

# Phosphorus Retention in Intact and Drained Prairie Wetland Basins: Implications for Nutrient Export

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## Abstract

Draining of geographically isolated (no defined inlet or outlet) freshwater mineral soil wetlands has likely converted areas that acted historically as important P sinks to sources of P. To explore the role of wetland drainage on nonpoint-source P pollution, differences in the chemical characteristics and P sorption parameters of drained and intact wetlands were investigated in a small watershed situated in the Prairie Pothole Region of southwestern Manitoba, Canada. Chemical characteristics and P sorption parameters varied across landscape positions, particularly for landscape positions that were submerged. Intact wetlands had slightly higher concentrations of organic and total P relative to drained wetlands, which is indicative of their P trapping capacity. More importantly, the maximum P sorption capacity and P buffering capacity of intact wetlands were 3.6 (1752 vs. 492 mg kg<sup>-1</sup>) and 17 (1394 vs. 84 L kg<sup>-1</sup>) times greater than those in drained wetlands. Conversely, equilibrium P concentrations and bioavailable P concentrations in drained wetlands were an order of magnitude greater than those in intact prairie wetlands. Our study suggests that intact prairie wetlands may be effective sinks for P. As a result, prairie wetlands may play an important role in mitigating nonpoint-source pollution. Conversely, our findings suggest that drained prairie wetlands are potentially a high risk for P export and should be treated as important critical source areas within prairie watersheds.

## Core Ideas

- Wetland drainage has converted P sinks to sources.
- Intact wetland sediment has higher P buffering capacity than drained wetlands.
- Wetland drainage increases nonpoint-source P pollution.

**E**UTROPHICATION as a result of P pollution has led to the degradation of aquatic ecosystems worldwide, altering ecosystem structure and function (Dodds et al., 2009). In North America and Europe, nonpoint sources are now the dominant supply of pollutants, including nutrients, to surface waters (Singh, 1997; Carpenter et al., 1998; Daniel et al., 1998; Kleinman et al., 2011; Xepapadeas, 2011; Lankoski and Ollikainen, 2013; Rahman, 2014; Wesström et al., 2014). In the Canadian Prairies, nonpoint P pollution is largely due to agriculture and agricultural intensification over the last century (Bunting et al., 2016).

One of the main mechanisms facilitating the transfer of P from agricultural landscapes to surface waters is surface drainage. This is of particular concern in the North American Prairie Pothole Region (PPR), where wetland drainage has reduced surface water storage, increased conveyance, expanded effective drainage area, and generally increased flows in larger streams and rivers (Blann et al., 2009). For the most part, surface drainage has targeted the conversion of geographically isolated (no defined inlet or outlet) freshwater mineral soil wetlands (where soils produce and accumulate little organic matter or peat) to annual cropland. Additionally, draining of isolated freshwater mineral soil wetlands has likely converted areas that acted as important P sinks to sources of P. It seems logical that drained wetlands should be considered critical source areas for P export, given the legacy P that would have accumulated in their soils and sediments prior to drainage of the wetland. This is especially important in the PPR, where human-induced hydrologic alteration of these systems (through surface drainage and ditching) results in increased connectivity to adjacent surface waters, thereby facilitating the transport of P.

In their natural isolated state, mineral wetlands of the PPR likely play an important role in mitigating water quality, as they are situated at the interface between upland and aquatic environments and typically act as nutrient sinks (Yang et al., 2010; Cheng and Basu, 2017). Phosphorus retention in wetlands is an important function in watershed nutrient cycling, particularly in drainage basins with significant nonpoint nutrient contributions from agriculture and/or urban sources (Reddy et al., 2005). Although there

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**Abbreviations:** EPC<sub>e</sub>, equilibrium phosphorus concentration; PEBC, phosphorus equilibrium buffering capacity; PPR, Prairie Pothole Region; S<sub>max</sub>, maximum phosphorus sorbed by soil; S<sub>max1</sub>, high-affinity maximum of phosphorus sorption; S<sub>max2</sub>, low-affinity maximum of phosphorus sorption; S<sub>e</sub>, originally sorbed phosphorus.

are many biotic and abiotic processes that regulate P retention in wetlands, biotic processes tend to be transitory in nature and are less important to long-term retention of P in wetland ecosystems than abiotic processes (Richardson, 1985; Reddy et al., 1999, 2005; Jamieson et al., 2002). The most important processes for the long-term retention of P in wetland systems are the sedimentation of particulate P and the sorption of soluble inorganic P to wetland sediments (Richardson, 1999; Jamieson et al., 2002; D'Angelo, 2005; Dunne and Reddy, 2005; Bruland and Richardson, 2006; Dunne et al., 2006a). Given that prairie wetlands have mineral soils and receive mostly dissolved inorganic P through spring runoff (Little et al., 2007; Jensen et al., 2011; Skopec and Eversizer, 2017), it is likely that long-term P retention in these systems is governed by sorption onto soils and sediments.

Although much research has been conducted on the P sorption capacity of wetlands, and most studies confirm the ability of intact wetlands to act as P sinks (Gale et al., 1994; Richardson, 1999; Bruland and Richardson, 2006; Dunne et al., 2006a), to our knowledge, no such work has been conducted in the Canadian or US portion of the PPR. Furthermore, there have been no comparisons between the chemistry and P sorption capacity of intact and drained wetland sediments within this region. This is important, as it is estimated that over the last 40 to 60 yr, >480,000 ha of wetlands have been drained in the Canadian PPR (Ducks Unlimited Canada, unpublished data, 2017). Therefore, the purpose of this study was (i) to examine and compare the soil and sediment chemistry between intact and drained isolated mineral wetland basins, (ii) to compare the P sorption capacity, equilibrium P concentration ( $EPC_0$ ), P equilibrium buffering capacity (PEBC), and (iii) to evaluate the relationships between soil and sediment characteristics and P sorption parameters.

## Materials and Methods

### Study Area

The Broughton's Creek watershed (26,034 ha) is located in the PPR of southwestern Manitoba, Canada (Fig. 1A), and is a tributary of the Little Saskatchewan River watershed. The watershed is a hummocky till plain and soils are dominated by the Newdale association (Yang et al., 2008). The Newdale soil series is characterized by an Orthic Black Chernozem solum on moderately to strongly calcareous, loamy morainal till of limestone, granitic, and shale origin (Podolsky, 1988). Agriculture is the dominant land use in the watershed (71.8%), followed by range land (10.8%), wetlands (9.5%), and forests (4.0%) (Yang et al., 2010). Historically, the Broughton's Creek watershed contained numerous depressions ranging from small potholes, to sloughs, to lakes that were left behind after the retreat of the Assiniboine glacial lobe between 20,000 and 12,000 BC (Yang et al., 2008). However, a change detection analysis conducted by Ducks Unlimited Canada (Boychuk, 2008) indicates that ~74% of the wetland basins (or 76% of wetland area) have been altered hydrologically through surface drainage and land use change between 1968 and 2005 (Fig. 1A).

### Wetland Basin and Catchment Characteristics

Six drained wetlands and six intact wetlands (Fig. 1B) were chosen as field sites within the Broughton's Creek watershed

for this study. All six drained wetlands and five intact wetlands were situated within agricultural fields, whereas one intact wetland was located in a wildlife management area dominated by grassland. All our study wetlands were seasonal or semipermanent according to Stewart and Kantrud (1971), based on current conditions for the intact wetlands and preimpact conditions for the drained wetlands. A topographic field survey was conducted in fall 2008 to determine the gross contributing area for each wetland (Supplemental Table S1). In addition, LiDAR (light detection and ranging) imagery was collected in fall 2009 and used to supplement the topographic information of the study wetlands and catchments that were not entirely captured in the initial topographic field survey. Our study wetlands ranged in size from 0.45 to 2.67 ha (mean size of intact wetlands = 1.07 ha, mean size of drained wetlands = 1.27 ha), and their catchments ranged in size from 1.89 to 16.34 ha (mean size of intact wetland catchments = 4.66 ha, mean size of drained wetland catchments = 8.79 ha). The ratios of wetland surface area to catchment for our study wetlands ranged between 3.1 and 10.8 (mean = 4.5 for intact wetlands, mean = 6.8 for drained wetlands). Estimates of maximum storage volume and depth are also provided in Supplemental Table S1.

The types of crops observed across the study sites were typical of a 2-yr spring wheat (*Triticum aestivum* L.)–canola (*Brassica napus* L.) crop rotation common to this agricultural region of Manitoba. However, winter wheat, flax (*Linum usitatissimum* L.), oats (*Avena sativa* L.), and peas (*Pisum sativum* L.) were also planted around some of the study wetlands. Nutrient application rates for the types of crop grown around our study wetlands are reported in Supplemental Table S2. Application rates reported for the types of crops grown in our study area were consistent across the drained and intact wetlands we sampled and generally ranged from 29.7 to 33.5 kg P ha<sup>-1</sup>, 87.2 to 112.9 kg N ha<sup>-1</sup>, and 2.9 to 3.5 kg K ha<sup>-1</sup> in 2008, and from 20.0 to 31.3 kg P ha<sup>-1</sup>, 71.1 to 100.1 kg N ha<sup>-1</sup>, and 2.9 to 3.7 kg K ha<sup>-1</sup> in 2009. Nutrient applications rates were notably different at a few sites where the wetland was embedded in grassland (Site I3, no nutrient applications) or fields where flax (Site I6 in 2008) and peas (Sites S1 and S2 in 2009) were planted.

### Phosphorus Concentrations in Snow, Overland Runoff, and Intact Wetlands

The majority of runoff entering the intact and drained basins each year is from snowmelt flowing over frozen soil and crop residue. Snow samples were collected in March 2009 from transects at each study wetland that extended from the upland landscape position to the basin center position. Samples were placed in plastic bags and thawed in the laboratory, and volumes were recorded for each sample. Additionally, runoff water quality samples (all study wetlands) and surface water samples from intact wetlands were collected for nutrient analysis. Runoff samples were collected using triangular stainless steel 1.2-m<sup>2</sup> runoff trays. Three trays were deployed in each wetland basin, with all trays deployed at the fringe of the crop–wetland vegetation interface of the intact wetlands and along the historical fringe of drained wetland basins. Runoff samples generated within a wetland study basin were combined to form one composite sample to reflect the nutrient concentrations associated with

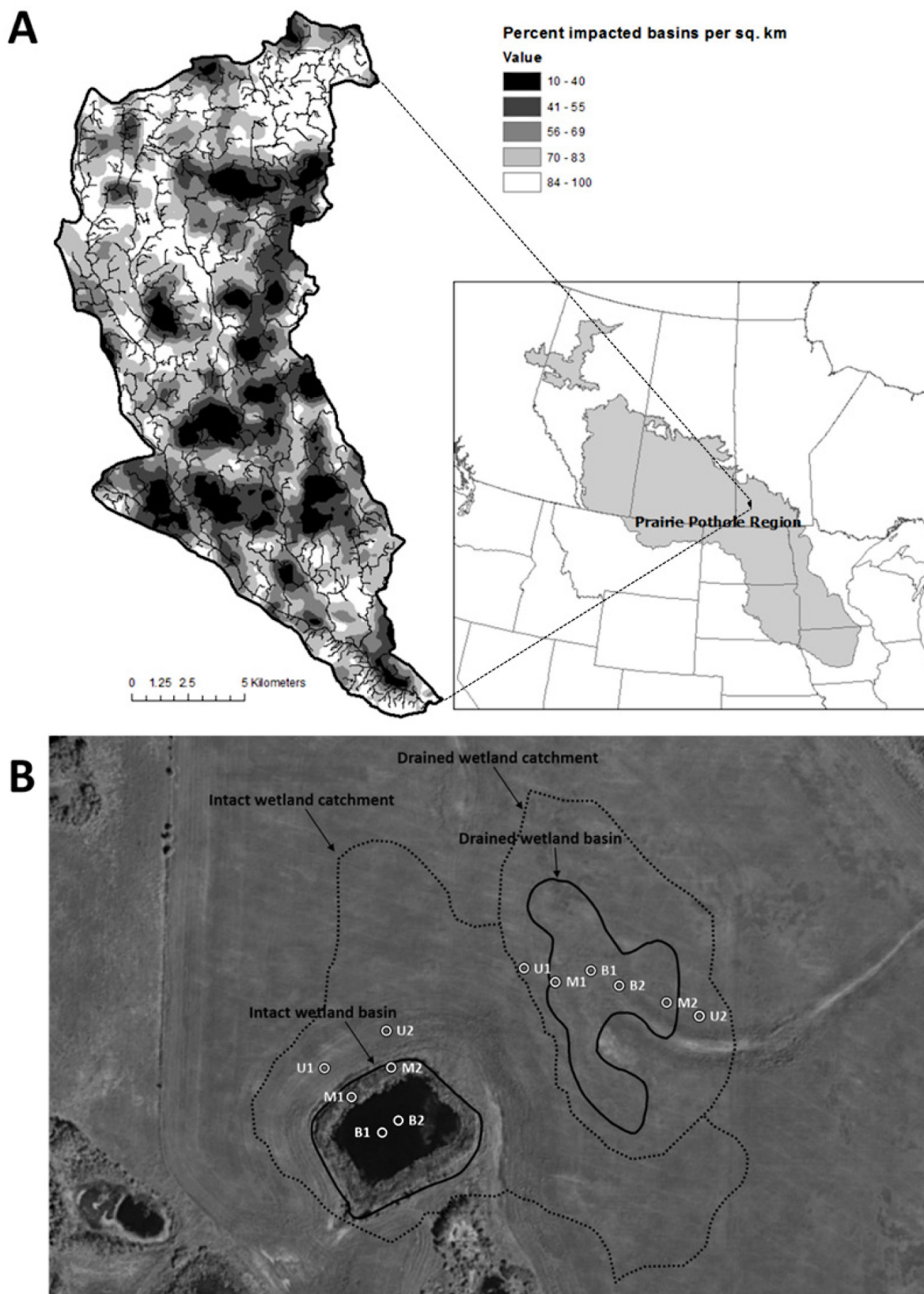


Fig. 1. (A) Location of the Broughton's Creek watershed and the percentage of wetlands basins affected. (B) Example of intact and drained wetland and duplicate soil-sediment sampling transects (B = basin center landscape position, M = midslope landscape position, U = upland landscape position).

runoff from the surrounding contributing areas. Water samples were also collected every second week from intact wetlands over the course of the 2008 and 2009 open-water seasons. Water samples were collected by taking a grab sample 10 cm below the

air-water interface from the side of a boat at the deepest point of the basin. All water samples (snow, runoff, and intact wetlands) were stored in the dark at 4°C until analysis. Samples were analyzed for total P and total dissolved P.



## Soil and Sediment Sampling

Two soil–sediment sampling transects were established at all 12 sites (Fig. 1B). Each transect was composed of an upland (non-wetland in both intact and drained sites), midslope (non-wetland in drained sites, wetland in intact sites), and basin center landscape position (non-wetland in drained sites, wetland in intact sites). Soil samples were taken in late September 2008 after crops were harvested. For each transect, at each unsubmerged landscape position, eight soil samples were collected using an Oakfield corer. The top 5 cm of each soil core from the eight samples were combined to form one composite soil sample. Sediment samples were collected at the basin center position (submerged landscape position) in each intact wetland from a boat using a handheld Watermark universal sediment corer. As for the soil cores, only the top 5-cm segment was collected from each sediment core. The sediment coring apparatus collected a larger volume of material relative to the Oakfield soil corer, and therefore only two sediment cores were required to generate a composite sample with enough sediment mass to complete all the required analyses. All samples were transported in a cooler to the laboratory, where they were stored at field moisture in the dark at 4°C and analyzed within 2 mo of being collected.

## Soil and Sediment Characteristics

Soil and sediment moisture and organic matter content were analyzed following the method of Dean (1974). All remaining soil and sediment analyses were conducted through the Department of Soil Science at the University of Manitoba following methods described in (Ige et al., 2005a). Mehlich-3 extractable P, Ca, Mg, Fe, Al, and Mn were determined by equilibrating 2.5 g of air-dried soil sample with 25 mL of Mehlich-3 extracting solution for 5 min and filtering through Whatman No. 40 filter paper (Mehlich, 1984). Total P was measured in soil and sediments by digesting samples with a  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$  mixture using the wet oxidation method described in Akinremi et al. (2003). Soil and sediment organic P was determined using the NaOH-EDTA (ethylenediaminetetraacetic acid) extraction procedure described in O'Halloran and Cade-Menun (2008). Bioavailable P, also known as Fe oxide-impregnated filter paper extractable P, was measured using Fe oxide-impregnated filter paper strips as described in Menon et al. (1989). The different soil extracts were analyzed colorimetrically for P using the molybdate blue method (Murphy and Riley, 1962). Extractable Ca, Mg, Fe, Al, and Mn were determined by inductively coupled plasma atomic emission spectrometry (Thermo iCAP 6500 Duo).

## Phosphorous Sorption Isotherms

Prior to conducting the sorption isotherm experiments, large visible pieces of plant debris and stones (when encountered) were removed from the samples using tweezers, and the remaining soil–sediment was homogenized. Fresh soil–sediment (1.0 g) was added to eight 50-mL Pyrex vials containing 25 mL of 0.01 M  $\text{CaCl}_2$  with seven increasing P concentrations of 0, 0.2, 0.5, 1.0, 5.0, 10.0, 20.0  $\text{mg P L}^{-1}$  ( $\text{KH}_2\text{PO}_4$ ). For each sample, one of the previous concentrations was randomly selected for duplicate analysis. Vials were placed on an end-over-end LabquakeR Thermolyne Shaker (eight rotations per minute) for 24 h in the dark at 20°C. Preliminary laboratory experiments demonstrated

that equilibrium was reached within 24 h. Equilibrated samples were immediately filtered on preweighed Whatman GF/C filter papers. With the filtrate removed, the Pyrex vials were rinsed several times to collect the entire suspended sample on the filter paper. Filter papers were dried in a desiccator for 24 h, transferred to a drying oven for 24 h at 100°C, and then weighed to determine the dry weight of the sample. Filtrate was analyzed immediately for soluble reactive P using the molybdenum ascorbic acid method (Stainton et al., 1978).

The total amount of P sorbed by soil–sediment ( $S$ ) was calculated using the following equation from (Kang et al., 2009):

$$S = S_o + S' \quad [1]$$

where  $S_o$  is an estimate of the P originally adsorbed ( $\text{mg kg}^{-1}$ ), and  $S'$  is the amount of added P sorbed by the soil and sediment ( $\text{mg kg}^{-1}$ ). The  $S'$  in soil and sediment was calculated by

$$S' = (C_o V - C_i V) / M \quad [2]$$

where  $C_o$  is the concentration of P added ( $\text{mg L}^{-1}$ ),  $V$  is the volume of liquid (L),  $C_i$  is the concentration of P in solution after 24-h equilibration ( $\text{mg L}^{-1}$ ), and  $M$  is the mass of dry soil and sediment (kg). We estimated  $S_o$  using the modified Freundlich equation with the exponent 1/3, as expressed by (Tolner and Füleky, 1995)

$$S' = k + C^{1/3} - S_o \quad [3]$$

where  $k$  is a dimensionless constant that gives the steepness of the slope for the sorption curve, and  $C$  is the P concentration at equilibrium ( $\text{mg L}^{-1}$ ). We chose to estimate the  $S_o$  using this equation based on previous studies (Tolner and Füleky, 1995; Anas et al., 1997) that concluded that the modified Freundlich equation was the most suitable for estimating this parameter compared with the Langmuir and two-surface Langmuir equations. Estimates of  $S_o$  were obtained by fitting the sorption data to the modified Freundlich isotherm equation using SigmaPlot version 11.0 for Windows (Systat Software, 2008).

After determining values for  $S_o$ , these were added to values of  $S'$  that were measured. Phosphorus sorption isotherms were modeled using the two-surface Langmuir equation as described in (Sui and Thompson, 2000; Bolster and Hornberger, 2007):

$$S_{\max} = S_{\max1} K_1 C / (1 + K_1 C) + S_{\max2} K_2 C / (1 + K_2 C) \quad [4]$$

where  $S_{\max}$  is the maximum P sorbed by soil ( $\text{mg kg}^{-1}$ ),  $S_{\max1}$  and  $S_{\max2}$  ( $\text{mg kg}^{-1}$ ) are the high- and low-affinity maxima of P sorption,  $K_1$  and  $K_2$  ( $\text{L mg}^{-1}$ ) are related to high- and low-affinity binding energies of P sorption, and  $C$  is the P concentration at equilibrium ( $\text{mg L}^{-1}$ ). Estimates of  $S_{\max1}$ ,  $S_{\max2}$ ,  $K_1$ , and  $K_2$  were obtained by fitting the sorption data to the two-surface Langmuir isotherm equation using SigmaPlot version 11.0 for Windows (Systat Software, 2008).

Quantity/intensity diagrams as described in (Sui and Thompson, 2000) were plotted to calculate the  $\text{EPC}_o$ , as well as the PEBC. The  $\text{EPC}_o$  is defined as the aqueous-phase P concentration at which there is no net exchange of P between water and soil–sediments. Soils–sediments will act as a sink for P when  $\text{EPC}_o$  is lower than P concentrations (dissolved) in overlying surface water; when  $\text{EPC}_o$  is higher than concentrations in

overlying surface water, soils–sediments will act as a source of P. The PEBC is a measure of a soil–sediment's ability to sorb further P additions, thereby reducing P concentration changes in water. Only data from the four lowest initial P concentrations (0.0, 0.2, 0.5, and 1.0 mg L<sup>-1</sup>) from each sorption isotherm were used. The intercept of the line in the quantity/intensity diagrams with the *x*-axis represents the EPC<sub>0</sub>, whereas the slope of the line represents the PEBC.

## Statistical Analyses

Mixed models (split-plot analyses) in SAS 9.2 (SAS Institute, 2010) were used for analyzing soil and sediment chemical properties, as well as P sorption parameters. Wetland ID (1, 2, 3, 4, 5, or 6) was included as a random effect, whereas wetland type (drained or intact), position (basin, midslope, or upland) and wetland × position were treated as fixed effects. Where residual analyses revealed heteroscedastic and non-normal errors, the response was natural log-transformed. Statistical contrasts were further used to help interpret significant fixed effects using the Tukey–Kramer adjustment. Simple Pearson correlations were used to examine the relationships between the various soil–sediment characteristics that we measured and the P sorption parameters that were generated from the P isotherm experiments. Correlations were compared at three levels (all landscape positions, submerged landscape positions, and nonsubmerged landscape positions). Separating submerged landscape positions (those continuously inundated [intact-basin center, *n* = 6] from nonsubmerged landscape positions [all other positions, *n* = 30]) was deemed important due the differences in redox conditions expected under contrasting moisture and O<sub>2</sub> regimes.

## Results and Discussion

### Phosphorus Concentrations in Snow, Overland Runoff, and Intact Wetlands

Total P concentrations in snow samples were generally low and consistent across all wetland sites, ranging from 0.009 to 0.026 mg L<sup>-1</sup> (Supplemental Table S3). Conversely, runoff samples were, on average, roughly two orders of magnitude greater than those measured in snow samples and ranged from 0.38 to 1.77 mg L<sup>-1</sup> (Supplemental Table S3). It is interesting to note that the lowest runoff concentrations of both total and dissolved P were recorded at the intact wetland site (I3), which was embedded in grassland and did not receive any nutrient applications. Mean total P concentrations measured in intact wetlands ranged from 0.06 to 1.19 mg L<sup>-1</sup> in 2008 and from 0.19 to 1.25 mg L<sup>-1</sup> in 2009 (Supplemental Fig. S1). As was the case for runoff concentrations, the lowest mean total P and total dissolved P concentrations occurred at the intact wetland site (I3) embedded in grassland. Phosphorus concentration in surface runoff across all sites and within intact wetlands almost always exceeded P guidelines for hypereutrophic systems.

### Chemical Characteristics of Soils and Sediments

As expected, chemical properties of soil and sediments differed between intact wetlands and drained wetlands (Table 1), especially between landscape positions that were always submerged (intact-basin center) and those that were rarely or never submerged (all other landscape positions). Moisture content (range

= 59.7–82.4%) and organic matter content (range = 17.9–36.2% dry wt.) for the intact-basin center landscape position were significantly higher than those at all other landscape positions (range = 4.6–21.7% and 7.4–27.2% dry wt. for moisture and organic matter, respectively; Table 1). More specifically, for wetland basin centers, moisture content (*p* < 0.0001) and organic matter content (*p* < 0.0001) were significantly higher in intact wetlands relative to drained wetlands. It is logical that organic matter content is higher in intact wetlands relative to drained wetlands given that submerged soils in the intact wetlands would often be anoxic and have reduced rates of decomposition, favoring the accumulation of organic matter, and this has been observed in the PPR (Badiou et al., 2011; Tangen et al., 2015).

Extractable soil and sediment cations of both drained and intact wetlands were dominated by Ca and Mg, consistent with the calcareous chernozemic soils of the study area (Pennock et al., 2010) and what has been reported for similar wetlands in the PPR (Arndt and Richardson, 1989). Mehlich-3-extractable Ca concentrations ranged between 3024 and 9537 mg kg<sup>-1</sup>, and Mehlich-3-extractable Mg concentrations ranged between 500 and 8645 mg kg<sup>-1</sup>. Concentrations of Ca were similar to those reported for alkaline soils in Manitoba (Ige et al., 2005b, 2008; Amarawansa et al., 2016). There was no statistically significant interaction between wetland type and landscape position (*p* = 0.3801), and mean concentrations were not significantly different between drained and intact wetland sites, as well as across landscape positions (Table 1). Although not statistically significant, Ca concentrations at the midslope position of the intact wetlands were notably higher than at all other landscape positions. This result seems to be driven by abnormally high concentrations that were measured at two of the intact wetlands. We surmise that these higher concentrations may be due to increased evaporation along the wetland edge (midslope position of intact wetlands) that can cause a buildup of CaCO<sub>3</sub> in the soils along wetland margins (Seelig and DeKeyser, 2006). Unlike Ca, there was a statistically significant interaction between wetland type and position (*p* = 0.0043). In addition, Mehlich-3-extractable Mg was significantly higher in intact wetlands than in drained wetlands for both the basin center (*p* = 0.0045) and midslope (*p* = 0.0007) landscape positions (Table 1) and was much higher than previously reported for alkaline soils in Manitoba (Ige et al., 2005b, 2008; Amarawansa et al., 2016). As mentioned above, high rates of evaporation may explain the elevated concentration of Mg in the wetland itself (basin center location), as well as in the soils adjacent to the intact wetlands (midslope location). It is also possible that these higher concentrations of Mg are related to the rapid leaching of Mg from wetland plants (Magee, 1993) and/or are because more Mg is cycled in surface soils by plants in semiarid regions (White, 1971) resulting in subsequent accumulation in wetland soils. The implications for the higher Mg concentrations found in intact wetlands (basin center position and midslope position) is important because Mg can play an important role in P cycling in alkaline soils (Racz and Soper, 1967). For example, increased availability of Mg can result in the preferential formation of more soluble amorphous P compounds bound with Mg and Ca, rather than the formation and precipitation of apatite and other more stable crystalline Ca-P compounds (Martens and Harriss, 1970; Jenkins et al., 1971; Ann et al., 1999).

**Table 1. Selected chemical properties (mean and SE) of sediments and soils collected from different landscape positions in six intact and six drained wetland basins in the Broughton's Creek watershed.**

Wetland catchment position	Moisture	Organic matter	Mehlich-3 Al	Mehlich-3 Ca	Mehlich-3 Fe	Mehlich-3 Mg	Mehlich-3 P	Bioavailable P	Organic P	Total P
	%	% dry wt.	mg kg <sup>-1</sup>							
Intact–basin center	71.6a† (0.5)	30.1a (1.5)	78.4a (10.1)	5295a (283)	674a (93)	2209a (210)	20.6a (2.0)	5.6a (1.3)	403ab (18)	852a (40)
Intact	15.0b (1.6)	16.5b (1.9)	28.4ab (9.2)	8343a (2280)	47cd (5)	3009a (759)	46.1a (10.0)	33.0bc (7.9)	450a (15)	870a (51)
Intact–upland	12.2b (2.2)	12.0b (1.5)	81.9a (25.0)	4392a (211)	50cd (4)	914b (211)	33.3a (5.9)	24.8bc (6.2)	424ab (27)	756a (47)
Drained–basin center	13.2b (1.2)	13.1b (1.6)	4.6b (1.8)	5527a (479)	178b (29)	936b (61)	80.6a (12.2)	64.2b (7.1)	322b (28)	789a (46)
Drained–midslope	14.6b (1.2)	13.3b (0.5)	47.4ab (25.7)	4985a (336)	78c (10)	785b (34)	33.3a (4.9)	27.8c (5.2)	388ab (17)	693a (38)
Drained–upland	12.6b (1.4)	10.8b (0.7)	69.8ab (31.5)	5126a (393)	41d (3)	745b (77)	31.2a (5.6)	24.6ac (7.0)	392ab (21)	738a (45)

† Different letters indicate statistically significant differences ( $p < 0.05$ ).

Mehlich-3-extractable Al concentrations were generally quite variable ( $<0.01$ – $341$  mg kg<sup>-1</sup>) but within the range reported by others for alkaline soils in Manitoba (Ige et al., 2005b, 2008; Amarawansa et al., 2016). Mean concentrations were fairly similar between drained and intact wetlands, as well as across landscape positions, with the exception of the drained-basin center position where the mean concentration was significantly lower than in intact wetlands ( $p = 0.001$ , Table 1). Additionally, mean Mehlich-3-extractable Al concentrations were significantly different ( $p = 0.019$ ) across the drained wetland sites and appeared to decrease from the upland landscape position to the basin center landscape position (Table 1). Mehlich-3-extractable Fe concentrations ranged between 26 and  $1454$  mg kg<sup>-1</sup>. Statistical contrasts revealed that there were significant differences among positions for both drained ( $p < 0.0001$ ) and intact wetlands ( $p < 0.0001$ ), with the basin center landscape position having higher concentrations than the midslope and upland landscape positions (Table 1). As was the case for Al, Fe concentrations for the basin center position of the intact wetlands and drained wetlands were significantly different ( $p < 0.0001$ ), and statistical contrasts revealed that concentrations were significantly higher in intact wetland basins ( $p < 0.001$ , Table 1). Similar to what was observed for Mg, Fe concentrations in intact wetlands for the basin center position were much higher than values reported for alkaline soils in Manitoba (Ige et al., 2005b, 2008; Amarawansa et al., 2016). Higher concentrations of both Al and Fe are likely associated with the increased organic matter content in sediments of the intact wetlands, which can result in strong organomineral associations through ligand exchange and/or polyvalent cation bridges (Lützow et al., 2006). Other reasons for elevated concentrations of Fe in intact wetland sediments may be due to accumulation of ferrous sulfide as a result of sulfate reduction or formation of Fe plaques associated with the roots of wetland plants (Kadlec and Wallace, 2009). However, the most likely reason for elevated Fe in intact wetlands is that Gleysolic soils are naturally rich in Fe (Bedard-Haughn, 2011). Although anoxic conditions in intact wetlands produce soluble and mobile ferrous Fe that could be lost from the system, this does not occur in geographically isolated prairie wetlands that have no surface outlets and little contact with groundwater. Even under fill-and-spill events, where water could potentially be lost from the wetland, Fe is likely retained in the system, as these events typically occur in the spring when water temperatures are low and the water column has been reoxygenated and is near saturation, resulting in the precipitation of dissolved Fe species. Conversely, the lower Fe concentration for the drained wetland basin center position than in the intact wetland is likely due to the production of soluble

ferrous Fe during anoxic periods resulting from saturated soil conditions that occur in these depressions during the spring snowmelt. Subsequently, the soluble Fe is removed from the system via the surface channel used to drain the wetland, reducing the pool of Fe in the basin center of drained wetlands.

Mehlich-3 P concentrations ranged between 4.7 and  $148.5$  mg kg<sup>-1</sup>. There were no statistically significant interactions between wetland type and position. However, the concentration of Mehlich-3 P appeared to be higher in the basin center landscape position of drained wetlands than in intact wetlands (Table 1). Concentrations across all landscape positions and both wetland types were within the range previously reported for alkaline soils of Manitoba (Ige et al., 2005b; Amarawansa et al., 2016). However, the mean Mehlich-3 P concentration for the basin center position of drained wetlands was roughly double the mean concentration for alkaline soils of Manitoba and was nearly 2.8 times greater than the concentration reported for the Newdale soil series (the dominant soil series in the Broughton's Creek watershed) by Amarawansa et al. (2016). The interaction between wetland type and position was not statistically significant for organic P ( $p = 0.3889$ ) or total P ( $p = 0.1854$ ) (Table 1). Bioavailable P was significantly higher at the basin center landscape position than at the upland and midslope positions for the drained wetland basins (Table 1), and this may be due to higher mineralization rates of organic matter after drainage occurs. Additionally, bioavailable P was an order of magnitude lower for the basin center landscape position in intact wetlands than in drained wetlands. This would suggest that wetland drainage results in the conversion of organic P to bioavailable P, which can easily be exported in drainage waters. This is supported by a number of other studies where the rewetting of dried or drained soils resulted in increases in bioavailable P concentrations (Bostic and White, 2007; Achat et al., 2012; Kröger et al., 2012; DeLonge et al., 2013). Other studies have demonstrated that reducing the hydraulic residence time of a wetland, or increasing the variability of the hydraulic residence time of a wetland, which leads to alternating drying and rewetting of sediments, also increased the amount of bioavailable P (Gilbert et al., 2014; Smith and Jacinthe, 2014; Attygalla et al., 2016).

### Phosphorus Sorption Parameters and Correlations with Soil and Sediment Characteristics

The two-surface Langmuir equation that we used shows a good fit to the P adsorption data from drained and intact wetland soil and sediments across all landscape positions. Examples of the



adsorption isotherms for the basin center position of drained and intact wetlands are presented in Fig. 2. Phosphorus sorption characteristics derived from the two-surface Langmuir equation for drained and intact wetland basins are given in Table 2.

The  $S_o$  ranged from 18 to 184 mg kg<sup>-1</sup>, and statistical contrasts revealed that there were significant differences among landscape positions within the intact ( $p < 0.0001$ ) and drained ( $p = 0.0002$ ) wetland basins. In both cases,  $S_o$  was significantly higher at the basin center landscape positions relative to other landscape positions (Table 2). Across all landscape positions  $S_o$  was significantly correlated with organic matter content, Mehlich-3 Mg, Mehlich-3 Fe, bioavailable P, and total P (Table 3). These correlations were notably stronger when only the nonsubmerged landscape positions were considered, with Mehlich-3 Ca, Mehlich-3 P, and organic P also being significantly correlated with  $S_o$ . For submerged intact wetland basin centers  $S_o$  was negatively correlated with Mehlich-3 P and bioavailable P. The chemical characteristics for both the basin center position of drained (nonsubmerged) and intact (submerged) wetlands, although different, seem to favor higher values of  $S_o$ . This may

be due to topographic influences that would tend to concentrate soluble and mobile P in these depositional environments.

The  $S_{max1}$ ,  $S_{max2}$ , and  $S_{max}$  ranged from 96 to 544, 221 to 3355, and 266 to 3527 mg kg<sup>-1</sup>, respectively, and values for upland soils (non-wetland soils) were similar to those reported for alkaline soils of Manitoba by Ige et al. (2005b), and for pastureland soils in Iowa (Hongthanat, 2010). The  $S_{max1}$  was significantly different among landscape positions for intact ( $p < 0.0001$ ) and drained wetlands ( $p = 0.0029$ ), with the basin center landscape positions having higher values than the midslope and upland landscape positions (Table 2). Between wetland types,  $S_{max1}$  was significantly higher for the basin center ( $p < 0.0001$ ) and midslope ( $p = 0.0007$ ) landscape positions in intact wetlands than in drained wetlands. The  $S_{max2}$  and  $S_{max}$  were also significantly different among landscape positions for intact wetlands ( $p < 0.0001$  and  $0.0001$ , respectively), with the basin center landscape positions having higher values than the midslope and upland landscape positions (Table 2). However, unlike  $S_{max1}$ , there were no statistical differences between landscape positions in the drained wetland sites for  $S_{max2}$  and  $S_{max}$ . As was the case for  $S_{max1}$ ,  $S_{max2}$  and  $S_{max}$  were significantly higher

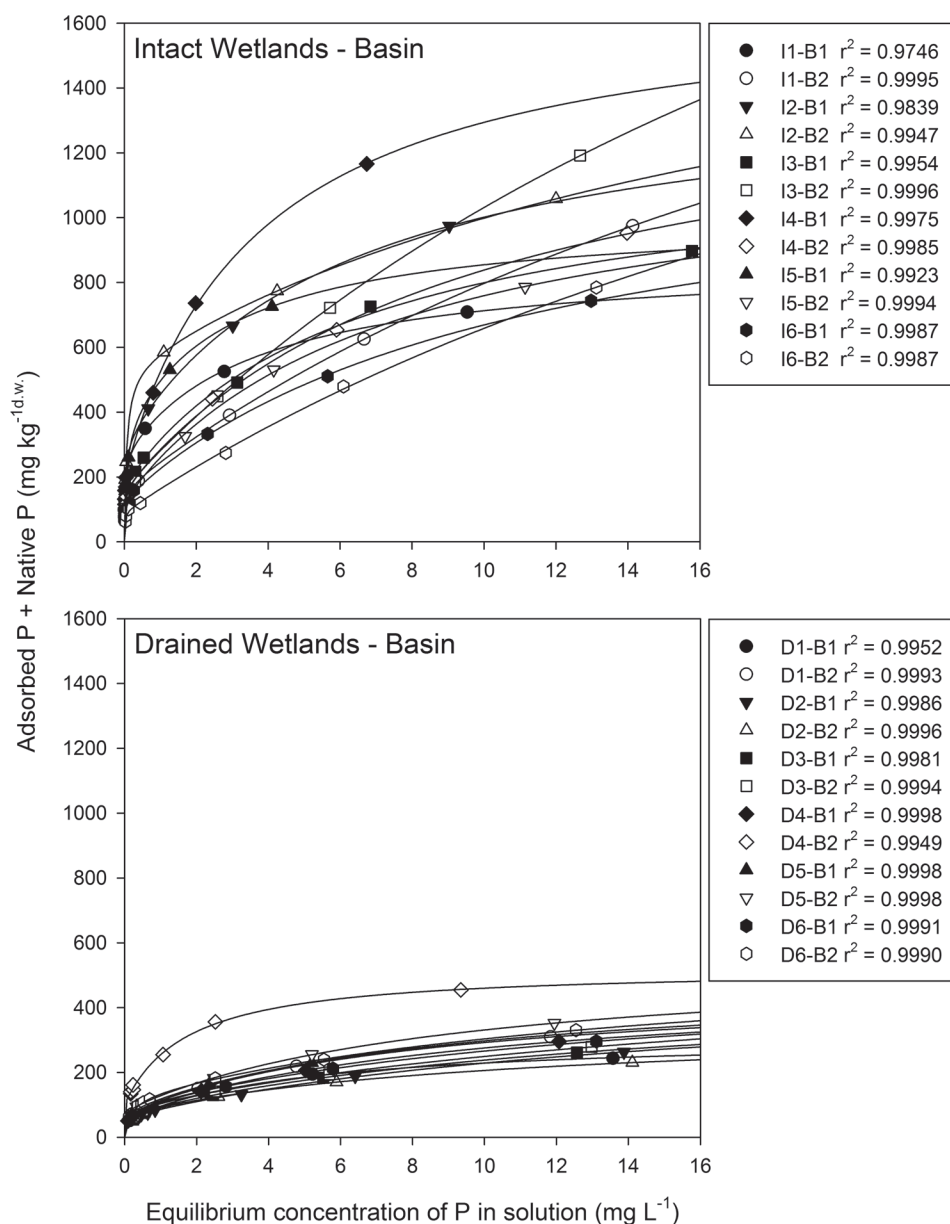


Fig. 2. Phosphorus sorption isotherms for duplicate soil-sediment samples collected from the basin center landscape position of drained (D1-D6) and intact wetlands (I1-I6) fitted using the two-surface Langmuir model.

**Table 2. Phosphorus sorption and buffering parameters (mean and SE) of sediments and soils collected from different landscape positions in six intact and six drained wetland basins in the Broughton's Creek watershed.**

Wetland catchment position	Parameter†							
	$S_o$	$S_{max1}$	$S_{max2}$	$S_{max}$	$K_1$	$K_2$	$EPC_o$	PEBC
	mg kg <sup>-1</sup>				L mg <sup>-1</sup>		mg kg <sup>-1</sup>	L kg <sup>-1</sup>
Intact–basin center	108a† (11)	227a (36)	1525a (241)	1752a (232)	39.7a (3.3)	0.076a (0.01)	0.021a (0.005)	1394a (541)
Intact	79a (9)	109b(24)	715b (87)	824b (107)	23.8ab (5.3)	0.077a (0.02)	0.275ab (0.081)	103b (47)
Intact–upland	43b (3)	54b (3)	439c (30)	493c (32)	28.1ab (1.8)	0.099a (0.01)	0.117 ab (0.032)	73b (8)
Drained–basin center	80a (8)	80b (8)	410bc (23)	492bc (27)	17.2b (1.6)	0.101a (0.02)	0.343b (0.061)	84b (17)
Drained–midslope	46b (5)	53b (4)	396c (38)	449c (40)	30.6ab (2.6)	0.081a (0.01)	0.185ab (0.039)	82b (26)
Drained–upland	41b (5)	51b (3)	435c (34)	486c (36)	36.1ab (1.3)	0.086a (0.01)	0.072ab (0.018)	79b (11)

†  $S_o$ , originally sorbed P;  $S_{max1}$ , high-affinity maximum of P sorption;  $S_{max2}$ , low-affinity maximum of P sorption;  $K_1$ , high-affinity binding energy of P sorption;  $K_2$ , low-affinity binding energy of P sorption;  $EPC_o$ , equilibrium P concentration; PEBC, P equilibrium buffering capacity.

‡ Different letters indicate statistically significant differences ( $p < 0.05$ ).

**Table 3. Correlation coefficients between relevant soil and sediment constituents and P sorption parameters of drained and intact wetland basins.**

Parameter†	Organic matter	Mehlich-3 Al	Mehlich-3 Ca	Mehlich-3 Fe	Mehlich-3 Mg	Mehlich-3 P	Bioavailable P	Organic P	Total P
All landscape positions									
$S_o$	0.62***	−0.12	0.27	0.57***	0.61***	0.33	−0.11*	0.14	0.58**
$S_{max1}$	0.76***	0.09	0.23	0.69***	0.60***	−0.02	−0.42*	0.02	0.47**
$S_{max2}$	0.80***	0.22	0.14	0.62***	0.77***	−0.23	−0.56***	0.22	0.49**
$S_{max}$	0.81***	0.19	0.15	0.63***	0.76***	−0.21	−0.56***	0.20	0.48**
$K_1$	−0.33	0.02	−0.15	−0.09	−0.19	0.65***	0.65***	0.12	0.09
$K_2$	−0.24	0.25	−0.17	−0.07	0.04	0.13	−0.35**	0.13	0.00
$EPC_o$	−0.51**	−0.29	−0.08	−0.32	−0.18	0.71***	0.78***	0.09	0.05*
PEBC	0.75***	0.20	0.26	0.82***	0.44**	−0.44**	−0.65***	−0.02	0.17
Submerged positions									
$S_o$	0.18	−0.77	0.42	−0.33	0.33	−0.85	−0.63*	0.12	−0.18
$S_{max1}$	−0.36	−0.26	−0.01	−0.06	−0.74	−0.51	0.16	−0.47	−0.30
$S_{max2}$	−0.28	0.39	0.05	0.26	0.50	−0.14	−0.11	−0.17	0.32
$S_{max}$	−0.59	−0.04	0.00	0.17	0.22	−0.68	−0.30	−0.42	−0.08
$K_1$	−0.13	0.10	−0.39	0.64	−0.93**	−0.29	0.71	−0.25	−0.66
$K_2$	−0.19	0.82*	−0.24	0.73	−0.03	0.06	0.50	−0.16	0.02
$EPC_o$	0.80*	−0.32	0.63	0.39	0.63	−0.17	−0.02	0.70	0.11
PEBC	0.20	−0.47	0.61	0.85*	−0.40	−0.41	0.31	0.07	0.05
Nonsubmerged positions									
$S_o$	0.82***	0.05	0.89***	0.81***	0.89***	0.86***	0.78***	0.88***	0.91***
$S_{max1}$	0.86***	0.12*	0.94***	0.83***	0.94***	0.81***	0.70**	0.92***	0.96***
$S_{max2}$	0.89***	0.26*	0.97***	0.76***	0.97***	0.68***	0.59***	0.97***	0.98***
$S_{max}$	0.89***	0.25*	0.97***	0.77***	0.97***	0.70***	0.60***	0.97***	0.98***
$K_1$	−0.52**	−0.25	−0.54**	−0.34	−0.50**	0.04	0.12	−0.50**	−0.50**
$K_2$	0.62***	0.23	0.71***	0.47**	0.72***	0.55**	0.54**	0.74***	0.73***
$EPC_o$	−0.29	−0.38*	−0.31	−0.15	−0.23	0.30	0.37*	−0.28	−0.26
PEBC	0.81***	0.25	0.87***	0.79***	0.81***	0.44*	0.32	0.84***	0.85***

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

†  $S_o$ , originally sorbed P;  $S_{max1}$ , high-affinity maximum of P sorption;  $S_{max2}$ , low-affinity maximum of P sorption;  $K_1$ , high-affinity binding energy of P sorption;  $K_2$ , low-affinity binding energy of P sorption;  $EPC_o$ , equilibrium P concentration; PEBC, P equilibrium buffering capacity.

for the basin center ( $p < 0.000$  and  $0.0001$ , respectively) and midslope ( $p = 0.0019$  and  $0.0009$ , respectively) landscape positions in intact wetlands than in drained wetlands. The  $S_{max1}$ ,  $S_{max2}$ , and  $S_{max}$  across all landscape positions were significantly correlated with organic matter content and total P (Table 3). This was also the case for nonsubmerged landscape positions. However, the  $S_{max1}$ ,  $S_{max2}$ , and  $S_{max}$  were not significantly correlated with sediment chemistry for the submerged landscape position (Table 3). Our inability to model a relationship for the submerged sites might be a result of the limited number of submerged sites ( $n = 6$ ) relative to the nonsubmerged sites ( $n = 30$ ). Overall,  $S_{max}$  was roughly 3.5

and 1.8 times higher for the basin center and midslope landscape position in intact wetlands than in drained wetlands. The range of maximum P sorption capacity we estimated for intact wetland sediments was similar to values previously reported for reservoirs, shallow polymictic lakes, pelagic sediments of subtropical palustrine forested wetlands (Lane and Autrey, 2016), stratified lakes (Cyr et al., 2009), and riverine wetlands (Bridgman et al., 2001) but were generally much higher than those reported for sediments of subtropical palustrine emergent wetlands (Lane and Autrey, 2016), stratified lakes (Cyr et al., 2009), riparian soils and stream sediments (Reddy et al., 1998; Dunne et al., 2006b; Heiberg et al.,



2010; Agudelo et al., 2011), estuarine sediments (Sundareshwar and Morris, 1999; Pant and Reddy, 2001; Wang and Li, 2010), constructed wetlands (Jamieson et al., 2002; Lai and Lam, 2009), and eutrophic lakes (Olila and Reddy, 1993; Zhou et al., 2005; Belmont et al., 2009; Huang et al., 2015; Zhang et al., 2016). One possible explanation for the higher P sorption capacity observed in our wetland soils relative to the surrounding uplands may be due to the large biomass of submerged macrophytes present in these systems. Jin et al. (2013) concluded that the presence of plant debris in systems with anoxic sediments enhanced P sorption and promoted P stabilization in sediments via microbial activity. Additionally, organic matter content is significantly higher in intact wetlands (basin center position) and potentially explains the elevated sorption capacity due to complexing of P with Fe and Mg compounds present in organic matter (Lane and Autrey, 2016).

The calculation of  $EPC_0$  according to P sorption isotherms is a widely used methodology for assessing the risk of P pollution from different soils (Pöthig et al., 2010). The  $EPC_0$  in our study ranged from 0.001 to 0.799  $\text{mg L}^{-1}$  across all sites and landscape positions. More specifically, the mean  $EPC_0$  for sediments from the basin center of intact wetlands (0.021  $\text{mg L}^{-1}$ , Table 2) is similar to those reported from other freshwater sediments (Sundareshwar and Morris, 1999; Belmont et al., 2009; Cyr et al., 2009; Lai and Lam, 2009; McDaniel et al., 2009) and constructed wetlands (Lai and Lam, 2009; Palmer-Felgate et al., 2011) but is much lower than those for subtropical wetland soils (Bhadha et al., 2010; Nair et al., 2015). The interaction between wetland type and landscape position was statistically significant ( $p < 0.0001$ ). Furthermore, statistical contrasts revealed that there was a significant difference among landscape positions within the drained wetlands ( $p = 0.0003$ ), where  $EPC_0$  was higher for the basin center landscape position than for the midslope and upland landscape positions (Table 2). Conversely,  $EPC_0$  values for intact wetland basins were lower ( $p < 0.0001$ ) for the basin center landscape position than the midslope and upland landscape positions (Table 2), resulting in the significant wetland type  $\times$  landscape position interaction. There was a significant difference between wetland types for the basin center landscape position ( $p < 0.0001$ ), with  $EPC_0$  values more than an order of magnitude higher in drained wetlands than in intact wetlands (Table 2). Across all landscape positions,  $EPC_0$  was significantly positively correlated with bioavailable P and Mehlich-3 P and negatively correlated with organic matter content of the soil-sediment (Table 3). Although a few parameters were significantly correlated with  $EPC_0$  for nonsubmerged landscape positions, correlation coefficients were all  $< 0.5$  (Table 3). Conversely, for submerged intact wetland basin centers,  $EPC_0$  was significantly correlated with organic matter content of the sediments.

Relative to the concentrations of P measured in snow collected from our study sites (mean = 0.014  $\text{mg L}^{-1}$ , range = 0.005–0.023  $\text{mg L}^{-1}$ ; Supplemental Table S3), the  $EPC_0$  of intact wetland basin centers was always lower or similar, indicating that these would have a low risk of P export. Conversely,  $EPC_0$  of drained wetland basin centers were an order of magnitude greater than concentrations measured in snow. As a result, the drained wetland basin centers have a high risk of exporting P during the snowmelt period. Surface runoff P concentrations (mean = 1.05  $\text{mg L}^{-1}$ , range = 0.029–9.34  $\text{mg L}^{-1}$ ; Supplemental Table S3) were also compared with  $EPC_0$  and were generally higher than  $EPC_0$ . This is not surprising given

that runoff samples were collected during the spring runoff period after water generated from snowmelt and precipitation interacted with thawing surface soils. However, 23% of the individual runoff samples collected had total dissolved P concentrations below the mean  $EPC_0$  for drained wetland basin centers, whereas the mean  $EPC_0$  for intact wetland basin centers was well below the concentrations measured in all runoff samples. This also suggests that drained wetlands are a greater risk for P pollution than intact wetlands. Lastly, monitoring of intact wetland water quality over the study period indicated that  $EPC_0$  for the most part were well below the total dissolved P concentrations across all sites (Supplemental Fig. S1). This would indicate that the intact wetlands we monitored were almost always a sink for P. In all, these results suggest that intact wetland sediments (basin center position) were likely a sink for P, whereas drained wetland soils (basin center position) likely behave as sources of P, and that the historical and ongoing surface drainage of prairie wetlands is potentially resulting in greater risk of P pollution to aquatic ecosystems in the Canadian Prairies.

The PEBC was significantly different among landscape positions for intact wetlands ( $p < 0.0001$ ), with the basin center landscape positions having higher values than the midslope and upland landscape positions (Table 2). There were no differences among landscape positions within the drained wetland sites. The PEBC was significantly higher for the basin center ( $p < 0.0001$ ) landscape positions in intact wetlands than in drained wetlands (Table 2). Given this finding, it appears that PEBC is significantly higher for sites that are submerged. In fact, PEBC was more than an order of magnitude greater for the intact wetlands basin center position (submerged sites) than for all other landscape positions across both wetland types. Correlation coefficients between soil-sediment characteristics and P sorption parameters (Table 3) indicate that PEBC is significantly positively correlated to Mehlich-3-extractable Fe concentrations. The PEBC values at our nonsubmerged sites (midslope and upland landscape positions) were similar to values reported for biosolids-amended soils in Iowa (Sui and Thompson, 2000), as well as for palustrine emergent wetland soils in agricultural regions of Florida (Lane and Autrey, 2016). Conversely, PEBC from the basin center position in intact wetlands in our study were roughly double the highest value recorded for wetlands in Florida and were more than an order of magnitude greater than those reported for palustrine emergent wetlands embedded in agricultural lands of the same region (Lane and Autrey, 2016). Although our sample size was fairly small ( $n = 6$ ), our results indicate that intact prairie wetlands have a relatively strong P buffering capacity, and this should be investigated further across a larger geographic extent. This suggests that maintaining intact wetlands in agricultural landscapes could help buffer against future losses of P. This is particularly important, given that non-point-source P pollution is increasing and negatively affecting water quality throughout the Canadian Prairies (Tiessen et al., 2010; Corriveau et al., 2013; Mekonnen et al., 2017).

## Conclusions

This study indicates some significant differences in soil and sediment characteristics and P sorption parameters between intact wetlands and drained wetlands, particularly for the basin center position. Overall, differences in chemical characteristics appeared

to be driven by whether or not a particular landscape position within a wetland was saturated or submerged. This is not unexpected given that oxidation–reduction potentials of submerged sites will be significantly different than those situated in more aerobic environments. In particular, organic matter, Mehlich-3 Fe and Mehlich-3 Mg were notably higher for submerged intact wetland basin centers. Similarly, the basin center and midslope landscape positions of intact wetlands appeared somewhat enriched (although not significantly) with regards to organic P and total P as a result of the chemical differences noted above, as well as due to the fact that, in their intact state, these wetlands are geographically isolated and act as strong depositional environments. Furthermore, intact wetlands also had higher P sorption capacities, as well as buffering capacities as demonstrated by the isotherm experiments. When taken together, this information suggests that intact prairie wetlands may be effective sinks for P, indicating they can potentially play an important role in mitigating nonpoint-source pollution in landscapes where these systems are abundant, such as the PPR. Conversely, the higher bioavailable P and EPC<sub>0</sub> suggest that drained prairie wetlands may be a high risk for P export and important critical source areas within prairie watersheds. Lastly, the fact that total P concentrations are similar between intact and drained wetlands indicates that increases in the risk of P pollution (as measured by differences in EPC<sub>0</sub> and PEBC) associated with drained wetlands are a result of conversion of immobile P to mobile forms that are readily bioavailable.

Future research should focus on examining P sorption capacities and buffering capacities in intact and drained wetlands across a range of soil types. Additionally, the speed at which P mobilization occurs after wetland drainage and the magnitude of mobilization changes with time should be investigated. Lastly, further studies should be conducted to determine the influence wetting and drying within intact wetlands on P sorption and buffering mechanisms to determine how these may be altered under a changing climate. Given the very heterogeneous nature of wetlands in the PPR, it would be beneficial to collect this information for wetlands spanning a range of hydroperiods, sizes, and dominant vegetation types to better understand and model the role of wetlands and wetland loss on nonpoint-source pollution at the landscape scale.

## Supplemental Material

A file if available online that contains a summary wetland and catchment characteristics, as well as information regarding total dissolved phosphorus concentrations in snow, runoff, and intact wetlands from our study sites.

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