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Land use and landscape position influence soil organic phosphorus speciation in a mixed land use watershed

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Abstract

Land use can significantly alter soil P forms, which will influence P loss in runoff. Organic P (P_o) compounds are an important component of soil P, but their forms and cycling in soils with different land uses are still poorly understood. In addition, streambanks are potential sources of P loss; P forms and concentrations in streambank soils may vary with land use, affecting potential P loss to water. This study used solution ^{31}P nuclear magnetic resonance spectroscopy to characterize and quantify P in interior and streambank soils (0–10 cm) under duplicate sites from four different land uses along streams in the Missisquoi River basin (VT, USA): silage corn, hay meadow, emergent wetlands, and forest. Orthophosphate monoesters were the dominant P compound class regardless of land use or landscape position. Forest soils had the lowest P_o concentrations, less labile P forms than other soils, and significantly lower concentrations of total inositol hexakisphosphates and total orthophosphate monoesters compared with corn soils. Riparian buffer zones for agricultural soils lowered P concentrations in streambank soils for many soil P pools relative to interior soils. The wetland soils of this study had P concentrations and P forms that were similar to those for interior agricultural soils and generally showed no reduction in P concentrations in streambank soils relative to interior soils. This is consistent with the role of wetlands as P sinks in the landscape but also suggests these wetlands should be carefully monitored to minimize P accumulation, especially in streambank soils.

Abbreviations: BMP, best management practice; DPS, degree of phosphorus saturation; FW, floodwater; IHP, inositol hexaphosphate; M/D ratio, ratio of orthophosphate monoesters to orthophosphate diesters (corrected for degradation); MRP, molybdate-reactive phosphorus; NETP, total P in NaOH-EDTA extracts; P_i , inorganic phosphorus; P-NMR, solution ^{31}P nuclear magnetic resonance spectroscopy; P_o , organic phosphorus; TP, total phosphorus; TP_o , total organic phosphorus.

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1 | INTRODUCTION

Phosphorus (P) runoff from land to water is a global concern. Phosphorus can be a limiting nutrient to algae in freshwater bodies, and algal blooms caused by transported nutrients can have negative economic effects on recreational and fishing activities and on human health if toxins are produced (Schoumans et al., 2014; Wilson et al., 2019). Reducing P inputs into water has been shown to control algal blooms (Schindler et al., 2016), and much effort has been invested into

reducing nutrient loads from land to water through the application of best management practices (BMPs) for agriculture, including reduced tillage and manure injection (Schoumans et al., 2014). However, water quality improvements have been less than expected, suggesting that more research is needed to fully understand soil P dynamics to minimize P loss from soil to water (Dodd & Sharpley, 2015; Miltner, 2015; Wilson et al., 2019).

When monitoring the potential for P transfer from soil to water, researchers have focused mostly on total P (TP) and short-term bioavailable inorganic P (P_i). The latter has been measured colorimetrically as water-extractable P or with standard soil test P methods such as modified Morgan's (ammonium acetate), Mehlich-3, or Olsen (Magdoff et al., 1999; Wilson et al., 2019; Young & Ross, 2018), because the most bioavailable P form for plants and algae is phosphate. However, other P species are readily converted to phosphate by hydrolysis, including organic P (P_o) species and complex P_i species such as polyphosphates (Condrón et al., 2005; Dodd & Sharpley, 2015). Soil P_o has been found to have a key role in ecosystem function and nutrient cycling, with P_o compounds comprising 30–65% of total soil P and having different degrees of bioavailability (Condrón et al., 2005). However, P_o is still inadequately understood in comparison to P_i , in part because identifying and quantifying P_o species in environmental samples is a complex task (Cade-Menun & Liu, 2014).

Land use and management have been shown to influence soil P forms and cycling (Liu et al., 2018; Zhou, et al., 2015). However, this relationship is complex and varies among soils because different biotic and abiotic factors play key roles in these processes (Stutter et al., 2015). Agricultural lands, including cropland and pastures, receiving inputs of chemical fertilizers or manure can be large sources of P from surface runoff or erosion into receiving waters (Wilson et al., 2019; Zaimes et al., 2008), whereas natural, unmanaged landscapes such as forests generally have low anthropogenic P inputs and thus lower potential P loss (MacDonald et al., 2012; Zhou et al., 2015). And while wetlands receive no direct fertilization, they capture and retain nutrient-rich runoff from adjacent lands (Singh et al., 2019; Walton et al., 2020; Weller et al., 1996). In general, most land use studies of P have focused on total P, labile P, or soil test P; few have used advanced spectroscopic techniques such as solution ^{31}P nuclear magnetic resonance spectroscopy (P-NMR) to investigate the effects of land use on P_o speciation.

To reduce P loss from agricultural lands, BMPs in use include reduced application rates of chemical fertilizers and manure, manure injection, and reduced tillage to prevent erosion (Miltner, 2015; Schoumans et al., 2014; Wilson et al., 2019). A widely implemented BMP is the establishment of riparian buffers between agricultural fields and water (Schoumans et al., 2014; Stutter et al., 2019), which puts distance between waterways and active agricultural practices that

Core Ideas

- Soil P concentrations were highest in hay and corn fields, with similar P_o forms.
- Forest soils had the lowest P_o concentrations and less labile P forms.
- Soil P_o concentrations were lower in streambanks than interior soils.
- Buffer strips for hay and corn fields reduced streambank P concentrations.
- Wetland soils had high streambank P concentrations, increasing potential for P loss.

can generate P loss (e.g., tillage, fertilization) and also reduces runoff-transported P by trapping sediments and colloids (particulate P) and sorbing dissolved P (Stutter et al., 2019). Riparian buffers can be vegetated strips, including grasses, shrubs or trees (Hénault-Ethier et al., 2019; Hoffmann et al., 2009), or wetlands (Walton et al., 2020), and their effectiveness depends on many factors, including soil type, vegetation, residence time, hydrology and runoff pathways, water saturation and redox, season, and width (Stutter et al., 2019).

Most studies have focused on changes in P concentration with land use with little regard to how P concentrations and speciation vary between the land use and its corresponding streambank. In a previous study in the Missisquoi River and its tributaries (VT, USA), we compared four types of land use (silage corn, hay meadow, emergent wetlands, and forest) and their corresponding streambanks and found that TP, soil test P (modified Morgan-extractable), and degree of P saturation (DPS) values of streambank soils varied significantly between each land use and its corresponding streambank, with the exception of forest sites (Perillo et al., 2019). However, more information about P speciation is needed to better understand P cycling in these soils. Therefore, the objective of this study was to use a subset of soils from the previous study, from four land use types (forests and wetlands without riparian buffers and corn fields and hay fields with riparian buffers), to characterize total P_o content and P speciation with P-NMR in soils from either (a) within fields ~10 m from streambanks (interior) or (b) streambanks associated with these fields. We hypothesized that land use and landscape position (interior versus streambank) would influence P speciation and P cycling, with differences among land use types and between interior and streambank samples.

2 | MATERIALS AND METHODS

2.1 | Study area and soil sampling

Detailed descriptions of the study area and sampling procedures are available in Perillo et al. (2019). Briefly, this

study focused on the Vermont portion of the Missisquoi River watershed that drains into Lake Champlain through the Missisquoi Bay (Supplemental Figure S1), with land use including forests (67.7%), agriculture (21.1%), urban (6.7%), and wetlands (1.4%). Between May and August 2015, soil samples (0–10 cm depth) were taken by trowel from forests, cornfields, hayfields, and emergent herbaceous wetlands, with eight sampling sites per land use (32 total), next to either the main stem of the Missisquoi River or its tributaries. Soils were mapped as fluvial Inceptisols (coarse-loamy to coarse-silty Fluvaqueptic Endoaquepts and Dystrudepts [Soil Survey Staff, 2017]). Eight of the 32 sites (two each of interior and streambank for each land use) were randomly chosen for the current study. For each of the selected sites (forests F1, F4; wetlands W2, W3; cornfields C2, C3; and hayfields H3 and H7; Supplemental Figure S1; Supplemental Table S1), the five streambank samples and interior samples were composited into a single sample each for streambank and interior per site for P-NMR analysis.

2.2 | Laboratory analysis

2.2.1 | General chemical analyses

All analyses used soils that were air-dried (3–4 d, room temperature) and sieved (<2 mm). Analyses for general soil properties (texture, pH [water], concentrations of total carbon [C], total nitrogen [N], TP, soil test P [modified Morgan's extract], oxalate-extractable aluminum [Al] and iron [Fe], and DPS) were conducted for Perillo et al. (2019) and are described in detail there. The results for the five replicate samples from these analyses were averaged into a single value each for interior and streambank per site. Total organic P (TP_o) concentrations were determined by the NaOH-EDTA extraction method (Bowman & Moir, 1993; Cade-Menun & Lavkulich, 1997); see the Supplemental Materials for more details.

Solution P-NMR

Samples for P-NMR were extracted with NaOH-EDTA, lyophilized, and analyzed on a Bruker 500 MHz spectrometer with a 5-mm probe (see the Supplemental Material for more details). Chemical shifts (Figure 1; Supplemental Table S2) were assigned to P compounds based on Cade-Menun (2015) and by spiking with reference compounds. Results were corrected for diester degradation products (Schneider et al., 2016), and concentrations were determined by multiplying percentages by the concentration of total P in the NaOH-EDTA extracts (NETP) for each sample.

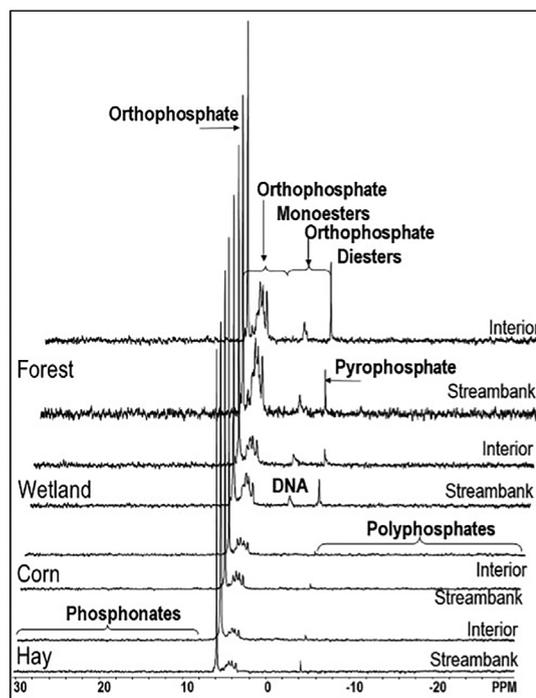


FIGURE 1 Examples of P-NMR spectra for streambank and interior samples of each land-use type. Spectra are plotted in full with 7 Hz line-broadening and are scaled to the height of the orthophosphate peak in each spectrum.

2.3 | Statistical analyses

Data were tested for normality with the Shapiro–Wilk test and transformed as needed, using $\log(n + 0.5)$ or $1/n$ for the general chemical properties and centered log ratios for the P-NMR data (Abdi et al., 2015). Two-factor ANOVA was conducted (land use, landscape position, and the land use \times landscape position interaction) with a standard least squares model, followed by Tukey's highest significant difference tests. Pearson pairwise correlations were also conducted for chemical data to other chemical data and to P-NMR data. All statistical analyses were performed using JMP (SAS Institute, v. 5.1), with $\alpha = .10$ (due to the small sample set, 16 samples total). The ANOVA results are shown in Supplemental Table S3.

3 | RESULTS AND DISCUSSION

3.1 | General chemical properties

The interaction of land use and landscape position was significant for TP concentrations, which were lower in forest samples (interior and streambank) than wetland, corn, and hay interior samples and lower in hay streambank than in hay interior samples (Table 1; Supplemental Table S3). There were

TABLE 1 General soil chemical properties and P-NMR results showing significant interactions of land use (forest, wetland, corn, or hay) and landscape position (interior or streambank) with ANOVA

Soil chemical properties	Forest		Wetland		Corn		Hay	
	Interior	Streambank	Interior	Streambank	Interior	Streambank	Interior	Streambank
Total P, mg kg ⁻¹	469 ± 19c	491 ± 72c	1086 ± 10ab	912 ± 169abc	1221 ± 186a	805 ± 165abc	1278 ± 209a	527 ± 188bc
Sand, g kg ⁻¹	686 ± 52ab	744 ± 7a	393 ± 199bc	522 ± 40abc	397 ± 44bc	588 ± 24abc	256 ± 91c	779 ± 63ab
Silt, g kg ⁻¹	214 ± 133bc	151 ± 73c	523 ± 164ab	413 ± 38abc	483 ± 21abc	318 ± 54abc	595 ± 16a	151 ± 62c
Monoester 1, ^a mg kg ⁻¹	1.2 ± 0.2b	0.6 ± 0.1b	8.4 ± 2.8a	4.9 ± 2.0a	12.5 ± 1.9a	5.8 ± 3.2a	10.2 ± 0.3a	1.6 ± 1.0b
Other diester 2, ^a mg kg ⁻¹	2.4 ± 0.6b	2.3 ± 0.4b	5.5 ± 2.2ab	4.2 ± 3.5b	3.6 ± 0.9b	4.0 ± 1.7b	12.0 ± 1.3a	1.8 ± 2.1b

Note: Values are mean ± SD ($n = 2$; $\alpha = .10$). Means with different letters in the same row are significantly different ($p < .10$).

^aMonoester 1 and Other diester 2 are general regions of P-NMR spectra.

TABLE 2 Soil general chemical properties for which there were no significant interactions of land use and landscape position with ANOVA (0–10 cm depth)

Soil chemical properties	Land use				Landscape position	
	Forest	Wetland	Corn	Hay	Interior	Streambank
TP _o , mg kg ⁻¹ ^a	81 ± 30	228 ± 134	288 ± 117	280 ± 198	302 ± 148x	139 ± 96y
TP _o , (% TP)	16.9 ± 6.70	22.7 ± 11.9	27.7 ± 6.91	35.5 ± 28.1	29.0 ± 9.78	22.4 ± 20.6
NETP Recovery, %	23.9 ± 6.59b	37.3 ± 12.8ab	61.1 ± 19.0a	56.5 ± 23.7ab	52.8 ± 18.9	36.5 ± 23.7
Soil test P, mg kg ⁻¹	0.90 ± 0.88b	1.50 ± 0.49ab	15.0 ± 18.8a	5.72 ± 6.69ab	9.75 ± 1.43x	1.82 ± 2.17y
Clay, g kg ⁻¹	233 ± 237	74.5 ± 23.2	108 ± 43.4	110 ± 63.0	114 ± 56	149 ± 177
Total N, g kg ⁻¹	1.35 ± 0.60	3.03 ± 1.26	2.38 ± 0.61	2.20 ± 1.64	2.86 ± 1.02x	1.61 ± 1.00y
Total C, g kg ⁻¹	17.5 ± 9.59	48.4 ± 26.2	27.3 ± 7.61	26.4 ± 21.3	37.8 ± 19.0x	22.0 ± 18.5y
pH in water	4.79 ± 0.69c	5.89 ± 0.29b	7.12 ± 0.39a	6.41 ± 0.19ab	5.99 ± 1.06	6.10 ± 0.92
Oxalate-extractable Al, mg kg ⁻¹	23.1 ± 10.9b	75.2 ± 21.5a	27.5 ± 11.2b	29.8 ± 20.4b	45.7 ± 28.7x	32.0 ± 23.9y
Oxalate-extractable Fe, mg kg ⁻¹	71 ± 27	141 ± 92	53 ± 61	90 ± 58	115 ± 64	141 ± 91.7
DPS, %	10.5 ± 0.17b	16.1 ± 3.93ab	31.7 ± 15.6a	27.0 ± 11.6 a	25.2 ± 16.4	17.4 ± 5.27
Est. porewater MRP ^b , mg L ⁻¹	0.23 ± 0.04b	0.30 ± 0.05ab	0.84 ± 0.59a	0.52 ± 0.33ab	0.64 ± 0.49x	0.30 ± 0.15y
Est. floodwater MRP ^b , mg L ⁻¹	0.15 ± 0.02b	0.18 ± 0.03ab	0.42 ± 0.26a	0.29 ± 0.16ab	0.34 ± 0.22x	0.18 ± 0.08y

Note: Values are mean ± SD ($n = 4$ for land use; $n = 8$ for landscape position). Means with different letters in the same row within either land use or landscape position are significantly different ($p < .10$).

^aDPS, degree of P saturation; NETP Recovery, recovery of soil total P in NaOH-EDTA extracts; soil test P method, modified Morgan extract; TP_o, total organic P.

^bPorewater and floodwater molybdate-reactive P (MRP) concentrations were estimated from log (STP) using equations in Young and Ross (2018).

no significant differences in TP_o concentrations among the land use types, but interior samples had significantly higher TP_o concentrations than streambanks (Table 2; Supplemental Table S3). Organic P as a percentage of TP (TP_o, %TP) was not significantly different with land use type or landscape position. Recovery of NETP was significantly lower in forest samples than in corn samples but did not significantly differ with landscape position (Table 2). Soil test P was significantly greater in corn soils than in forest soils and was greater in interior samples compared with streambanks (Table 2). There were significant interactions of land use and landscape position for sand and silt contents (Table 1; Supplemental Table S3), with significantly more sand and less

silt in forest interiors than in hay interiors and in hay streambanks compared with hay interiors. There were no significant differences among land use types or with landscape position for clay content (Table 2; Supplemental Table S3). Soil C and N concentrations did not differ significantly among the land use types (Table 2) but were significantly greater for interior than streambank samples. Soil pH was significantly higher in corn soils than wetland and forest soils but did not differ with landscape position. Oxalate-Al concentrations were significantly higher in wetland samples than other land uses and in interior samples relative to streambanks, but there were no significant differences with land use or landscape position for oxalate-Fe concentrations (Table 2). There were no significant

TABLE 3 Correlations of soil parameters with other soil parameters and with P forms determined by P-NMR

	TP	TP _o	Soil test P	N	C	pH	Sand	Silt	Clay	OxalateAl	OxalateFe	DPS
TP _o ^a	.67											
Soil test P	.80	.68										
Total N	.77	.63	.68									
Total C	.71	.53	.63	.97								
pH	.48	.45	.56									
Sand	-.84	-.78	-.65	-.70	-.66							
Silt	.86	.72	.65	.72	.70		-.97					
Oxalate Al	.55		-.65	.77	.81		-.62	.69				
Oxalate Fe				.71	.71		-.44	.43				
DPS	.78	.54	.80	.45		.77	-.48	.49		.72		
NETP	.47	.85	.65	.43		.59						.61
Orthophosphate	.65	.62	.66			.86	-.56	.56				.81
Pyrophosphate	-.63	-.58				-.63	.51	-.52				-.63
Polyphosphate	-.52	-.51	-.63	-.51	-.56		.64	-.70		-.57	-.47	
Total polyphosphate	.65	.76	.66	.81	.70		-.56	.53				.53
NMR total P _i	.82	.87	.80	.60	.49	.70	-.73	.73				.80
scyllo-IHP ^a									.62			.43
D-chiro-IHP	.54	.47	.58			.81	-.44					.62
Total IHP	.79	.90	.79	.67	.61	.55	-.75	.75				.70
Nucleotides						-.66					.50	
Glucose 6-phosphate						.62						.55
Unknown 5 ppm		.46										
Monoester 1	.81	.57	.72	.61	.60	.66	-.72	.75		.52		.65
Total monoesters	.80	.92	.81	.70	.63	.53	-.78	.77		.44	.48	.70
DNA			-.52			-.64						
Other diester 1		-.55	-.55			-.53						
Total diesters	.75	.81	.67	.86	.79		-.73	.71		.60	.48	.49
NMR total P _o	.80	.89	.78	.76	.72	.45	-.76	.77		.54		.64

Note. Only significant correlations ($\alpha = .10$) are shown.

^aNETP Recovery, recovery of soil total P in NaOH-EDTA extracts; DPS, degree of P saturation; IHP, inositol hexakisphosphate; modified Morgan extraction; monoesters, orthophosphate monoesters; NMR total P_i, total inorganic P calculated from NMR data; NMR total P_o, total organic P calculated from NMR data; soil test P, diesters, orthophosphate diesters; TP, total P; TP_o, total organic P. Total orthophosphate monoesters and total orthophosphate diester concentrations were corrected for diester degradation.

differences in DPS with landscape position (Table 2), whereas DPS was significantly greater in soils from corn and hay sites than from forest sites.

Total P, TP_o, and soil test P were positively correlated with each other and with C and N concentrations, pH, silt, DPS, and NETP recovery and were negatively correlated with sand concentration (Table 3). None of these P pools was significantly correlated with oxalate-Fe concentrations, whereas TP was positively correlated and soil test P was negatively correlated with oxalate-Fe.

The Lake Champlain watershed is mostly forested and agricultural (66 and 25%, respectively; Mears & Markowitz, 2013), so these results represent the major non-urban land use. Differences in general soil properties observed here are con-

sistent with those reported for the larger sample set by Perillo et al. (2019) and likely both cause and are caused by the sampled land uses. For example, the coarser texture of these forest soils may have influenced their use for farming. In contrast, agricultural practices in corn and hayfields have altered soil chemistry relative to forest soils (e.g., liming increased soil pH, while fertilization increased TP and soil test P concentrations). Increased TP in fertilized agricultural soils relative to unfertilized forest has been widely reported worldwide (MacDonald et al., 2012; Zhou et al., 2015), and reduced tillage or no-till on these fertilized agricultural sites (Supplemental Table S1) will stratify soil P, leaving surface-applied chemical fertilizers or injected manure near the soil surface, increasing P concentrations (Abdi et al., 2014; Cade-Menun et al.,

2015). The TP and soil test P concentrations in wetland soils, which were not significantly different from fertilized agricultural soils but were significantly higher than forest soils (Tables 1 and 2), could indicate that P has been transported into these wetlands and subsequently retained (e.g., Walton et al., 2020; Weller et al., 1996), or may reflect past agricultural use. The higher oxalate-Al concentration in wetland soils compared with soils of other land use types, combined with higher total C concentrations, suggests that the wetlands may have more organically-complexed Al, which could explain why DPS in these wetland soils was not significantly different from corn and hay soils (Table 2).

Hay interior soils had significantly higher TP concentrations than hay streambank soils (Table 1). Soil test P concentrations were generally greater in interior than streambank soils and were driven by differences between interior and streambank soils for corn (25 ± 24 vs. 4.2 ± 4.0 mg kg⁻¹) and hay (10 ± 1.2 vs. 1.2 ± 0.3 mg kg⁻¹) soils than forest (1.2 ± 0.1 vs. 0.6 ± 0.1 mg kg⁻¹) or wetland (1.8 ± 0.3 vs. 1.3 ± 1.2 mg kg⁻¹) soils. Interior TP_o concentrations were significantly different from streambank concentrations and were driven more by differences between interior and streambank soils for hay (403 ± 176 vs. 157 ± 163 mg kg⁻¹), corn (373 ± 8 vs. 203 ± 108 mg kg⁻¹), and wetlands (333 ± 71 vs. 125 ± 76 mg kg⁻¹) than forest soils (98 ± 30 vs. 64 ± 28 mg kg⁻¹). The corn and hay fields had riparian buffers between the fields and streambanks (Supplemental Table S1), as is recommended or required in Vermont and Quebec (Hénault-Ethier et al., 2019; Young & Ross, 2018). These results show that riparian buffers effectively provide an offset between fertilized agricultural soils and adjacent streams, especially for the hay fields of this study. Riparian buffers may also intercept transported nutrients in runoff (Stutter et al., 2019), and the lack of significant differences in DPS between interior and streambank soils suggests this might be occurring. However, the hay streambank soils differ significantly in texture from the hay interior soils, which could affect P sorption and retention. Further investigation is warranted.

3.2 | P speciation by P-NMR

3.2.1 | Inorganic P

Orthophosphate concentration and NETP recovery were significantly lower in forest soils than other land use types (Tables 2 and 4; Supplemental Table S3). Prior research has shown that NaOH-EDTA extracts organic P plus labile and moderately labile orthophosphate; the unextracted P is poorly soluble P_i compounds such as hydroxyapatite (Cade-Menun et al., 2015; Liu et al., 2020). Thus, phosphate in these forest soils was less soluble than in corn soils, and concentrations were lower. This is consistent with lower soil

test P concentrations for these forest soils (Table 2) and with the positive correlation of orthophosphate with soil test P and TP (Table 3). Orthophosphate was also positively correlated with TP_o, pH, silt, and DPS, and was negatively correlated with sand content. There were no significant differences in orthophosphate concentrations with landscape position, likely due to high variability in the interior samples (Table 4).

There were no significant differences among land use types or landscape position for pyrophosphate, which was negatively correlated with TP, TP_o, pH, silt, and DPS (Tables 3 and 4). Polyphosphate concentrations were significantly higher in corn soils than in forest soils and in interior samples compared with streambanks and were correlated positively with sand content and correlated negatively with TP, TP_o, soil test P, C, N, silt, and oxalate-Al. Total polyphosphate concentrations (pyrophosphate + polyphosphate) did not differ significantly with land use but were higher in interior than streambank samples and were correlated negatively with sand and positively with TP, TP_o, soil test P, C, N, DPS, and silt. Total P_i concentrations, dominated by orthophosphate, were significantly lower in forest soils than other land use types and in streambanks compared with interior soils and were correlated positively with TP, TP_o, soil test P, C, N, pH, DPS, and silt and correlated negatively with sand content (Table 3). The higher P_i in agricultural lands reflects the added fertilizers (Supplemental Table S1), including manure, which often has high P_i concentrations (Toor et al., 2005). A review of P-NMR studies of agricultural soils found that P_i, especially orthophosphate, was high in all fertilized soils regardless of fertilizer type (Cade-Menun, 2017). The high P_i in wetland soils, comparable to agricultural soils, reflects higher P retention in poorly drained soils and is consistent with results from other studies in nearby watersheds (Young & Ross, 2016; Young et al., 2013).

3.2.2 | Organic P

Total P_o concentration determined by P-NMR was significantly higher in corn than forest samples and in interior versus streambank samples (Table 4), with concentrations comparable to those determined for TP_o (Table 2). Concentrations of total P_o by NMR were correlated positively with TP, TP_o, soil test P, C, N, pH, silt, oxalate-Al, and DPS and correlated negatively with sand content (Table 3). There were no significant differences with land use type or landscape position for phosphonates, which were low for all samples and were not significantly correlated with any soil parameters (Tables 4; Supplemental Table S3).

Orthophosphate monoesters were dominated by total IHP, which was significantly higher in corn soils than forest soils and higher in interior samples than in streambank samples. Four IHP stereoisomers were identified, of which *myo*-IHP

TABLE 4 Phosphorus species present in NaOH-EDTA extracts of soils, analyzed by P-NMR spectra

Phosphorus species ^a	Land use				Landscape position	
	Forest	Wetland	Corn	Hay	Interior	Streambank
—mg P kg ⁻¹ —						
Inorganic P (P _i)						
Orthophosphate	33 ± 8.9b	180 ± 83a	379 ± 253a	288 ± 196a	320 ± 231	119 ± 91
Pyrophosphate	5.6 ± 3.4	7.7 ± 5.0	5.3 ± 0.8	8.2 ± 4.4	8.9 ± 3.6	4.5 ± 1.8
Polyphosphates	4.9 ± 0.8b	9.0 ± 5.8ab	12.0 ± 5.8a	9.9 ± 5.7ab	11.4 ± 5.8x	6.5 ± 3.4y
Total polyphosphates	10.5 ± 3.1	16.8 ± 10.5	17.3 ± 5.4	18.1 ± 10.0	20.4 ± 7.5x	11.0 ± 4.5y
Total P _i	43 ± 11b	197 ± 85a	396 ± 257a	306 ± 205a	341 ± 234x	130 ± 95y
Organic P (P _o)						
Phosphonates	1.7 ± 0.4	5.5 ± 3.6	7.8 ± 6.1	3.7 ± 2.2	6.3 ± 4.8	3.0 ± 2.4
Orthophosphate monoesters						
<i>myo</i> -IHP	15.6 ± 6.2	35.0 ± 16.0	59.0 ± 26.9	41.5 ± 28.3	49.4 ± 26.3	26.1 ± 18.0
<i>scyllo</i> -IHP	4.2 ± 1.7	12.3 ± 6.1	19.9 ± 9.3	15.2 ± 10.5	17.3 ± 9.9	8.4 ± 5.8
<i>neo</i> -IHP	2.0 ± 0.7	6.3 ± 3.3	7.7 ± 4.6	4.9 ± 3.7	7.0 ± 4.0	3.4 ± 2.5
<i>D-chiro</i> -IHP	2.9 ± 0.8b	11.6 ± 4.5b	24.4 ± 11.2a	11.5 ± 8.4b	17.1 ± 11.2	8.1 ± 7.7
Total IHP	24 ± 6.8b	65 ± 24ab	111 ± 48a	73 ± 249ab	91 ± 47x	46 ± 33y
α-glycerophosphate	1.6 ± 0.5	3.7 ± 2.3	6.1 ± 2.1	4.7 ± 4.2	5.3 ± 2.9	2.7 ± 2.3
β-glycerophosphate	3.2 ± 0.9	7.2 ± 4.4	12.2 ± 4.2	9.4 ± 8.7	10.5 ± 5.9	5.5 ± 4.9
Nucleotides	8.8 ± 3.6	17.8 ± 15.6	17.8 ± 11.2	14.5 ± 10.6	21.1 ± 11.6	8.4 ± 4.0
Choline phosphate	1.4 ± 0.4	5.0 ± 2.2	5.1 ± 1.8	5.5 ± 3.5	5.6 ± 2.9	2.9 ± 1.4
Glucose 6-phosphate	0.8 ± 0.3b	2.7 ± 0.5a	4.6 ± 2.4a	4.3 ± 1.7a	3.9 ± 2.3	2.3 ± 1.5
Unknown 5 ppm	2.4 ± 1.0	7.4 ± 3.1	14.3 ± 8.1	10.0 ± 5.5	11.0 ± 6.7	6.0 ± 5.4
Monoester 2	11.2 ± 4.4	28.2 ± 16.1	49.5 ± 23.9	30.4 ± 18.5	42.1 ± 22.2	17.5 ± 9.7
Monoester 3	2.4 ± 0.9	6.6 ± 4.9	8.7 ± 4.1	8.6 ± 4.1	7.9 ± 4.2	5.3 ± 4.3
Total orthophosphate monoesters		122 ± 51ab	202 ± 87a	138 ± 82ab	169 ± 85x	83 ± 56y
Orthophosphate diesters						
DNA	4.5 ± 1.5	16.5 ± 16.0	3.3 ± 2.2	8.6 ± 5.8	12.0 ± 12.1	4.4 ± 2.7
Other diester 1	4.6 ± 1.6	10.4 ± 4.9	6.8 ± 4.1	10.0 ± 8.0	11.0 ± 5.7	4.9 ± 2.2
Total orthophosphate diesters	25 ± 7	60 ± 44	50 ± 16	54 ± 39	66 ± 33x	29 ± 13y
M/D ratio ^a	2.3 ± 0.8	2.9 ± 0.7	3.9 ± 0.7	1.8 ± 0.4	2.7 ± 1.3	2.8 ± 0.8
Total P _o	70 ± 19b	187 ± 90ab	260 ± 106a	195 ± 123ab	241 ± 108x	115 ± 71y

Note. Values are means ± SD ($n = 4$ for land use; $n = 8$ for landscape position). Means with different letters in the same row within either land use or landscape position are significantly different ($p < .10$).

^aIHP, inositol hexakisphosphate; M/D ratio, ratio of orthophosphate monoesters to orthophosphate diesters, using data corrected for diester degradation.

was the predominant form for all land use types. There were no significant differences in concentrations of *myo*-, *scyllo*-, or *neo*-IHP with land use type or landscape position. Concentrations of *D-chiro*-IHP were significantly higher in corn soils than other land use types but did not differ with landscape position. There were no significant correlations to soil parameters for concentrations of *myo*- and *neo*-IHP. Total IHP and *D-chiro*-IHP concentrations were positively correlated with TP, TP_o, soil test P, silt, and DPS and negatively correlated with sand. Total IHP concentrations were also positively correlated with C and N concentrations and pH. Only *scyllo*-IHP

was significantly correlated with clay content, and this was the only soil parameter with which *scyllo*-IHP was significantly and positively correlated (Table 3).

Glucose 6-phosphate concentrations were significantly lower in forest soils than other land use types but were unaffected by landscape position. Concentrations of choline phosphate, the unknown peak at 5 ppm, and the general orthophosphate monoester categories of Monoester 2 and Monoester 3 were not significantly different among land use classes or landscape position; nor were the degradation compounds α- and β-glycerophosphates and nucleotides (Table 4).

There was, however, a significant interaction of land use and landscape position for P concentration in the Monoester 1 category (Table 1), with significantly lower concentrations in the forest interior and streambank soils and in the hay streambank soils. The exact identification of compounds in this region is unknown, but they are likely some type of inositol phosphate (Turner & Richardson, 2004; Turner et al., 2012). After correcting for degradation compounds, total orthophosphate monoester concentrations were significantly higher in corn than forest soils and in interior versus streambank soils (Table 4). There were no significant correlations to soil parameters for α - and β -glycerophosphates, choline phosphate, Monoester 2, Monoester 3, Other Diester 2, and the monoester-to-diester ratio calculated after correction for degradation products (M/D ratio; Table 3). Total monoesters and Monoester 1 concentrations were correlated positively with TP, TP_o, soil test P, DPS, and silt contents and correlated negatively with sand. Soil pH was correlated positively with glucose 6-phosphate, Monoester 1, and total Monoesters concentrations and correlated negatively with nucleotides. Oxalate-Al concentration was positively correlated with Monoester 1 and total monoesters; oxalate-Fe was positively correlated with nucleotides and total monoesters.

After correcting for degradation, there were no significant differences in total orthophosphate diester concentrations with land use, but concentrations were higher in interior samples than in streambank samples (Table 4). There were no significant differences with land use type or landscape position for DNA or the Other Diester 1 category, which contains lipoteichoic acid and phospholipids not degraded to glycerophosphate during extraction and analysis (Cade-Menun, 2015). There was a significant interaction of landscape position and land use for the Other Diester 2 category, with significantly higher concentrations in interior hay samples compared with corn and forest interior samples and all streambank samples (Table 1). Unfortunately, the P compounds producing peaks in this region remain unidentified, so the implications of this difference are unclear. Concentrations of P in the Other Diester 1 category were correlated negatively with TP_o and soil test P and correlated positively with pH, whereas DNA concentrations were negatively correlated with soil test P and pH (Table 3). Other Diester 2 concentrations had no significant correlations to soil parameters.

The M/D ratio (Table 4) showed no significant differences with land use or landscape position. For these soils, mean ratios ranged from 1.8 to 3.9, indicating that orthophosphate monoesters were the dominant P_o compound class in these soils. This ratio was not significantly correlated to any of the soil parameters measured for this study.

The forms and concentrations of soil P_o are governed by inputs, transformations, and retention. For many of the iden-

tified P_o compounds or compound classes (e.g., Monoester 1), little is known about their cycling in soils. As such, we focus on the P_o compounds for which more information is available.

Inputs

Soil P_o compounds may originate from plant material, they may be synthesized by soil microbes, or they may be added to soils as agricultural chemicals or fertilizers. Within phosphate monoesters, the inositol hexaphosphates (IHPs) are a dominant group of compounds in most soils (Giles et al., 2011). These exist in a number of stereoisomers, of which *myo*-IHP (phytate) is known to originate directly from plants; the origins of other IHP stereoisomers are unknown, but they may be directly synthesized by soil microbes or transformed from one IHP stereoisomer into another (Giles et al., 2011). Differences in inputs of these stereoisomers are expected given the different plant species associated with each land use type and in the buffer strips for the corn and hay fields. However, the lack of significant differences for concentrations of all but *D-chiro*-IHP was unexpected, given the potential inputs with manure and higher P concentrations overall for the corn and hay fields. This may instead reflect differences in retention, which is discussed in more detail below. Other P_o compounds as well as pyrophosphate and polyphosphate can originate from plant material or soil microbes (Condrón et al., 2005; Nelson et al., 2020; Noack et al., 2014). Some phosphonate compounds can be added to agricultural soils as fungicides and herbicides (Cade-Menun, 2015); however, the low phosphonate concentrations and the lack of significant differences among land use types suggest that is not a significant source for these soils. The addition of organic fertilizers such as manure to agricultural lands can also add a range of P_o compounds, including phosphonates and *myo*-IHP, but the specific compounds added will vary with the source and treatment (e.g., composting) of manure (Cade-Menun et al., 2015; Toor et al., 2005). The P_o compounds added in manure to these soils are unknown because manure samples were not analyzed for this study.

Transformations

Forms of P_o input into soils from plants, manure, etc., can be transformed into other P_o compounds by various processes. Soil microbes may epimerize one IHP stereoisomer into another (Giles et al., 2011), and soil enzymes released by plants and microbes can hydrolyze P_o compounds to release bioavailable P_i (Nannipieri et al., 2011). Phosphatase activity was not assayed for this study. However, a recent land use study of agricultural soils in Saskatchewan, Canada, showed significantly lower phosphatase activities but a greater abundance of P cycling genes in fertilized cropland than in grazed planted and native pastures, which was thought to be linked to fertilization and disturbance (Liu et al., 2018). As such,

we would expect to see differences in phosphatase activities with land use in the soils of this study, too, and potentially also differences with landscape position, resulting in differences in transformation of P_o compounds. Additionally, P_o compounds can be transformed to bioavailable forms by enzymatic hydrolysis if transported to waterbodies in runoff or erosion (Giles et al., 2015; Stout et al., 2016).

Retention

Sorption and precipitation affect P_i and P_o compounds, although the degree of retention differs among P_o compounds. Both DNA and IHP stereoisomers can strongly sorb to soil minerals, especially at acidic soil pH. The sorption of DNA increases below its isoelectric point at pH 5 (Condrón et al., 2005), and DNA was negatively correlated with pH for the soils of this study despite a lack of significant differences in DNA concentrations with landscape position or land use. Soil pH also affects the sorption and precipitation of IHP stereoisomers, as do other soil properties, including clay content and Al- and Fe-(oxy)hydroxides (Condrón et al., 2005; Turner & Blackwell, 2013). In soils with neutral or alkaline pH, *myo*-IHP added from manure or plant material degrades rapidly to orthophosphate (Doolette et al., 2010; Leytem et al., 2006). In contrast, a recent soil chronosequence study showed that concentrations of *myo*- and *scyllo*-IHP increased with decreasing pH and increasing concentrations of oxalate-Fe and -Al, despite relatively low inputs of these compounds from overlying forests (Nelson et al., 2020). In the current study, there were no significant differences with land use or landscape position for *myo*- and *scyllo*-IHP, although total IHP was significantly greater in corn than other land use types and in interior versus streambank soils, and *myo*-IHP was significantly correlated with soil chemical properties. This suggests that no single factor controls the cycling of P_o compounds in these soils; although inputs of *myo*- and *scyllo*-IHP may have been greater in corn fields, turnover was likely also greater in the higher pH corn soils. In contrast, retention was likely greater in the lower pH forest soils. Disturbance may also affect IHP storage, with forest soils less disturbed than corn fields and interior soils more disturbed than streambanks (Liu et al., 2018; Williams & Anderson, 1968). The M/D ratio is used by many groups to estimate lability of P_o compounds, with the assumption that soils with high ratios will have higher retention of P_o and lower lability, whereas soils with low ratios will have higher turnover and less retention (Liu et al., 2018; Nelson et al., 2020). In these soils, the M/D ratio was significantly higher in soils under corn than forests and in interior soils compared with streambanks, but there were no significant correlations of the M/D ratio to any soil parameters, including those controlling P retention (e.g., pH, oxalate-Al, and oxalate-Fe). This suggests that the M/D ratio should be used very cautiously as a proxy for P retention or turnover and that further investigation

into turnover of specific P compounds in these soils is warranted.

3.3 | Water quality implications

The risk of P loss from land to water depends on many factors, including soil P concentrations, bioavailability of P forms, soil factors influencing P retention, and transportation mechanisms of P from land to water. The forest soils of this study had lower P concentrations in various measured P pools, including TP and soil test P, than interior soils of agricultural lands receiving P fertilizer and P forms that were less labile. The interior agricultural soils had the highest concentrations of P in various P pools and more labile P, which was not unexpected due to regular manure applications. Using BMPs can help prevent P loss from agricultural soils, and many of the recommended BMPs are in use on these lands, including manure injection and reduced tillage (Miltner, 2015; Schoumans et al., 2014; Wilson et al., 2019). More important, however, is the use of buffer strips, which was associated with reduced TP_o , soil test P, and total N in streambank relative to interior samples.

Soil factors influencing P retention include texture, pH, and mineralogy. Forest soils and hay streambanks were coarser textured than the other soils, which would reduce P retention. Soil pH affects P retention processes including sorption and precipitation and was significantly higher in corn than wetland and forest soils but did not differ with landscape position. Phosphorus retention is also influenced by Al- and Fe-(oxy)hydroxides, which can be assessed with oxalate extraction. Oxalate-Al concentrations were significantly higher in wetland samples than other land uses, but there were no significant differences with land use for oxalate-Fe concentrations or for oxalate-Al and oxalate-Fe with landscape position. However, redox is an important factor controlling P solubilization from Fe-(oxy)hydroxides, especially under saturated conditions that may occur seasonally for soils in this region (Hénault-Ethier et al., 2019; Young & Ross, 2018). In a microcosm study using soils from the same region as the current study, Young and Ross (2018) studied P desorption potential and P mobilization to floodwater (FW) under moderately reducing conditions that mimicked saturated riparian environments. They found that, with time, FW remained oxidized and FW-molybdate-reactive P (MRP) decreased, whereas porewater (PW) became reduced and PW-MRP increased. They also showed relationships of FW-MRP and PW-MRP with soil test P. We used the equation from Figure 2c in Young and Ross (2018) to estimate FW-MRP and PW-MRP in the samples from this study: $\log(\text{PW MRP}) = 1.183(\log \text{soil test P}) - 1.42$, and $\log(\text{FW MRP}) = 1.01(\log \text{STP}) - 1.87$. Estimated FW-MRP and PW-MRP were significantly lower in forest soils than the other land uses, and in streambank than

interior soils (Table 2). In particular, the estimated PW-MRP and FW-MRP concentrations in wetland soils were not significantly different from those for the agricultural soils. However, riparian wetlands are likely to have reducing conditions more frequently throughout the year than agricultural soils, increasing the risk of P loss (Dupas et al., 2015; Hénault-Ethier et al., 2019; Young & Ross, 2018).

Phosphorus can move from land to water in dissolved or particulate forms, and it is widely recognized that riparian buffers can intercept nutrients in runoff in either of these physical forms (Hénault-Ethier et al., 2019; Stutter et al., 2019). Thus, although the agricultural soils have high P concentrations in interior soils, the riparian buffers will likely reduce P loss directly from the interior soils to streams. This is not the case for wetland soils, with similar TP concentrations in interior and streambank samples. However, it should be noted that wetland streambank TP concentrations were significantly lower than interior TP concentrations when all 32 sites of the previous study were assessed (Perillo et al., 2019), suggesting that the results from the current study may not necessarily apply to all wetland soils in this region. Nonetheless, the results here support the need to assess and manage riparian wetlands on a regular basis because they can shift from a P sink to a P source with changing conditions, such as drying and rewetting or redox cycles (Dupas et al., 2015).

4 | CONCLUSIONS

Significant differences were observed in P forms and concentrations with land use and landscape position. Forest soils had significantly lower concentrations of TP and some P_o compound classes, including total IHP and total orthophosphate monoesters. Soils from wetlands and hay and corn fields had the highest concentrations in all P pools and no significant differences in soil P_o forms. Buffer strips appeared to reduce streambank TP concentrations for the agricultural soils, particularly for hay fields, and streambank concentrations were significantly lower than interior soils for total polyphosphate, total IHP, total orthophosphate monoesters, and total orthophosphate diesters. Wetland soil P concentrations and forms were not significantly different from the agricultural soils and were also similar for interior and streambank soils, resulting in high P concentrations adjacent to streambanks. This increases the potential for P loss to streams from wetland sites relative to agricultural fields with buffer strips.

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DATA AVAILABILITY STATEMENT

Data can be made available by request to authors.

AUTHOR CONTRIBUTIONS

Vanesa L. Perillo, Conceptualization, Data curation, Formal analysis, Methodology, Writing-original draft, Writing-review & editing; Barbara J. Cade-Menun, Formal analysis, Investigation, Methodology, Writing-original draft, Writing-review & editing; Monika Ivancic, Methodology, Writing-review & editing; Donald S. Ross, Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing-review & editing; Beverley C. Wemple, Conceptualization, Funding acquisition, Writing-review & editing.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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