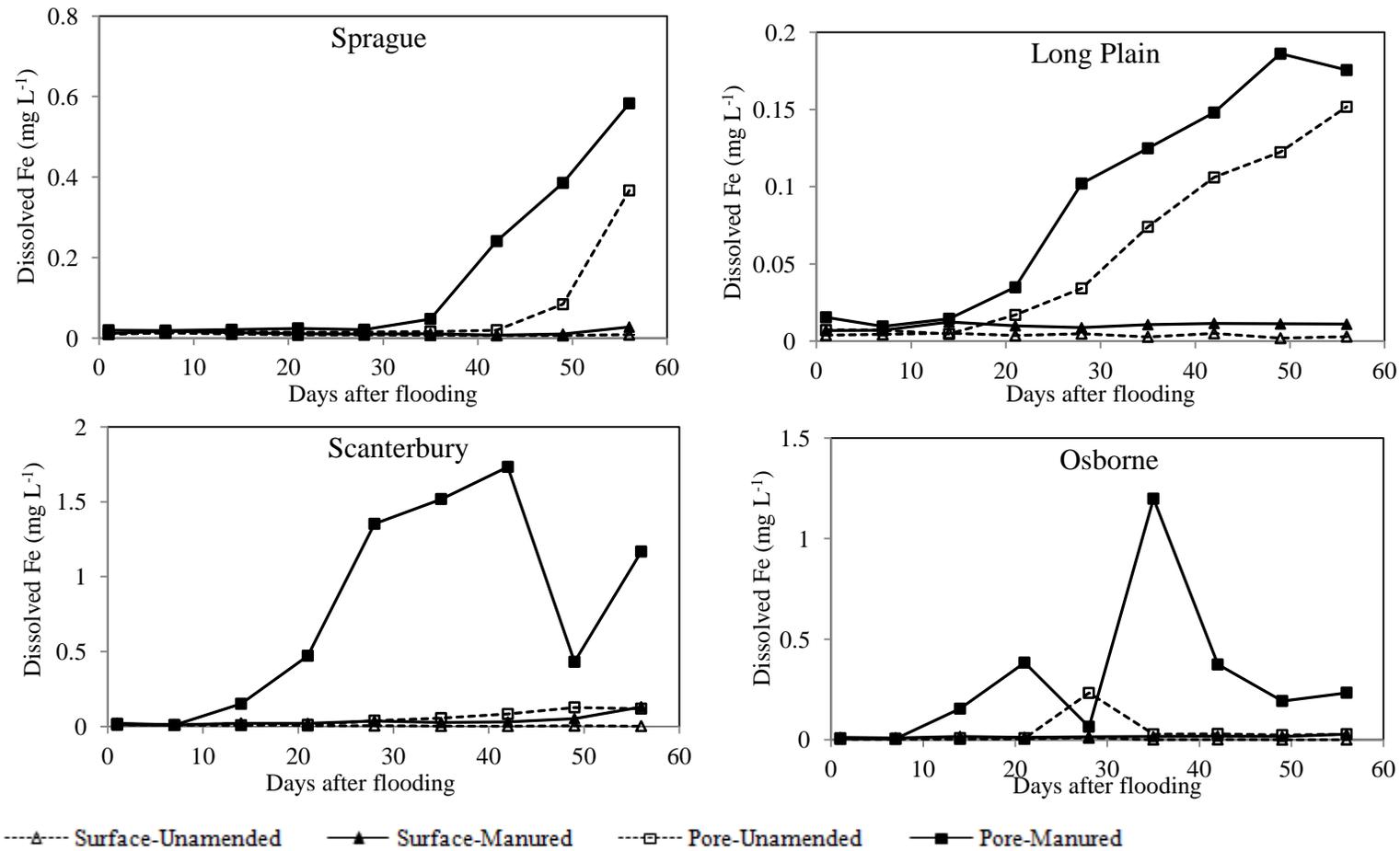
Appendix 3. D; Figure IIIc. Variation of Fe (mg L^{-1}) concentration in surface and pore water over the flooding period in Sprague, Long Plain, Scanterbury, and Osborne series.

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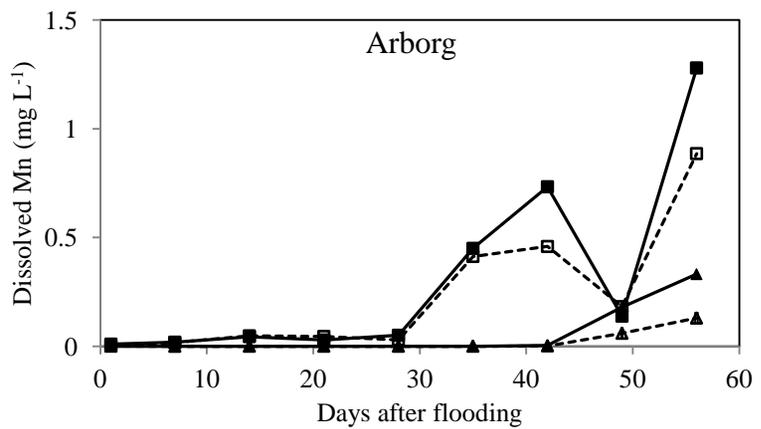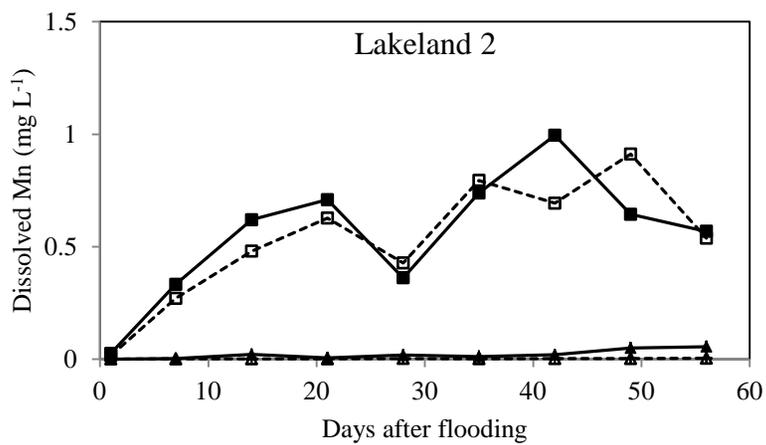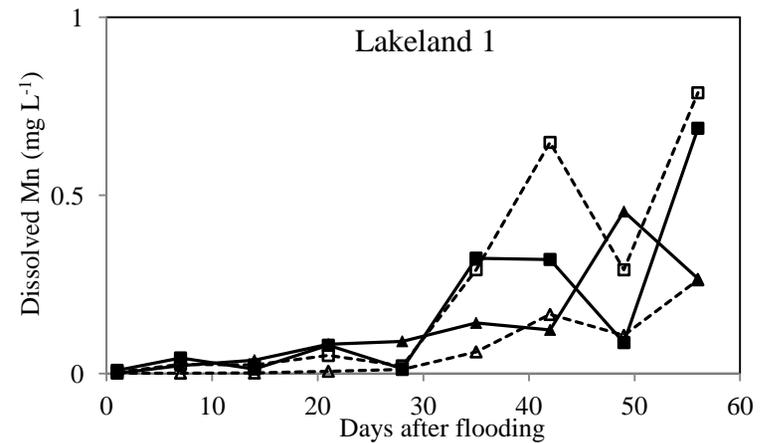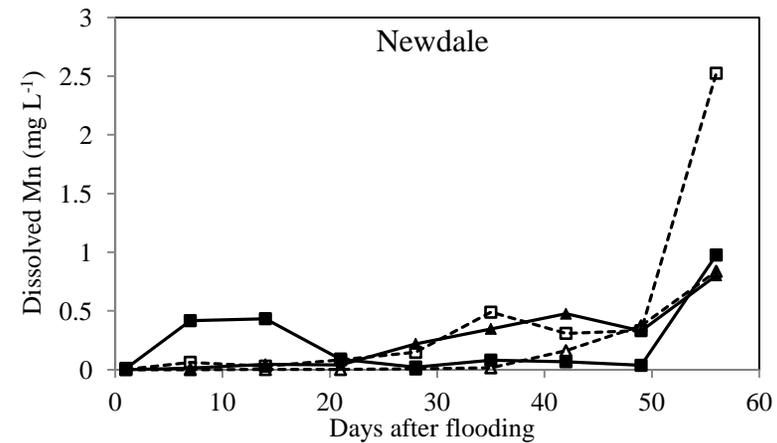
Appendix 3. D; Figure IVa. Variation of Mn (mg L^{-1}) concentration in surface and pore water over the flooding period in Newdale, Lakeland 1, Lakeland 2, and Arborg series.
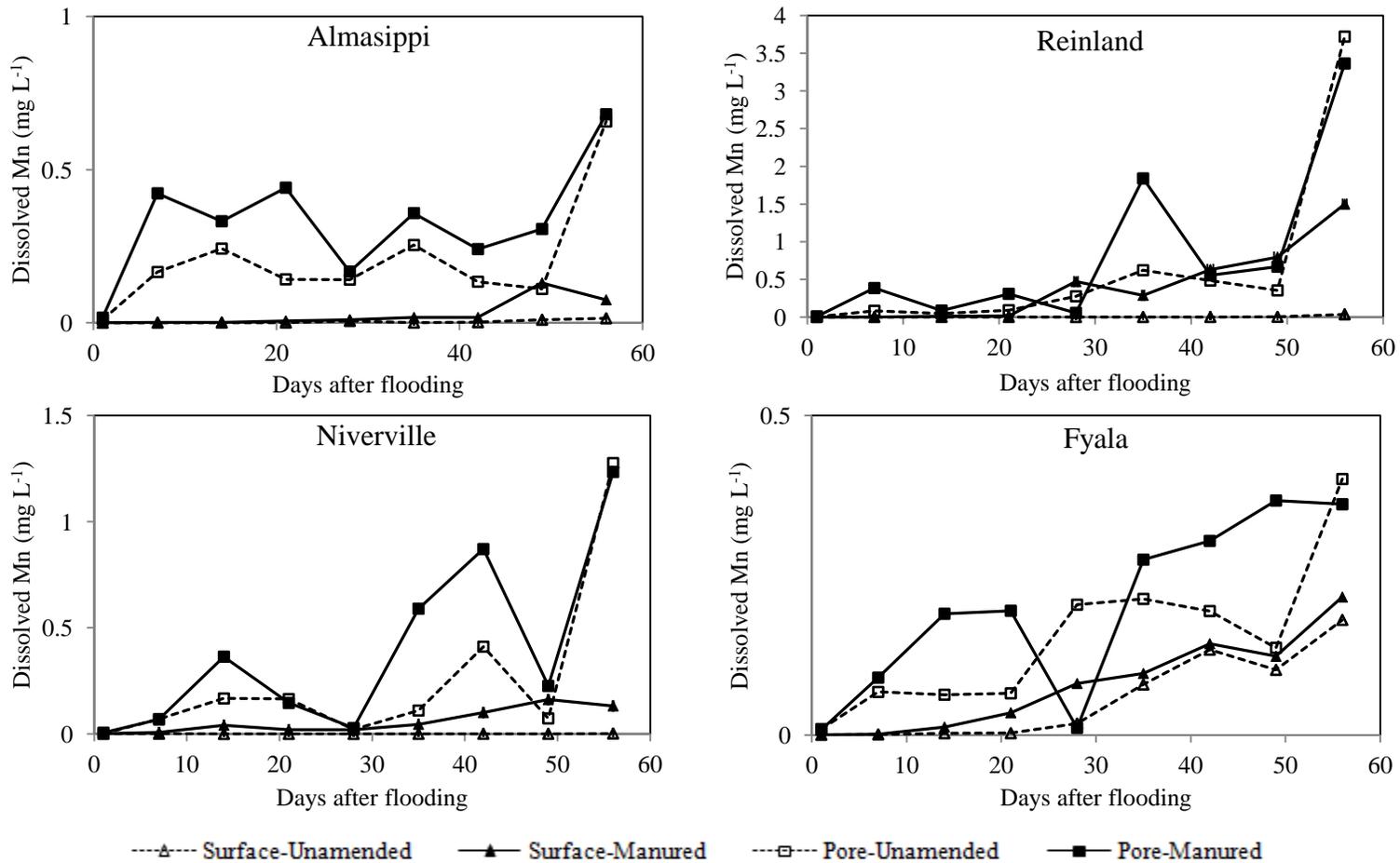
Appendix 3. D; Figure IVb. Variation of Mn (mg L^{-1}) concentration in surface and pore water over the flooding period in Almasippi, Reinland, Niverville, and Fyala series.
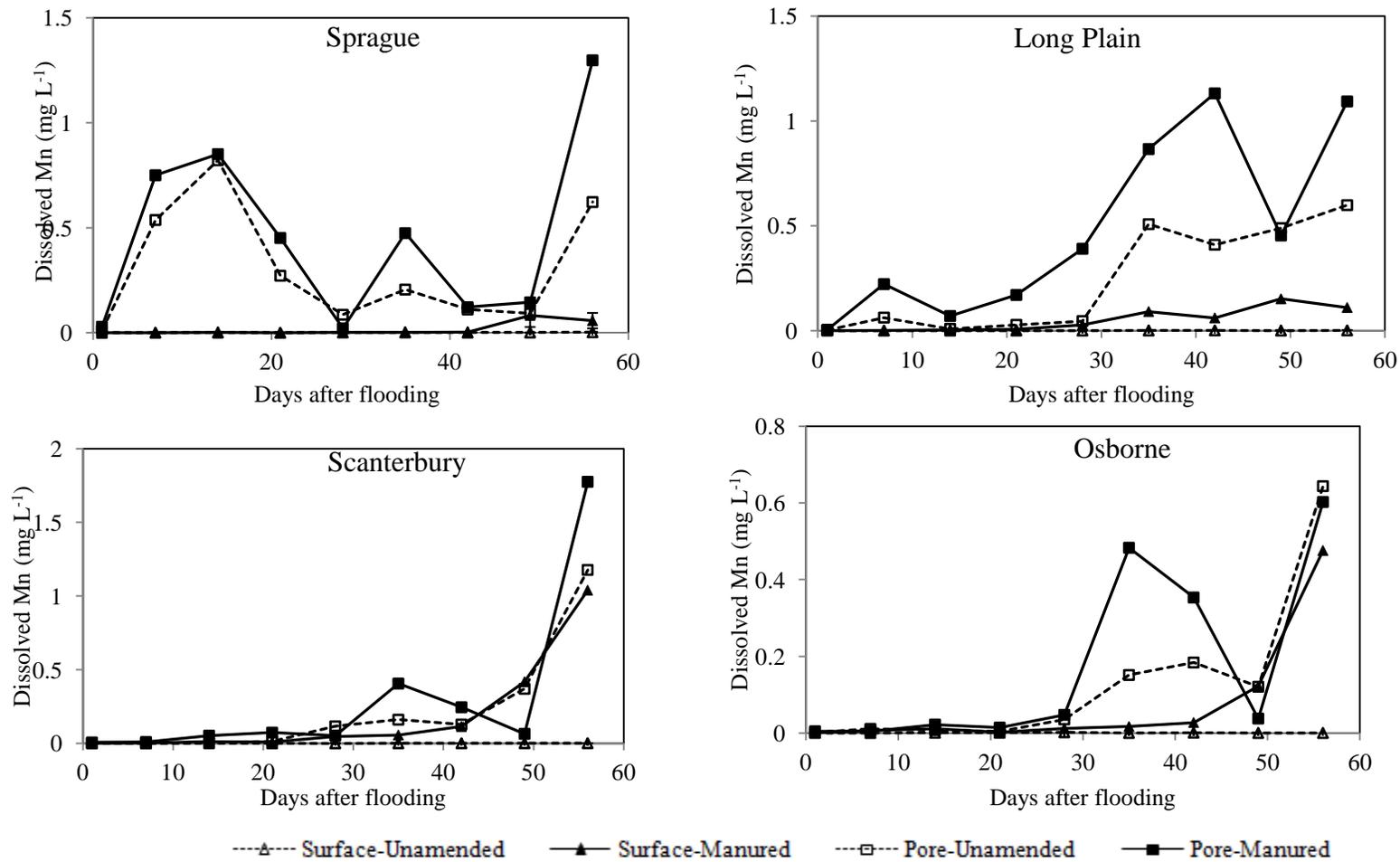
Appendix 3. D; Figure IVc. Variation of Mn (mg L^{-1}) concentration in surface and pore water over the flooding period in Sprague, Long Plain, Scanterbury, and Osborne series.
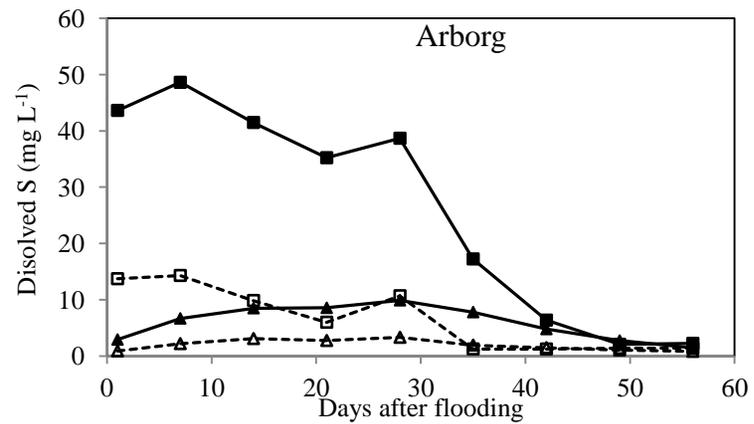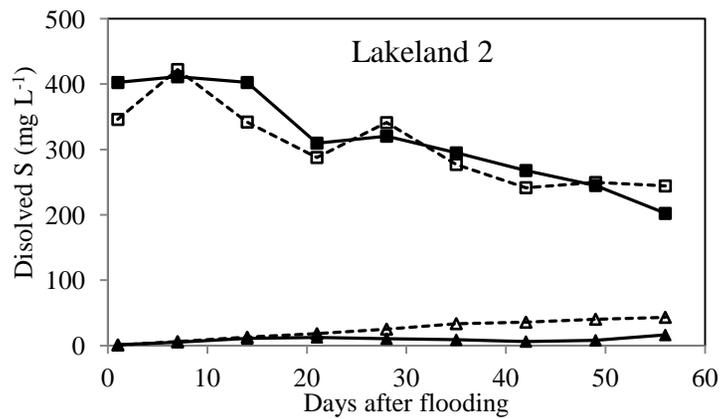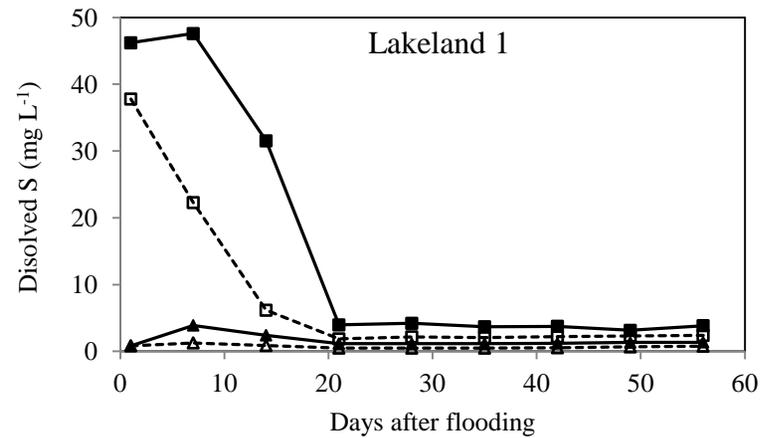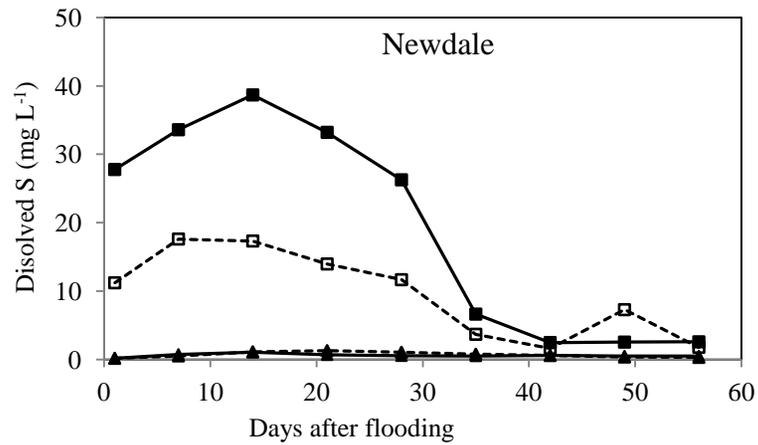
Appendix 3. D; Figure Va. Variation of S (mg L^{-1}) concentration in surface and pore water over the flooding period in Newdale, Lakeland 1, Lakeland 2, and Arborg series.
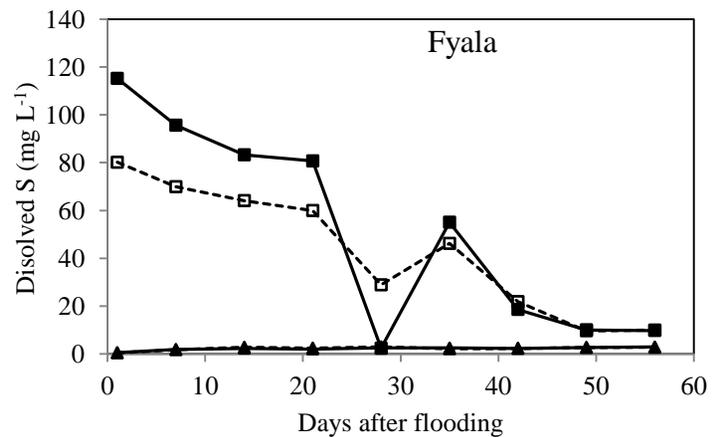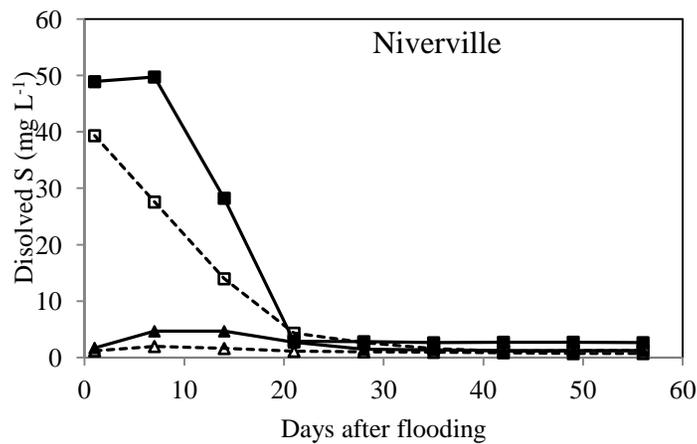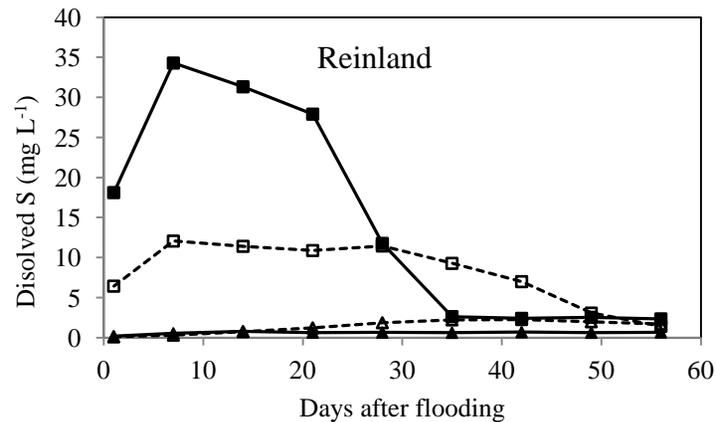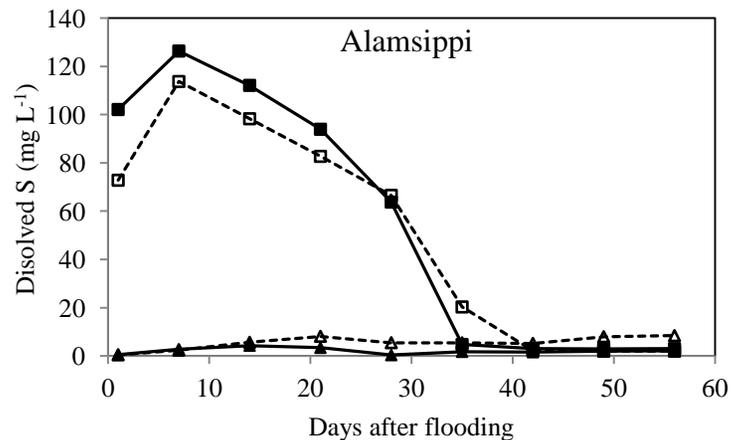
Appendix 3. D; Figure Vb. Variation of S (mg L^{-1}) concentration in surface and pore water over the flooding period in Almasippi, Reinland, Niverville, and Fyala series.

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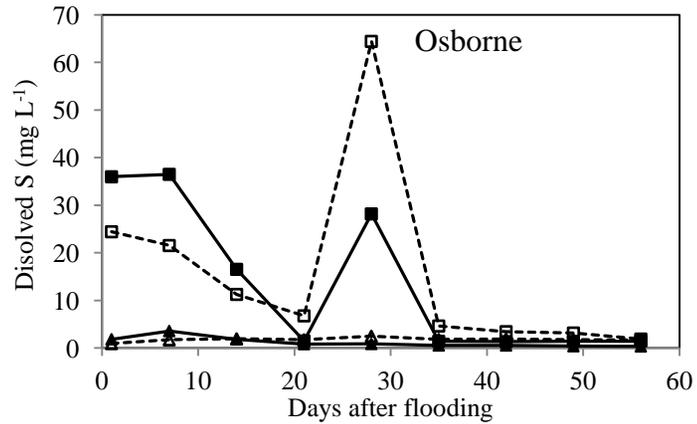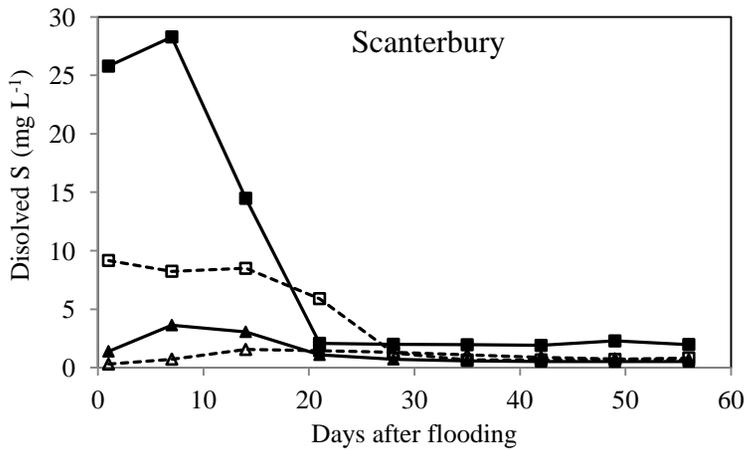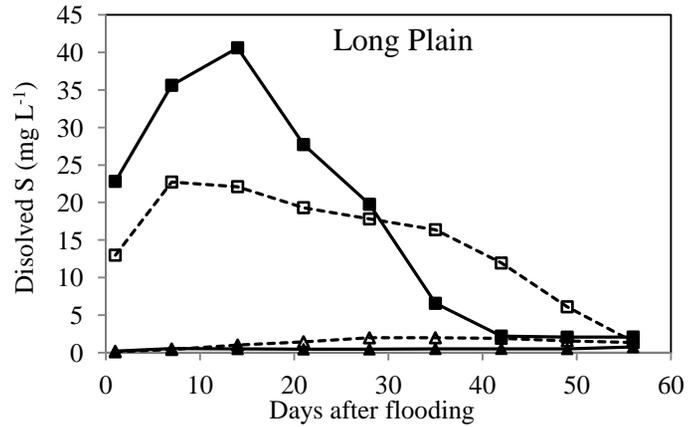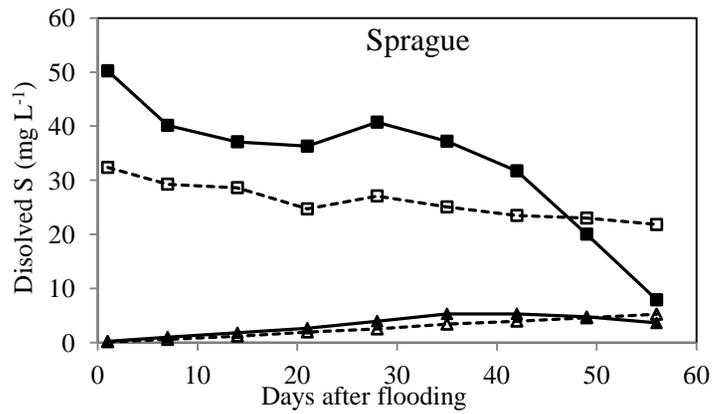
Appendix 3. D; Figure Vc. Variation of S (mg L^{-1}) concentration in surface and pore water over the flooding period in Sprague, Long Plain, Scanterbury, and Osborne series.

Appendix 3.E; Effect of soil series, manure treatment, and flooding on phosphorus sorption capacity (P150).

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	323.1c	512.6a	380.3bc	501.4ab
Lakeland 1	639.8a	609.8a	623.1a	616.4a
Lakeland 2	502.0b	515.3ab	534.8ab	642.0a
Arborg	582.0b	747.0a	604.8b	770.3a
Almasippi	363.1ab	455.9ab	340.3b	485.3a
Reinland	132.6b	228.1ab	157.6b	284.8a
Niverville	537.6a	601.4a	533.1a	605.9a
Fyala	593.7b	679.8ab	587b	725a
Sprague	343.1a	293.1a	329.8a	274.2a
Long Plain	359.8b	369.8b	303.7b	517.6a
Scanterbury	663.1a	685.9a	663.1a	764.8a
Osborne	674.8b	814.2a	674.8b	814.2a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	0.001
Soil * Treatment			11	0.131
Flooding			1	<0.0001
Soil * Flooding			11	<0.0001
Treatment * Flooding			1	0.0024
Soil * Treatment * Flooding			11	0.012
CV[‡] (%)				7

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡]CV - coefficient of variation

Appendix 3.F; Table I. Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable Al content of soils.

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	314.7a	181.0b	205.7b	150.0b
Lakeland 1	233.7a	200.0a	214.0a	206.0a
Lakeland 2	76.5a	57.8a	74.0a	50.5a
Arborg	735.7a	699.7a	698.7a	679.0a
Almasippi	5.75a	0.12a	8.34a	0.17a
Reinland	240.7a	246.0a	234.0a	224.7a
Niverville	72.6ab	56.7ab	94.3a	31.6b
Fyala	220.3a	201.3a	224.0a	195.0a
Sprague	134.3a	128.0a	133.7a	119.0a
Long Plain	23.8a	15.6a	17.7a	13.3a
Scanterbury	680.3ab	706.0a	720.0a	643.3b
Osborne	742.7a	700.3ab	737.3a	661.3b
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	<0.0001
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	0.15
Soil * Treatment * Flooding			11	<0.0011
CV[‡] (%)				6

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]CV - coefficient of variation

Appendix 3.F; Table II. Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable Fe content of soils.

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	234.3b	502.0a	224.0b	489.0a
Lakeland 1	135.3b	236.0a	128.7b	240.3a
Lakeland 2	231.7a	210.7a	230.3a	234.0a
Arborg	291.7b	440.3a	270.3b	434.7a
Almasippi	187.0b	342.7a	211.3b	346.3a
Reinland	189.0b	219.3ab	192.0b	248.7a
Niverville	119.0b	272.0a	143.3b	291.7a
Fyala	208.3b	309.7a	200.0b	302.7a
Sprague	462.7a	505.0a	472.3a	484.0a
Long Plain	199.7c	237.7bc	289.0a	272.7ab
Scanterbury	188.7c	369.0b	208.7c	492.0a
Osborne	271.7c	357.3b	279.3c	507.0a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	<0.0001
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	0.0002
Soil * Treatment * Flooding			11	<0.0001
CV‡ (%)				5

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]CV - coefficient of variation

Appendix 3.F; Table III. Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable Ca content of soils.

Soil Series	Treatment		Flooding status	
	Unamended	**Manured**	**Before flooding**	**After flooding**
		mg kg^{-1}		
Newdale	4120a	4123a	4302a	3942b
Lakeland 1	7230a	7286a	7325a	7192a
Lakeland 2	7525a	7492a	7713a	7303b
Arborg	6205a	6088a	6357a	5937b
Almasippi	5630a	5555a	5872a	5313b
Reinland	3445a	3497a	3417a	3525a
Niverville	7980a	8012a	8068a	7923a
Fyala	7517a	7592a	7727a	7382b
Sprague	3737a	3815a	3852a	3700a
Long Plain	5575b	5981a	5757a	5800b
Scanterbury	5545a	5588a	5625a	5508a
Osborne	5130a	5215a	5193a	5152a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	0.023
Soil * Treatment			11	0.0025
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	0.029
Soil * Treatment * Flooding			11	0.063
CV[‡] (%)				2

[†]Mean values followed by the same lowercase letter within a row for treatment or for flooding status are not significantly different

[‡]CV - coefficient of variation

Appendix 3.F;   Table IV. Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable Mg content of soils.

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	980.7a	901.3a	986.3a	960a
Lakeland 1	1603.3a	1653.3a	1660a	1643.3a
Lakeland 2	1750a	1666.7b	1780ab	1713.3ab
Arborg	1750a	1690a	1750a	1700a
Almasippi	1426.7a	1446.7a	1483.3a	1393.3a
Reinland	565a	596.3a	630a	580a
Niverville	1776.7b	1880a	1873.3ab	1856.7ab
Fyala	1670a	1680a	1750a	1690a
Sprague	742ab	704.7b	806a	768.7ab
Long Plain	665.3b	690ab	767a	768.7a
Scanterbury	1513.3b	1593.3ab	1610a	1586.7ab
Osborne	1973.3a	1930a	1966.7a	1933.3a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	0.009
Flooding			1	0.0002
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	<0.0001
Soil * Treatment * Flooding			11	0.0018
CV‡ (%)				2

[†]Mean values followed by the same lowercase letter within a row are not significantly different
[‡]CV - coefficient of variation

Appendix 3.F; Table V. Effect of soil series, manure treatment and flooding on Mehlich-3 extractable Mn content of soils.

Soil Series	Unamended		Manured	
	Before flooding	**After flooding**	**Before flooding**	**After flooding**
	mg kg^{-1}			
Newdale	244.3ab	268.3a	217.3b	252.1a
Lakeland 1	77.1b	189a	73.9b	190.0a
Lakeland 2	51.9b	61.9a	50.7b	65.0a
Arborg	70.4a	59.9ab	66.1ab	55.7b
Almasippi	77.4a	82.3a	78.7a	76.9a
Reinland	140.7a	160.3a	138.3a	151.6a
Niverville	85.8a	93.5a	96.5a	89.5a
Fyala	36.9b	59.2a	40.0b	66.6a
Sprague	52.5a	54.5a	50.5a	53.7a
Long Plain	93.7ab	101.1a	85.1b	104.9a
Scanterbury	47.6b	130.6a	53.6b	127.4a
Osborne	46.8b	60.9a	46.0b	63.8a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	0.312
Soil * Treatment			11	0.0010
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	0.884
Soil * Treatment * Flooding			11	0.005
CV[‡] (%)				5

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]CV - coefficient of variation

Appendix 3.G; Table I. Effect of soil series, manure treatment, and flooding on Mehlich-3 extractable phosphorus measured by molybdate blue method.

Soil Series	Unamended		Manured	
	Before flooding	After flooding	Before flooding	After flooding
		mg kg^{-1}		
Newdale	28.9a[†]	30.6a	41.2a	41.7a
Lakeland 1	19.6d	29.6c	74.9a	48.1b
Lakeland 2	94.7a	96.8a	119.8a	119.9a
Arborg	96.5a	99.6a	122.0a	118.6a
Almasippi	17.7b	22.2b	40.1a	34.4a
Reinland	14.9c	21.4bc	29.1ab	37.0a
Niverville	51.0a	54.2a	75.1a	67.0a
Fyala	68.5a	79.5a	84.3a	98.4a
Sprague	27.3c	32.5bc	44.9ab	53.2a
Long Plain	23.1c	29.3bc	39.9ab	50.9a
Scanterbury	25.3a	28.3a	34.8a	28.1a
Osborne	37.9a	40.8a	52.1a	45.8a
Analysis of variance (ANOVA)			df	$P > F$
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	<0.0001
Flooding			1	0.0006
Soil * Flooding			11	0.0019
Treatment * Flooding			1	<0.0001
Soil * Treatment * Flooding			11	0.0005
CV[‡] (%)				12

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]CV - coefficient of variation

Appendix 3.G; Table II. Effect of soil series, manure treatment, and flooding on water extractable phosphorus.

Soil Series	Unamended		Manured	
	Before flooding	After flooding	Before flooding	After flooding
	mg kg^{-1}			
Newdale	3.76b[†]	15.6a	5.78b	18.1a
Lakeland 1	5.05b	11.0a	7.86ab	12.3a
Lakeland 2	8.51a	1.84b	11.6a	2.75b
Arborg	13.1a	9.61a	14.9a	13.2a
Almasippi	1.93b	1.62b	4.64a	2.95ab
Reinland	4.41b	4.48b	9.36a	8.27ab
Niverville	2.65b	2.82b	8.26a	2.30b
Fyala	12.7a	4.63b	15.4a	6.05b
Sprague	6.00a	6.98a	8.26a	6.28a
Long Plain	4.04a	3.04a	3.80a	2.82a
Scanterbury	4.21a	4.21a	6.76a	6.78a
Osborne	3.10b	5.49ab	6.22a	5.93ab
Analysis of variance (ANOVA)			df	$P > $ F
Soil			11	<0.0001
Treatment			1	<0.0001
Soil * Treatment			11	<0.0001
Flooding			1	<0.0001
Soil * Flooding			1	<0.0001
Treatment * Flooding			1	0.0002
Soil * Treatment * Flooding			11	0.0014
CV[‡] (%)				21

[†]Mean values followed by the same lowercase letter within a row are not significantly different

[‡]CV - coefficient of variation

Appendix 3,H. Table I. Correlation coefficients (*r*) between changes in DRP concentration and changes in dissolved Ca, Mg, Fe, Mn and S concentrations in soil pore water of unamended and manured soils during flooding.

	Unamended soils					Manured soils				
	1-7 days	1-14 days	1-21 days	1-42 days	1-56 days	1-7 days	1-14 days	1-21 days	1-42 days	1-56 days
Ca	0.22	0.12	0.10	0.17	-0.24	-0.04	-0.21	-0.36	0.08	-0.64*
Mg	0.10	-0.18	0.01	0.24	0.36	-0.20	-0.36	-0.51	-0.54	-0.65*
Fe	0.82**	0.20	0.29	0.22	-0.10	0.10	-0.08	0.06	-0.29	0.17
Mn	0.48	0.68*	0.45	0.47	0.89***	-0.01	0.41	0.17	0.65*	0.78**
S	0.06	-0.44	-0.59*	-0.26	-0.26	-0.12	-0.19	-0.75**	-0.22	-0.52

*,**,*** Significant at the 0.05, 0.01 and 0.001 probability levels respectively.

Appendix 3.H. Table II. Correlation coefficients (*r*) between changes in DRP concentration and changes in dissolved Ca, Mg, Fe, Mn and S concentrations in surface water of unamended and manured soils during flooding.

	Unamended soils					Manured soils				
	1-7 days	1-14 days	1-21 days	1-42 days	1-56 days	1-7 days	1-14 days	1-21 days	1-42 days	1-56 days
Ca	0.79**	0.61*	0.73**	0.78**	-0.61*	0.62*	0.66*	0.81**	0.79**	0.17
Mg	0.27	0.32	0.25	0.43	0.35	-0.12	0.05	0.15	0.05	0.32
Fe	0.29	-0.13	-0.03	0.10	0.34	-0.30	-0.03	-0.43	-0.27	-0.15
Mn	0.33	0.15	0.10	0.23	0.93***	-0.42	-0.03	0.10	0.06	0.88**
S	0.27	0.32	0.48	0.26	0.08	-0.23	0.57	0.67*	0.63*	0.41

*,**,*** Significant at the 0.05, 0.01 and 0.001 probability levels respectively.

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Appendix 3.I; Table I. Fitted model equations for predicting absolute and relative changes in DRP during flooding in surface flood water of unamended and manured soil.

Response variable		Fitted model equation[†]	$r^{2\ddagger}$	Root mean PRESS[§]
ΔDRP_{abs}	Unamended	$\Delta DRP_{abs} = -0.53 + 0.020\ M3P_{ICP}$	0.94	0.28
		$\Delta DRP_{abs} = -1.024 + 0.006\ HCl\text{-}Pi$	0.35	0.99
	Manuered	$\Delta DRP_{abs} = -1.87 + 0.311\ DPS2 + 0.167\ DPS3$	0.89	0.42
ΔDRP_{ratio}	Unamended	$\Delta DRP_{ratio} = -0.19 + 0.015\ HCl\text{-}Pi + 0.268\ DPS3 + 0.025\ H_2O\text{-}Pi - 0.038\ Clay$	0.95	0.40
		$\Delta DRP_{ratio} = 1.91 + 0.483\ DPS3$	0.42	1.10
		$\Delta DRP_{ratio} = -1.36 + 0.020\ HCl\text{-}Pi + 0.032\ H_2O\text{-}Pi$	0.65	0.69
		$\Delta DRP_{ratio} = -2.38 + 0.028\ HCl\text{-}Pi$	0.55	0.88
		$\Delta DRP_{ratio} = 7.99 - 0.068\ Clay$	0.38	1.02
ΔDRP_{ratio}	Manured	$\Delta DRP_{ratio} = 5.18 + 0.314\ DPS3 + 0.612\ DPS1 - 0.007\ P150 - 0.042\ Caly$	0.84	0.57
		$\Delta DRP_{ratio} = 1.91 + 0.483\ DPS3$	0.76	0.57
		$\Delta DRP_{ratio} = 10.9 - 0.122\ Clay$	0.55	0.91

[†]ΔDRP_{abs} = Absolute change in dissolved reactive P concentration during flooding; Ols-P - Olsen extractable P; $M3P_{ICP}$ = Mehlich-3 extractable P measured by ICP-AES; DPS1 - Ols-P / (2 * P150) + Ols-P * 100; DPS2 - $M3P_{MRP}$/ (2 * P150) + $M3P_{MRP}$ * 100; DPS3 - $M3P_{ICP}$ / (2 * P150) + $M3P_{ICP}$ * 100; HCl-Pi = 1 M HCl extractable P

[‡]Equivalent to variability explained by the fitted model

[§]Root mean predicted residual sums of squares

Appendix 3.J; Table I. Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 29 predictors in the preliminary model for estimation of pore water dissolved reactive P at 21 days of flooding (DRP21P).

Soil property	Unamended		Manured		All	
	B	VIP[†]	B	VIP	B	VIP
DRP1P	0.141	*1.58*	0.134	*1.35*	0.144	1.58
M3P$_{ICP}$	0.124	*1.53*	0.137	*1.59*	0.124	1.59
WEP	0.122	*1.51*	0.110	*1.35*	0.119	1.53
M3P$_{MRP}$	0.109	*1.47*	0.095	*1.40*	0.108	1.51
Ols-P	0.088	*1.36*	0.087	*1.30*	0.086	1.39
DRP1SU	0.084	*1.31*	0.134	*1.48*	0.139	1.59
DPS2	0.086	*1.27*	0.056	0.55	-0.025	0.41
DPS3	0.108	*1.27*	0.100	*1.08*	0.109	1.30
HCl-Pi	0.117	*1.08*	0.146	*1.36*	0.109	1.08
Residual P	0.072	*1.04*	0.019	*1.00*	0.036	0.93
DPS1	0.053	*1.04*	0.037	0.76	0.058	1.39
M3Ca	0.073	0.97	0.101	*1.21*	0.071	1.00
NaOH-Pi	-0.02	0.95	-0.039	0.92	-0.021	0.94
Silt	0.054	0.93	0.032	0.96	0.031	0.85
NaHCO$_3$-Pi	0.000	0.90	-0.025	0.64	0.010	0.83
M3Al	-0.089	0.90	-0.113	*1.01*	-0.090	0.88
CEC	0.018	0.89	0.041	*1.03*	0.021	0.89
Sand	0.022	0.84	0.007	0.79	0.017	0.77
Clay	-0.057	0.83	-0.026	0.60	-0.038	0.67
P150	-0.050	0.82	-0.048	0.83	-0.046	0.79
NaOH-Pt	-0.030	0.80	-0.093	*1.02*	-0.083	0.88
M3Mg	0.014	0.78	0.03	0.84	0.017	0.81
Labile	-0.003	0.58	-0.021	0.49	0.012	0.65
HCl-Po	-0.014	0.57	-0.094	0.88	-0.084	0.78
M3Mn	-0.016	0.43	0.022	0.46	0.005	0.42
SOM	0.039	0.37	0.101	0.94	-0.046	0.57
pH	0.017	0.27	0.069	0.62	-0.005	0.26
H$_2$O-Pi	-0.008	0.19	-0.019	0.41	0.010	0.48
M3Fe	-0.019	0.18	-0.054	0.55	-0.024	0.23

[†]Significant VIP values exceeding 0.8 are in italics

Appendix 3.J; Table II. Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 29 predictors in the preliminary model for estimation of surface flood water dissolved reactive P at 21 days of flooding (DRP21SU).

Soil property	Unamended		Manured		All	
	B	VIP[†]	B	VIP	B	VIP
DRP1P	0.134	*1.56*	0.120	*1.26*	0.135	*1.50*
M3P$_{ICP}$	0.120	*1.53*	0.139	*1.61*	0.129	*1.60*
WEP	0.115	*1.50*	0.128	*1.48*	0.127	*1.55*
M3P$_{MRP}$	0.104	*1.46*	0.086	*1.37*	0.104	*1.48*
DRP1SU	0.090	*1.36*	0.125	*1.46*	0.143	*1.60*
Ols-P	0.080	*1.34*	0.071	*1.21*	0.075	*1.33*
DPS2	0.083	*1.28*	0.080	0.77	-0.034	0.49
DPS3	0.104	*1.27*	0.089	*1.00*	0.101	*1.23*
Residual P	0.076	*1.08*	0.058	*1.11*	0.055	*1.01*
DPS1	0.049	*1.04*	0.009	0.67	0.035	0.95
HCl-Pi	0.110	*1.04*	0.182	*1.65*	0.138	*1.31*
Silt	0.066	*1.00*	0.071	*1.12*	0.057	0.96
NaOH-Pi	-0.016	0.95	-0.043	0.92	-0.029	0.96
M3Al	-0.089	0.92	-0.132	*1.18*	-0.111	*1.05*
NaHCO$_3$-Pi	0.010	0.91	-0.034	0.59	-0.005	0.80
Clay	-0.068	0.90	-0.069	0.84	-0.068	0.86
M3Ca	0.058	0.90	0.105	*1.25*	0.075	*1.02*
CEC	0.025	0.89	0.066	*1.14*	0.044	0.96
Sand	0.025	0.85	0.024	0.84	0.029	0.82
P150	-0.051	0.82	-0.048	0.84	-0.049	0.81
NaOH-Pt	-0.011	0.78	-0.007	0.64	-0.043	0.61
M3Mg	0.002	0.76	0.006	0.79	-0.002	0.80
Labile	0.010	0.59	-0.036	0.48	-0.004	0.62
HCl-Po	0.008	0.57	0.015	0.36	-0.036	0.36
M3Mn	-0.010	0.42	-0.033	0.48	-0.018	0.43
pH	-0.035	0.39	0.005	0.20	-0.047	0.49
H$_2$O-Pi	0.005	0.18	-0.049	0.52	-0.013	0.46
SOM	0.007	0.13	0.033	0.48	0.021	0.28
M3Fe	-0.002	0.09	-0.024	0.36	-0.011	0.13

[†]Significant VIP values exceeding 0.8 are in italics

Appendix 3.J; Table III. Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 29 predictors in the preliminary model for estimation of soil pore water dissolved reactive P at 42 days of flooding (DRP42P).

Soil property	Unamended		Manured		All	
	B	VIP[†]	B	VIP	B	VIP
M3P$_{ICP}$	0.075	*1.61*	0.109	*2.03*	0.164	*1.58*
WEP	0.075	*1.59*	0.095	*1.76*	0.156	*1.51*
M3P$_{MRP}$	0.074	*1.59*	0.084	*1.55*	0.088	*1.42*
DRP1SU	0.070	*1.50*	0.092	*1.71*	0.272	*1.56*
Ols-P	0.068	*1.46*	0.080	*1.48*	0.077	*1.32*
DRP1P	0.067	*1.43*	0.086	*1.59*	0.137	*1.44*
DPS2	0.065	*1.40*	0.035	0.64	-0.090	*0.47*
DPS3	0.060	*1.29*	0.086	*1.59*	0.169	*1.38*
M3Ca	0.053	*1.13*	0.067	*1.25*	0.112	*1.00*
Silt	0.052	*1.11*	0.042	0.77	-0.017	0.86
DPS1	0.051	*1.10*	0.049	0.91	0.056	*1.05*
HCl-Pi	0.047	*1.01*	0.098	*1.82*	0.205	*1.35*
CEC	0.047	*1.01*	0.050	0.92	0.038	0.89
Residue	0.043	0.93	0.026	0.47	-0.158	1.03
NaHCO$_3$-Pi	0.043	0.92	-0.001	0.01	-0.078	0.88
NaOH-Pi	0.038	0.81	0.021	0.39	0.000	0.91
Sand	-0.037	0.79	-0.016	0.29	-0.024	0.79
M3Mg	0.035	0.75	0.020	0.37	-0.057	0.80
NaOH-Pt	0.033	0.70	0.004	0.08	-0.010	0.64
Labile	0.031	0.66	-0.015	0.27	-0.121	0.83
HCl-Po	0.026	0.56	-0.006	0.12	-0.026	0.49
P150	0.024	0.50	-0.003	0.06	-0.044	0.80
Clay	0.022	0.46	-0.001	0.02	0.040	0.78
M3Mn	-0.020	0.42	-0.028	0.52	-0.012	0.45
H$_2$O-Pi	0.012	0.27	-0.015	0.27	-0.119	0.74
SOM	0.009	0.18	0.016	0.31	-0.032	0.47
M3Fe	-0.004	0.08	-0.005	0.08	0.017	0.24
pH	-0.002	0.05	0.021	0.39	0.036	0.29
M3Al	0.001	0.03	-0.033	0.61	-0.023	0.85

[†]Significant VIP values exceeding 0.8 are in italics

Appendix 3.J; Table IV. Partial least squares (PLS) regression coefficients and variable influence on projection (VIP) values for 29 predictors in the preliminary model for estimation of surface flood water dissolved reactive P at 42 days of flooding (DRP42SU).

Soil property	Unamended		Manured		All	
	B	VIP[†]	B	VIP	B	VIP
M3P$_{ICP}$	0.120	*1.52*	0.147	*1.69*	0.136	*1.65*
M3P$_{MRP}$	0.105	*1.46*	0.100	*1.41*	0.109	*1.49*
WEP	0.109	*1.45*	0.145	*1.62*	0.136	*1.61*
DRP1SU	0.103	*1.42*	0.101	*1.27*	0.120	*1.43*
DRP1P	0.111	*1.39*	0.153	*1.55*	0.148	*1.59*
HCl-Pi	0.145	*1.33*	0.180	*1.64*	0.153	*1.42*
Ols-P	0.072	*1.30*	0.082	*1.28*	0.082	*1.36*
DPS2	0.078	*1.24*	0.102	0.97	0.007	0.37
DPS3	0.096	*1.20*	0.121	*1.29*	0.119	*1.36*
Silt	0.080	*1.07*	0.039	0.94	0.049	0.90
M3Ca	0.076	*1.00*	0.082	*1.03*	0.071	0.97
M3Al	-0.099	0.99	-0.118	*1.03*	-0.106	0.99
DPS1	0.033	0.99	0.034	0.79	0.047	*1.00*
NaOH-Pi	-0.025	0.97	-0.043	0.85	-0.029	0.94
CEC	0.045	0.96	0.039	0.93	0.036	0.89
Residue	0.045	0.94	0.034	0.97	0.035	0.93
NaHCO3-Pi	0.010	0.92	-0.035	0.60	-0.007	0.80
Clay	-0.062	0.87	-0.087	0.86	-0.076	0.88
Sand	0.016	0.84	0.051	0.80	0.038	0.82
NaOH-Pt	-0.016	0.78	-0.010	0.54	-0.034	0.53
M3Mg	0.003	0.78	-0.026	0.70	-0.017	0.78
P150	-0.039	0.78	-0.072	0.84	-0.059	0.83
Labile	0.012	0.60	-0.046	0.57	-0.012	0.64
HCl-Po	0.002	0.57	0.011	0.26	-0.024	0.25
M3Mn	-0.034	0.51	-0.036	0.45	-0.031	0.47
pH	-0.031	0.35	0.029	0.32	-0.027	0.36
H$_2$O-Pi	0.008	0.19	-0.051	0.56	-0.017	0.49
SOM	-0.004	0.15	0.018	0.30	0.005	0.18
M3Fe	-0.004	0.08	-0.011	0.22	-0.001	0.05

[†]Significant VIP values exceeding 0.8 are in italics

Appendix 3.J; Table V. Partial least squares analysis (PLS) for dissolved reactive phosphorus in surface flood and soil pore water at 21 and 42 days after flooding.

Response variable		Fitted model equation[†]	$r^{2\ddagger}$	Root mean PRESS[§]
DRP21P	Unamended	DRP21P = -0.15 + 0.010 M3P$_{ICP}$ + 0.88 DRP1P	0.93	0.35
	Manured	DRP21P = 0.69 + 0.014 M3P$_{ICP}$ + 3.25 DRP1SU - 0.01 NaOH-Pt	0.87	0.56
	Both	DRP21P = -0.29 + 0.010 M3P$_{ICP}$ + 2.9 DRP1SU	0.80	0.53
DRP21SU	Unamended	DRP21SU = -0.192 + 0.007 M3P$_{ICP}$ + 0.633 DRP1P	0.92	0.41
	Manured	DRP21SU = -2.01 + 0.011 M3P$_{ICP}$ + 0.005 HCl-Pi + 2.63 DRP1SU	0.90	0.44
	Both	DRP21SU = -0.60 + 0.01 M3P$_{ICP}$ + 2.774 DRP1SU	0.79	0.54
DRP42P	Unamended	DRP42P = -0.57 + 0.031 M3P$_{ICP}$	0.87	0.44
	Manured	DRP42P = -1.75 + 0.020 M3P$_{ICP}$ + 0.010 HCl-Pi	0.73	0.56
	Both	DRP42P = -0.48 + 0.009 M3P$_{ICP}$ + 0.097 WEP + 0.011 M3P$_{MRP}$ + 2.17 DRP1SU	0.75	0.56
DRP42SU	Unamended	DRP42SU = -0.57 + 0.031 M3P$_{ICP}$	0.87	0.44
	Manured	DRP42SU = -1.52 + 0.014 M3P$_{ICP}$ + 0.137 WEP + 0.007 HCl-Pi	0.72	0.61
	Both	DRP42SU = -1.19 + 0.007 M3P$_{ICP}$ + 0.076 WEP + 0.003 HCl-Pi + 0.518 DRP1P	0.86	0.46

[†] DRP21P = Dissolved reactive P concentration in pore water at 21 days of flooding; DRP21SU = Dissolved reactive P concentration in surface flood water at 21 days of flooding; DRP42P = Dissolved reactive P concentration in pore water at 42 days of flooding; DRP42SU = Dissolved reactive P concentration in surface flood water at 42 days of flooding; DRP1P = Dissolved reactive P concentration in soil pore water at 1 day of flooding; DRP1SU = Dissolved reactive P concentration in surface flood water at 1 day of flooding M3P$_{ICP}$ = Mehlich-3 extractable P measured by ICP-AES; NaOH-Pt = 0.1 M NaOH extractable P; HCl-Pi = 1 M extractable P; WEP = water extractable P

[‡]Equivalent to variability explained by the fitted model

[§]Root mean predicted residual sums of squares

$$y = 0.937x + 0.057$$
$$r^2 = 0.93$$

$$y = 0.845x + 0.051$$
$$r^2 = 0.83$$

$$y = 0.730x + 0.220$$
$$r^2 = 0.79$$
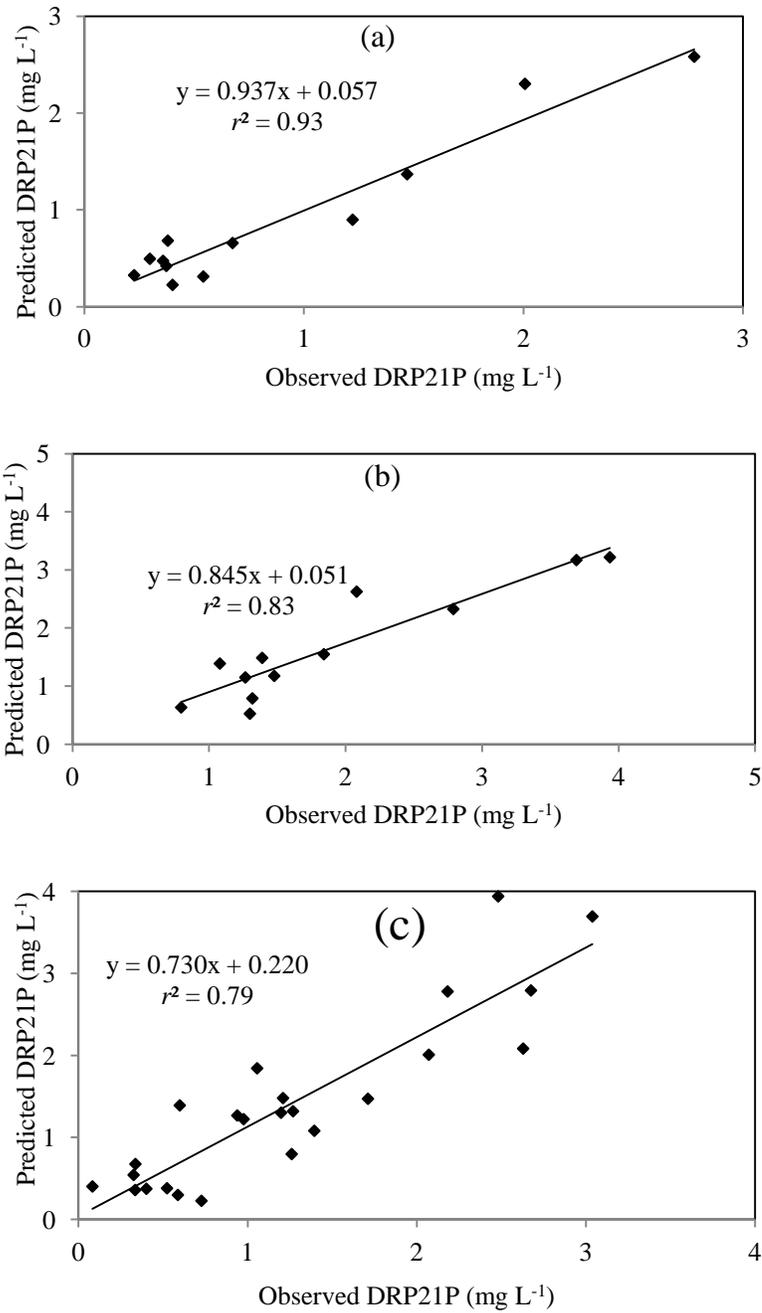
Appendix 3.J; Figure I.   Predicted dissolved reactive phosphorus concentration in pore water of (a) unamended, (b) manured, and (c) combined soils after 21 days of flooding from the one factor partial least square models (Appendix 3.J; Table V) versus observed values.

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Graph (a): $y = 0.908x + 0.039$, $r^2 = 0.91$

Graph (b): $y = 0.877x + 0.059$, $r^2 = 0.88$

Graph (c): $y = 0.785x + 0.190$, $r^2 = 0.79$

Axis labels: Predicted DRP21SU (mg L^{-1}); Observed DRP21SU (mg L^{-1})
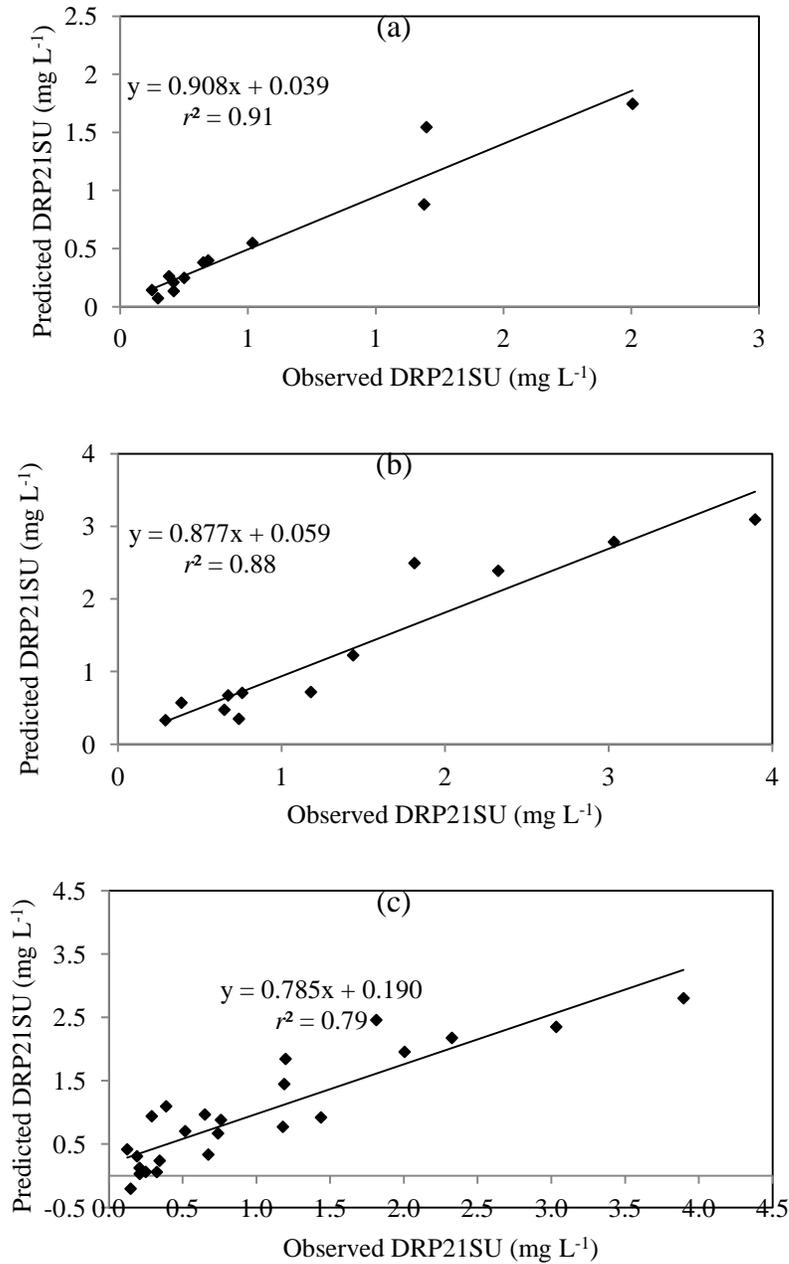
Appendix 3.J; Figure II.   Predicted dissolved reactive phosphorus concentration in surface flood water of (a) unamended, (b) manured, and (c) combined soils after 21 days of flooding from the one factor partial least square models (Appendix 3.J; Table V) versus observed values.
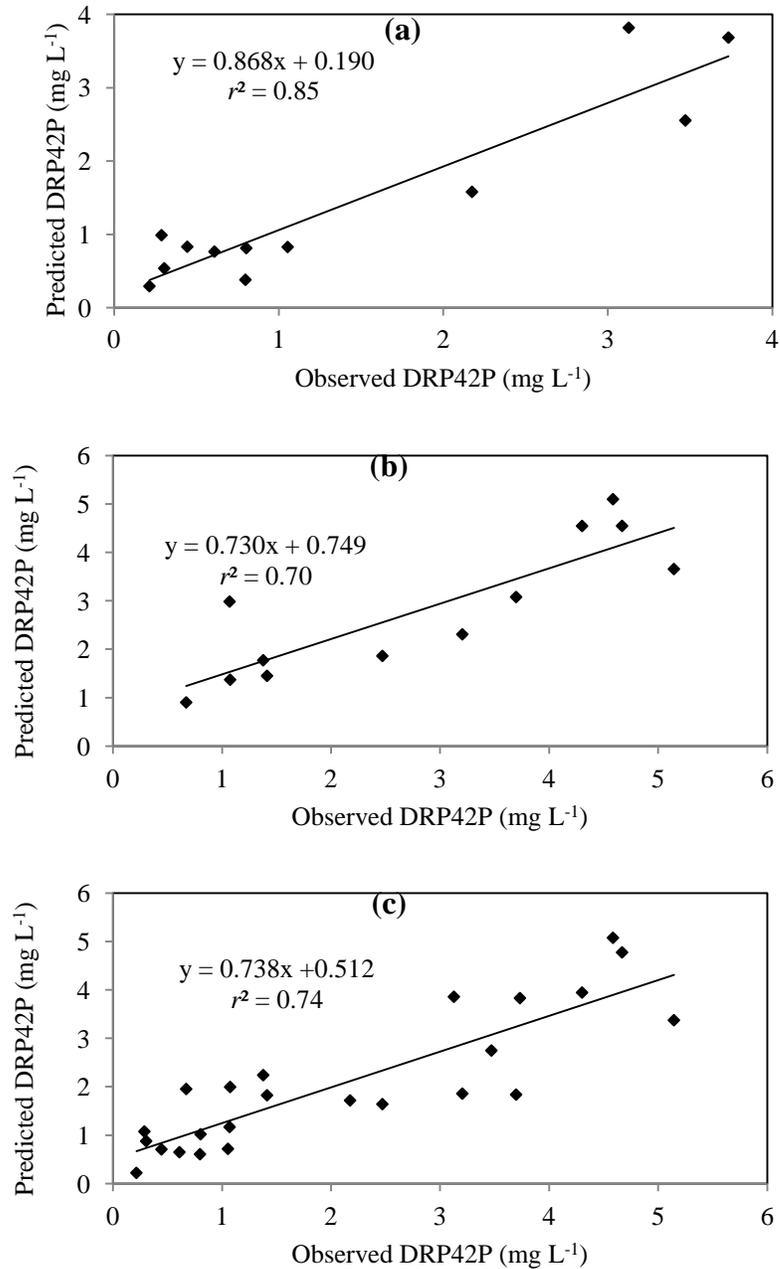
Appendix 3.J; Figure III. Predicted dissolved reactive phosphorus concentration in soil pore water of (a) unamended, (b) manured, and (c) combined soils after 42 days of flooding from the one factor partial least square models (Appendix 3.J; Table V) versus observed values.

(a)

y = 1.413x + 0.412
r^2 = 0.85

(b)

y = 1.157x + 1.115
r^2 = 0.85

(c)

y = 0.854x + 0.141
r^2 = 0.86
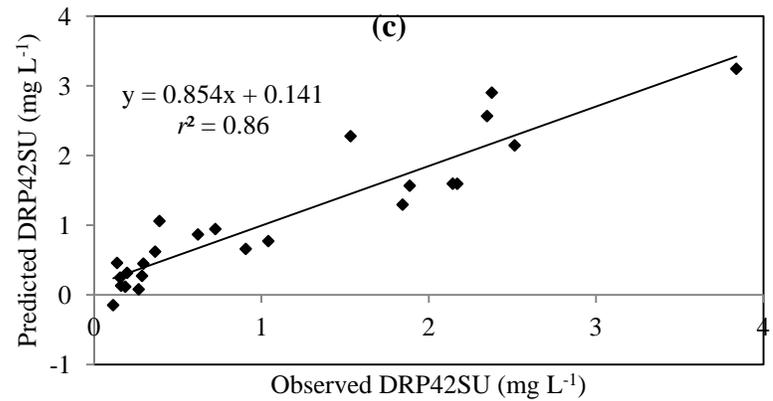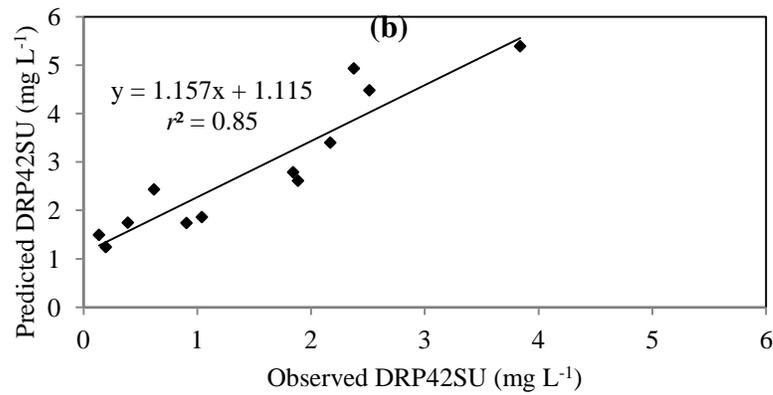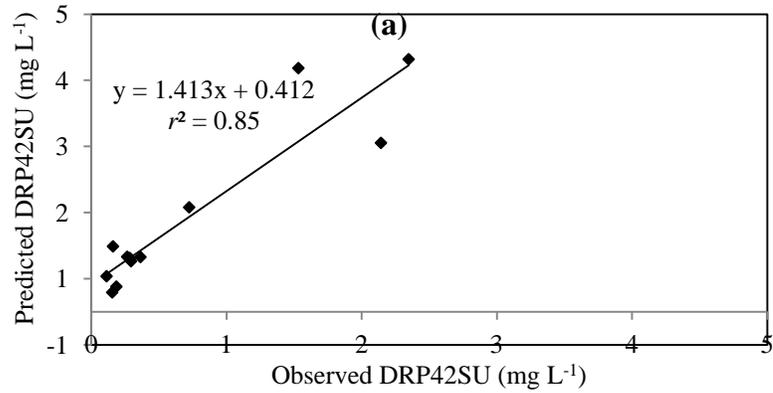
Appendix 3.J; Figure IV. Predicted dissolved reactive phosphorus concentration in surface flood water of (a) unamended, (b) manured, and (c) combined soils after 42 days of flooding from the one factor partial least square models (Appendix 3.J; Table V) versus observed values.

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