Running title (optional): Soil P forms in a mixed land-use watershed

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

Land Use and Landscape Position Influence Soil Organic Phosphorus Speciation in a Mixed Land-Use Watershed

Vanesa L. Perillo[1, 2],[*] Barbara Cade-Menun[3], Monika Ivancic[4], Donald S. Ross[1], Beverley C. Wemple[5]

1. Dept. of Plant and Soil Science, University of Vermont, 63 Carrigan Dr., Burlington, VT, 05405

2. V.L. Perillo present address: Instituto Argentino de Oceanografía (CONICET-UNS), Camino La Carrindanga Km 7, Bahía Blanca, 8000, Argentina;

3. Agriculture & Agri-Food Canada, Swift Current Research and Development Centre, Box 1030, Gate 4, Airport Rd., Swift Current, SK, Canada S9H 3X2;

4. Dept. of Chemistry, 82 University Pl., University of Vermont, Burlington, VT, 05405

5. Geography Dept., University of Vermont, 94 University Pl, Burlington, VT 05405.

[*]Corresponding author (vperillo@criba.edu.ar)

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

-

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 (P-NMR) 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 to corn soils. Riparian buffer zones for agricultural soils lower 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.

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, Carpenter, Chapra, Hecky & Orihel, 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, Kryshko, Jokela, Durieux & Bu, 1999; Young & Ross, 2018; Wilson et al., 2019), 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 (Condron, Turner & Cade-Menun, 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 (Condron, Turner & Cade-Menun, 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 (Zhou, et al., 2015; Liu et al., 2018). 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 (Zaimes, Schultz, & Isenhart 2008; Wilson et al., 2019), while natural, unmanaged landscapes such as forests generally have low anthropogenic P inputs and thus lower potential P loss (MacDonald, Bennett & Taranu, 2012; Zhou et al., 2015). And while wetlands receive no direct fertilization, they capture and retain nutrient-rich runoff from adjacent lands (Weller, Watzin & Wang, 1996; Singh et al., 2019; Walton et al., 2020). 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 (Schoumans et al., 2014; Miltner, 2015; Wilson et al., 2019). A widely implemented BMP is the establishment of riparian buffers between agricultural fields and water (Schoumans et al., 2014; Stutter, Kronvang, hUallacháin, & Rozemeijer, 2019), which puts distance between waterways and active agricultural practices that 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, Kronvang, hUallacháin, & Rozemeijer, 2019). Riparian buffers can be vegetated strips, including grasses, shrubs or trees (Hoffmann, Kjaergaard, Uusi-Kämppä, Bruun Hansen, & Kronvang, 2009; Hénault-Ethier et al., 2019) 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, Kronvang, hUallacháin, & Rozemeijer, 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, Ross, Wemple, Balling & Lemieux, 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.

MATERIALS AND METHODS

Study Area and Soil Sampling

Detailed descriptions of the study area and sampling procedures are available in Perillo, Ross, Wemple, Balling & Lemieux (2019). Briefly, this study focused on the Vermont portion of the

Missisquoi River watershed that drains into Lake Champlain, through the Missisquoi Bay (Supplemental Fig. 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 Fluvaquentic 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 Fig. S1; Supplementary 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.

Laboratory Analysis

General Chemical Analyses

All analyses used soils that were air-dried (3-4 days, 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, Ross, Wemple, Balling & Lemieux (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 Supplementary Materials (SM) for more details.

Solution 31P nuclear magnetic resonance spectroscopy

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 SM for more details. Chemical shifts (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, Cade-Menun, Lynch, & Voroney, 2016), and concentrations were determined by multiplying percentages by the concentration of total P in the NaOH-EDTA extracts (NETP) for each sample.

Statistical Analyses

Data were tested for normality with the Shapiro-Wilks 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, Cade-Menun, Ziadi & Parent, 2015). Two-factor analysis of variance (ANOVA) was conducted (land use, landscape position and the land use*landscape position interaction) with a standard least squares model, followed by Tukey's highest significant differences (HSD) tests. Pearson pair-wise 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 $\alpha = 0.10$ (due to the small sample set, 16 samples total). The ANOVA results are shown in Table S3.

RESULTS AND DISCUSSION

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 in hay streambank than hay interior samples (Tables 1, S3). There were no significant differences in TP_o concentrations among the land use types, but interior samples had significantly higher TP_o concentrations than streambanks (Tables 2, S3). Organic P as a percentage of TP (TP_o, % TP) was not significantly different with land use type or landscape position. Recovery of TP in the NaOH-EDTA extracts (NETP) was significantly lower in forest samples than corn samples, but did not significantly differ with landscape position (Table 2). Soil test P was significantly greater in corn than forest soils and in interior samples compared to streambanks (Table 2). There were significant interactions of land use and landscape position for sand and silt contents (Tables 1, S3), with significantly more sand and less silt in forest interiors than hay interiors and in hay streambanks compared to hay interiors. There were no significant differences among land use types or with landscape position for clay content (Tables 2, 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 differences in DPS with landscape position (Table 2), while 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, while 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 consistent with those reported for the larger sample set by Perillo, Ross, Wemple, Balling & Lemieux (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, Bennett & Taranu, 2012; Zhou et al., 2015), and reduced tillage or no-till on these fertilized agricultural sites (Table S1) will stratify soil P, leaving surface-applied chemical fertilizers or injected manure near the soil surface, increasing P concentrations (Abdi, Cade-Menun, Ziadi, & Parent, 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, 2), could indicate that P has been transported into these wetlands and subsequently retained (e.g., Weller, Watzin & Wang, 1996; Walton et al., 2020), or may reflect past agricultural use. The higher oxalate-Al concentration in wetland soils compared to 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}) 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}). 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 (Table S1), as is recommended or required in Vermont and Quebec (Young & Ross, 2018; Hénault-Ethier et al., 2019). 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, Kronvang, hUallacháin, & Rozemeijer, 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.

Phosphorus Speciation by P-NMR

Inorganic P

Orthophosphate concentration and NETP recovery were significantly lower in forest soils than other land use types (Table 3, 4, 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, TPo, pH, silt and DPS (Tables 3, 4). Polyphosphate concentrations were significantly higher in corn than forest soils and in interior samples compared to streambanks, and were correlated positively with sand content and 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 to interior soils, and were correlated positively with TP, TP_o, soil test P, C, N, pH, DPS and silt, and negatively with sand content (Table 3). The higher P_i in agricultural lands reflects the added fertilizers (Table S1), including manure, which often has high P_i concentrations (Toor, Cade-Menun & Sims, 2005). A review of P-NMR studies of agricultural soils found that P_i, especially orthophosphate, was high in all fertilized soils, regardless of fertilizers 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, Cade-Menun, & Liu, 2013; Young & Ross, 2016).

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 3), 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 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 3, 4).

Orthophosphate monoesters were dominated by total IHP, which was significantly higher in corn than forest soils, and in interior than streambank samples. Four IHP stereoisomers were identified, of which *myo*-IHP 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, TPo, 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 3). 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, Cheesman, Godage, Riley, & Potter, 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 and Other Diester 2, and the monoester-to-diesters 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 negatively with sand. Soil pH was correlated positively with glucose 6-phosphate, Monoester 1, and total Monoesters concentrations, and 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 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 to 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 positively with pH, while 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 3) showed no significant differences with land use or landscape position. For these soils, mean ratios ranged from 1.8-3.9, indicating that orthophosphate monoesters were the dominant P 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 identified P_o compounds or compound classes (e.g. Monoester 1), little is known about their cycling in soils. As such, discussion will 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 (IHP) are a dominant group of compounds in most soils (Giles, Cade-Menun & Hill, 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, Cade-Menun & Hill, 2011). Differences in inputs of these stereoisomers is 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 signficant 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 (Condron, Turner & Cade-Menun, 2005; Noack, Smernik, McBeath, Armstrong & McLaughlin, 2014; Nelson, Cade-Menun, Walker & Sanborn, 2020). Some phosphonate compounds can be added to agricultural soils as fungicides and herbicides (Cade-Menun, 2015); however, the low phosphonate concentrations and lack of significant differences among land use types suggests 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 (Toor, Cade-Menun & Sims, 2005; Cade-Menun et al., 2015). 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, Cade-Menun & Hill, 2011), and soil enzymes released by plants and microbes can hydrolyze P_o compounds to release bioavailable P_i (Nannipieri, Giagnoni, Landi & Renella, 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 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, Nguyen & Jaisi, 2016).

Retention: Sorption and precipitation will affect P_i and P_o compounds, although the degree of retention will differ among P_o compounds. Both DNA and IHP stereoisomers can strongly sorb to soil minerals, especially at acidic soil pH. The sorption of DNA will increase below its isoelectric point at pH 5 (Condron, Turner & Cade-Menun, 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 will also affect the sorption and precipitation of IHP stereoisomers, as will other soil properties including clay content and Al- and Fe-(oxy)hydroxides (Condron, Turner & Cade-Menun, 2005; Turner & Blackwell, 2013). In soils with neutral or alkaline pH, *myo*-IHP added from manure or plant material will degrade rapidly to orthophosphate (Leytem, Smith, Applegate & Thacker, 2006; Doolette, Smernik & Doughterty, 2010). 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, Cade-Menun, Walker & Sanborn, 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, and that inputs of *myo*- and *scyllo*-IHP may have been greater in corn fields, but turnover was greater in the higher pH corn soils while retention was 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 that streambanks (Williams & Anderson, 1968; Liu et al., 2018). 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, while soils with low ratios will have higher turnover and less retention (Liu et al., 2019; Nelson, Cade-Menun, Walker & Sanborn, 2020). In these soils, the M:D ratio was significantly higher in soils under corn than forests, and in interior soils compared to streambanks, but there were no significant correlations of the M:D ratio to any soil parameters, including those controlling P retention (pH, oxalate-Al and -Fe, etc.). This suggests that the M:D ratio should be used very cautiously as a proxy for P retention or turnover, and further investigation into turnover of specific P compounds in these soils is warranted.

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 (Schoumans et al., 2014; Miltner, 2015; 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 will also be 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 (Young & Ross, 2018; Hénault-Ethier et al., 2019). In a microcosm study using soils from the same region as the current study, Young & Ross (2018) studied P desorption potential and P mobilization to floodwater under moderately reducing conditions that mimicked saturated riparian environments. They found that, with time, floodwater (FW) remained oxidized and FW-MRP decreased, while porewater (PW) became reduced and PW-MRP increased. They also showed relationships of FW- and PW-MRP with soil test P. We used the equation from Fig. 2c in Young & Ross (2018) to estimate FW- and PW-MRP in the samples from this study: log (PW MRP) = 1.183 (log soil test P) – 1.42, and log (FW MRP) = 1.01 (log STP) – 1.87. Estimated FW-MPR 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- 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; Young & Ross, 2018; Hénault-Ethier et al., 2019)

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, Kronvang, hUallacháin, & Rozemeijer, 2019). Thus, while 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, Ross, Wemple, Balling & Lemieux, 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).

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 streambanks 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.

ACKNOWLEDGEMENTS

This work was funded by the United States Geological Survey through The Vermont Water Resources and Lake Studies Center and interns funded by the National Science Foundation under VT EPSCoR Grant No. EPS-1101317. We are thankful to Joel Tilley for his advice in the laboratory, and to students Courtney Balling, Hannah Boudreau, Hope Zabronsky, Alexander Morton, Brendan Hennessey from The University of Vermont, and Nicolás Gomez (Universidad de Puerto Rico, PR), and Erin Buckley (St. Michael's College, VT), who helped with field and laboratory work through the Research on Adaptation to Climate Change program.

SUPPLEMENTAL MATERIAL

Supplementary materials are included with this paper and contain tables of general properties of the studied soils, chemical shifts of compounds identified by P-NMR, and the results of ANOVA and correlation analyses. Figures include a map of the study sites and P-NMR spectra showing details of the orthophosphate monoester region.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY

Data can be made available by request to authors.

AUTHOR CONTRIBUTIONS

Vanesa L. Perillo: Conceptualization; Data curation; Formal analysis; Methodology; Writing original draft; Review & editing. **B. Cade-Menun:** Formal analysis; Investigation; Methodology; Writing - original draft; 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

ORCID

Vanesa L. Perillo: https://orcid.org/0000-0002-6031-3119

B. Cade-Menun: https://orcid.org/0000-0003-4391-3718

Donald S. Ross: https://orcid.org/0000-0002-5390-6602

Beverley C. Wemple: https://orcid.org/0000-0002-3155-9099

REFERENCES

Abdi, D., Cade-Menun B. J., Ziadi N., & Parent L. -É. (2014). Long-term impact of tillage practices and phosphorus fertilization on soil phosphorus forms as determined by ^{31}P nuclear magnetic resonance spectroscopy. *Journal of Environmental Quality, 43,* 1431–1441. doi: 10.2134/jeq2013.10.0424.

Abdi, D., Cade-Menun B. J., Ziadi N., & Parent L. -É. (2015). Compositional statistical analysis of soil ^{31}P-NMR forms. *Geoderma, 257–258,* 40–47.

Bowman, R. A., & Moir, J. O. (1993). Basic EDTA as an extractant for soil organic phosphorus. *Soil Science Society of America Journal, 57*(6), 1516–1518.

Cade-Menun, B. J. (2015). Improved peak identification in ^{31}P-NMR spectra of environmental samples with a standardized method and peak library. *Geoderma, 257–258*, 102–114. doi: 10.1016/j.geoderma.2014.12.016.

Cade-Menun, B. J. (2017). Characterizing phosphorus forms in cropland soils with solution ^{31}P-NMR: Past studies and future research needs. *Chemical & Biological Technologies in Agriculture, 4,* 17. doi: 10.1186/s40538-017-0098-4.

Cade-Menun, B. J., He, Z., Zhang, H., Endale, D. M., Schomberg, H. H., & Liu, C. W. (2015). Stratification of phosphorus forms from long-term conservation tillage and poultry litter application. *Soil Science Society of America Journal,* 79(2): 504–516. doi: 10.2136/sssaj2014.08.0310.

Cade-Menun, B. J., & Lavkulich, L. M. (1997). A comparison of methods to determine total, organic, and available phosphorus in forest soils. *Communications in Soil Science and Plant Analysis, 28*(9–10), 651–663.

Cade-Menun, B., & Liu, C. W. (2014). Solution phosphorus-31 nuclear magnetic resonance spectroscopy of soils from 2005 to 2013: a review of sample preparation and experimental parameters. *Soil Science Society of America Journal, 78*(1):19–37.

Condron, L. M., Turner B. L., & Cade-Menun B. J. (2005). Chemistry and dynamics of soil organic phosphorus. In: Sims, J.T. and Sharpley, A.N., editors, Phosphorus: agriculture and the environment. Monograph no 46. Soil Science Society of America, Madison, WI. p. 87–121

Dodd, R. J., & Sharpley, A. N. (2015). Recognizing the role of soil organic phosphorus in soil fertility and water quality. Resour. Conserv. Recycl. 105:282–293.

Doolette, A. L., Smernik, R.J. & Dougherty, W. J. (2010). Rapid decomposition of phytate applied to a calcareous soil demonstrated by a solution ^{31}P NMR study. *European Journal of Soil Science, 61,* 563-575.

Dupas, R., Gruau, G., Gu, S., Humbert, G., Jaffrézic, A. & Gascuel-Odoux, C. (2015). Groundwater control of biogeochemical processes causing phosphorus release from riparian wetlands. *Water Research, 84*, 307-314. doi: 10.1016/j.watres.2015.07.048.

Giles, C., Cade-Menun, B., & Hill, J. (2011). The inositol phosphates in soils and manures: abundance, cycling, and measurement. *Canadian Journal of Soil Science 91*(3), 397–416.

Giles, C. D., Lee, L. G., Cade-Menun, B. J., Hill, J. E., Isles P. D. F., Schroth, A. W., Druschel, G. K. (2015). Characterization of organic phosphorus form and bioavailability in lake sediments using ^{31}P nuclear magnetic resonance and enzymatic hydrolysis. *Journal of Environmental Quality,* 44(3):882–894.

Hénault-Ethier, L., Lucotte, M., Smedbol, É., Pedrosa Gomes, M., Maccario, S., Lamoreaux Laprise, M. E., … Labrecque, M. (2019). Potential efficiency of grassy or shrub willow buffer strips against nutrient runoff from soybean and corn fields in southern Quebec, Canada. *Journal of Environmental Quality, 48,* 352-361. doi: 10.2134/jeq2016.10.0391.

Hoffmann, C. C., Kjaergaard, C., Uusi-Kämppä, J., Bruun Hansen, H. C., & Kronvang, B. (2009). Phosphorus retention in riparian buffers: Review of their efficiency. *Journal of Environmental Quality, 38,* 1942-1955.

Leytem, A. B., Smith, D. R., Applegate, T. J. & Thacker, P. A. (2006). The influence of manure phytic acid on phosphorus solubility in calcareous soils. *Soil Science Society of America Journal, 70*, 1629-1638.

Liu, J., Cade-Menun B. J., Yang, J., Hu, Y., Liu, C. W., Tremblay, J., … & Bainard, L. (2018). Long-term land use affects phosphorus speciation and the composition of phosphorus cycling genes in agricultural soils. *Frontiers in Microbiology, 9*, 1643. doi: 10.3389/fmicb.2018.01643.

Liu, J., Han, C., Yang, J., Cade-Menun, B.J., Hu, Y.F., Li, J., … & Ma, Y. (2020). The chemical nature of soil phosphorus in response to long-term fertilization practices: Implications for sustainable phosphorus management. *Journal of Cleaner Production, 272,* 123093

MacDonald, G. K., Bennett, E.M., & Taranu, Z.E. (2012). The influence of time, soil characteristics and land-use history on soil phosphorus legacies: a global meta-analysis. *Global Change Biology, 18,* 1904-1917.

Magdoff, F. R., Hryshko, C., Jokela, W. E., Durieux, R. P., & Bu, Y. (1999). Comparison of phosphorus soil test extractants for plant availability and environmental assessment. *Soil Science Society of America Journal, 63*(4), 999–1006.

Mears, D., & Markowitz, D. (2013). Missisquoi Bay Basin Water Quality Management Plan. Vermont Agency of Natural Resources, Vermont, USA.

Miltner, R J. (2015). Measuring the contribution of agricultural conservation practices to observed trends and recent condition in water quality indicators in Ohio, USA. *Journal of Environmental Quality, 44,* 1821-1831, doi: 10.2134/jeq2914.12.0550.

Nannipieri, P., L. Giagnoni, L. Landi, and G. Renella. 2011. Role of phosphatase enzymes in soil. Phosphorus in action. Springer. p. 215–243

Nelson, L.-A., B.J. Cade-Menun, I.J. Walker, and P. Sanborn. 2020. Soil phosphorus dynamics across a Holocene chronosequence of Aeolian sand dunes in a hypermaritime environment on Calvert Island, BC, Canada. Front. For. Glob. Change 3:83. doi: 10.3389/ffgc.2020.00083.

Noack, S.R., R.J. Smernik, T.M. McBeath, R.D. Armstrong, and M.J. McLaughlin. (2014). Assessing crop residue phosphorus speciation using chemical fractionation and solution 31P nuclear magnetic resonance spectroscopy. *Talanta. 126,* 122–129.

Perillo, V. L., Ross, D. S., Wemple, B. C., Balling C., & Lemieux, L. E. (2019). Stream corridor soil phosphorus availability in a forested–agricultural mixed land use watershed. *Journal of Environmental Quality, 48*(1), 185–192. doi: 10.2134/jeq2018.05.0186.

Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E., & Orihel, D. M. (2016). Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science & Technology, 50*(17), 8923–8929. doi: 10.1021/acs.est.6b02204.

Schneider, K. D., Cade-Menun, B. J., Lynch, D. H. & Voroney, R. P. (2016). Soil phosphorus forms from organic and conventional forage fields. *Soil Science Society of America Journal, 80*(2), 328–340.

Schoumans, O. F., Chardon, W. J., Bechmann, M. E., Gascuel-Odoux, C., Hofman, G., Kronvang, B., … & Dorioz, J. –M. (2014). Mitigation options to reduce phosphorus losses from the agricultural section and improve surface water quality: A review. *Science of the Total Environment, 468-469,* 1255-1266. doi:20.2026.j.scitotenv.2013.08.061.

Singh, N. K., Courevitch, J. D., Wemple, B. C., Watson, K. B., Rizzo, D. M., Polansky S., & Ricketts, T. H. (2019). Optimizing wetland restoration to improve water quality at a regional scale. *Environmental. Research Letters, 14,* 064006. doi:10.1088/1748-9326/ab1827.

Soil Survey Staff. (2017). Natural Resources Conservation Service, United States Department of Agriculture. https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx (accessed 8 May 2017).

Stout, L. M., Nguyen T. T., & Jaisi, D. P. (2016). Relationship of phytate, phytate-mineralizing bacteria, and beta-propeller phytase genes along a coastal tributary to the Chesapeake Bay. *Soil Science Society of America Journal, 80*(1), 84–96. doi: 10.2136/sssaj2015.04.0146.

Stutter, M., Kronvang, B., hUallacháin, D. Ó. & Rozemeijer, J. (2019). Current insights into the effectiveness of riparian management, attainment of multiple benefits and potential technical enhancements. *Journal of Environmental Quality, 48,* 236-247.

Stutter, M. I., Shand, C. A., George, T. S., Blackwell, M. S. A., Dixon, L., Bol, R., … & Haygarth, P. M. (2015). Land use and soil factors affecting accumulation of phosphorus species in temperate soils. *Geoderma 257–258*, 29–39. doi: 10.1016/j.geoderma.2015.03.020.

Toor, G. S., Cade-Menun, B. J., & Sims, J. T. (2005). Establishing a linkage between phosphorus forms in dairy diets, feces, and manures. *Journal of Environmental Quality,* 34(4):1380–1391.

Turner, B. L., & Blackwell, M. S. A. (2013). Isolating the influence of pH on the amounts and forms of soil organic phosphorus. Eur. J. Soil Sci. 64(2):249–259. doi: 10.1111/ejss.12026.

Turner, B. L., & Richardson, A. E. (2004). Identification of *scyllo*-inositol phosphates in soil by solution phosphorus-31 nuclear magnetic resonance spectroscopy. *Soil Science Society of America Journal, 68,* 802-808.

Turner, B. L., Cheesman, A. W., Godage, H. Y., Riley, A. M., & Potter, B.V. L. (2012). Determination of *neo*- and D-*chiro*-inositol hexakisphosphate in soils by solution ^{31}P NMR spectroscopy. *Environmental Science & Technology, 46,* 4994-5002.

Walton, C. R., Zak, D., Audet, J., Petersen, R. J., Lange, J., Oehmke, C., … & Hoffmann, C. C. (2020). Wetland buffer zones for nitrogen and phosphorus retention: Impacts of soil type, hydrology and vegetation. *Science of the Total Environment, 727,* 138709. doi: 10.1016/j.scitotenv.2020.138709.

Weller, C. M., Watzin M. C. & Wang, D. (1996). Role of wetlands in reducing phosphorus loading to surface water in eight watersheds in the Lake Champlain Basin. *Environmental Management, 20,* 731-739.

Williams, C.H., and G. Anderson. 1968. Inositol phosphates in some Australian soils. Soil Res. 6(1):121–130.

Wilson, R. S., Beetstra, M. A., Reutter, J. M., Hesse, G., DeVanna Fussell, K. M., Johnson, L T., … & Winslow, C. (2019). Commentary: Achieving phosphorus reduction targets for Lake Erie. *Journal of Great Lakes Research, 45,* 4-11. doi: 10.1016/j.jglr.2018.11.004.

Young, E. O., & Ross, D. S. (2016). Total and labile phosphorus concentrations as influenced by riparian buffer soil properties. *Journal of Environmental Quality, 45*(1), 294–304. doi: 10.2134/jeq2015.07.0345.

Young, E. O., & Ross, D. S. (2018). Phosphorus mobilization in flooded riparian soils from the Lake Champlain basin, VT, USA. *Frontiers in Environmental Science,* 6, 120. doi: 10.3389/fenvs2018.00120.

Young, E. O., Ross, D. S., Cade-Menun, B. J., & Liu C. W. (2013). Phosphorus speciation in riparian soils: A phosphorus-31 nuclear magnetic resonance spectroscopy and enzyme hydrolysis study *Soil Science Society of America Journal, 77*(5), 1636–1647.

Zaimes, G. N., Schultz, R. C., & Isenhart, T.M. (2008). Streambank soil and phosphorus losses under different riparian land-uses in Iowa. *Journal of the American Water Resources Association, 44*(4), 935–947.

Zhou, B., Vogt, R. D., Lu, X., Yang, X., Lü, C., Mohr, C. W., & Zu L. (2015). Land use as an explanatory factor for potential phosphorus loss risk, assessed by P indices and their governing parameters. *Environmental Science: Processes & Impacts, 17,*1443-1454. doi: 10.1039/c5em00244c.

FIGURE CAPTIONS

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.

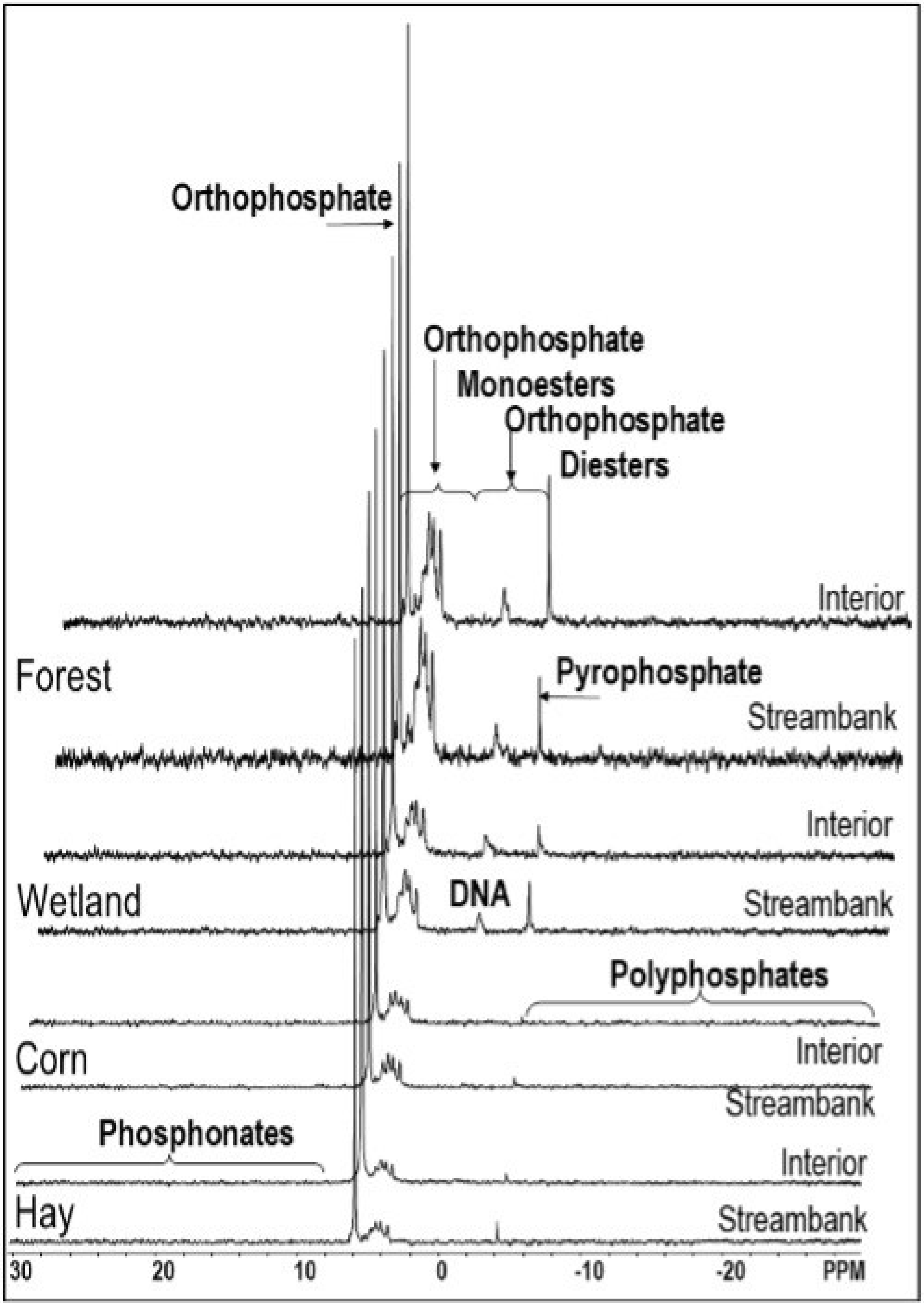

Table 1. General soil chemical properties and P-NMR results showing significant interactions of land use and landscape position with ANOVA. Values are mean ± std. dev., n = 2, α = 0.10.

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

Note: Means with different letters in the same row are significantly different (*p* < 0.10)

[a] Monoester 1 and Other Diester 2 are general regions of P-NMR spectra. See text for more details.

Table 2. Soil general chemical properties for which there was no significant interactions of land use and landscape position with ANOVA (0-10 cm depth). Values are mean ± std. dev. (n = 4 for land use, n = 8 for landscape position).

	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 ± 148 x	139 ± 96 y
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 ± 6.59 b	37.3 ± 12.8 ab	61.1 ± 19.0 a	56.5 ± 23.7 ab	52.8 ± 18.9	36.5 ± 23.7
Soil test P, mg kg^{-1}	0.90 ± 0.88 b	1.50 ± 0.49 ab	15.0 ± 18.8 a	5.72 ± 6.69 ab	9.75 ± 1.43 x	1.82 ± 2.17 y
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 ± 1.02 x	1.61 ± 1.00 y
Total C, g kg^{-1}	17.5 ± 9.59	48.4 ± 26.2	27.3 ± 7.61	26.4 ± 21.3	37.8 ± 19.0 x	22.0 ± 18.5 y
pH in water	4.79 ± 0.69 c	5.89 ± 0.29 b	7.12 ± 0.39 a	6.41 ± 0.19 ab	5.99 ± 1.06	6.10 ± 0.92
Oxalate-extractable Al, mg kg^{-1}	23.1 ± 10.9 b	75.2 ± 21.5 a	27.5 ± 11.2 b	29.8 ± 20.4 b	45.7 a ± 28.7	32.0 b ± 23.9
Oxalate-extractable Fe, mg kg^{-1}	71 ± 27	141 ± 92	53 ± 61	90 ± 58	115 ± 64	141 ± 91.7
DPS, %	10.5 ± 0.17 b	16.1 ± 3.93 ab	31.7 ± 15.6 a	27.0 ± 11.6 a	25.2 ± 16.4	17.4 ± 5.27
Est. porewater MRP[b], mg L^{-1}	0.23 ± 0.04 b	0.30 ± 0.05 ab	0.84 ± 0.59 a	0.52 ± 0.33 ab	0.64 ± 0.49 x	0.30 ± 0.15 y
Est. floodwater MRP [b], mg L^{-1}	0.15 ± 0.02 b	0.18 ± 0.03 ab	0.42 ± 0.26 a	0.29 ± 0.16 ab	0.34 ± 0.22 x	0.18 ± 0.08 y

Note: Means with different letters in the same row within either land use or landscape position are significantly different ($p < 0.10$)

[a] TP$_o$, total organic P; NETP Recovery, recovery of soil total P in NaOH-EDTA extracts; soil test P method, modified Morgan extract; DPS, degree of P saturation. See text for more details about methods.

[b] Porewater and floodwater molybdate-reactive P (MRP) concentrations were estimated from log (STP) using equations in Young & Ross (2018). See text for more details.**Table 3.** Correlations of P forms determined by P-NMR with soil parameters (n = 16). Only significant correlations ($\alpha = 0.10$) are shown.

	TP	TP_o	Soil test P	N	C	pH	Sand	Silt	Clay	Oxalate Al	Oxalate Fe	DPS
TP_o[a]	0.67											
Soil test P	0.80	0.68										
Total N	0.77	0.63	0.68									
Total C	0.71	0.53	0.63	0.97								
pH	0.48	0.45	0.56									
Sand	-0.84	-0.78	-0.65	-0.70	-0.66							
Silt	0.86	0.72	0.65	0.72	0.70		-0.97					
Oxalate Al	0.55		-0.65	0.77	0.81		-0.62	0.69				
Oxalate Fe				0.71	0.71		-0.44	0.43				
DPS	0.78	0.54	0.80	0.45		0.77	-0.48	0.49		0.72		
NETP	0.47	0.85	0.65	0.43		0.59						0.61
Orthophosphate	0.65	0.62	0.66			0.86	-0.56	0.56				0.81
Pyrophosphate	-0.63	-0.58				-0.63	0.51	-0.52				-0.63
Polyphosphate	-0.52	-0.51	-0.63	-0.51	-0.56		0.64	-0.70		-0.57	-0.47	
Tot Polyphosphate	0.65	0.76	0.66	0.81	0.7		-0.56	0.53				0.53
NMR Total P_i	0.82	0.87	0.80	0.60	0.49	0.70	-0.73	0.73				0.80

	TP	TP_o	Soil test P	N	C	pH	Sand	Silt	Clay	Oxalate Al	Oxalate Fe	DPS
scyllo-IHP[a]									0.62			0.43
D-*chiro*-IHP	0.54	0.47	0.58			0.81	-0.44					0.62
Total IHP	0.79	0.90	0.79	0.67	0.61	0.55	-0.75	0.75				0.70
Nucleotides						-0.66					0.50	
Glucose 6-phosphate						0.62						0.55
Unknown 5 ppm		0.46										
Monoester 1	0.81	0.57	0.72	0.61	0.60	0.66	-0.72	0.75		0.52		0.65
Total Monoesters	0.80	0.92	0.81	0.70	0.63	0.53	-0.78	0.77		0.44	0.48	0.70
DNA			-0.52			-0.64						
Other diester 1		-0.55	-0.55			0.53						
Total Diesters	0.75	0.81	0.67	0.86	0.79		-0.73	0.71		0.60	0.48	0.49
NMR Total P_o	0.80	0.89	0.78	0.76	0.72	0.45	-0.76	0.77		0.54		0.64

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

Table 4. Phosphorus species present (mg P kg^{-1}) in NaOH-EDTA extracts of soils, analyzed by P-NMR spectra. Values are means ± std. dev.; n = 4 for land use and n = 8 for landscape position.

	Land Use				Landscape Position	
	Forest	**Wetland**	**Corn**	**Hay**	**Interior**	**Streambank**
Inorganic P (P_i)						
Orthophosphate	33 ± 8.9 b	180 ± 83 a	379 ± 253 a	288 ± 196 a	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 ± 0.8 b	9.0 ± 5.8 ab	12.0 ± 5.8 a	9.9 ± 5.7 ab	11.4 ± 5.8 x	6.5 ± 3.4 y
Total Polyphosphates	10.5 ± 3.1	16.8 ± 10.5	17.3 ± 5.4	18.1 ± 10.0	20.4 ± 7.5 x	11.0 ± 4.5 y
Total P_i	43 ± 11 b	197 ± 85 a	396 ± 257 a	306 ± 205 a	341 ± 234 x	130 ± 95 b
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						
myo-IHP[a]	15.6 ± 6.2	35.0 ± 16.0	59.0 ± 26.9	41.5 ± 28.3	49.4 ± 26.3	26.1 ± 18.0
scyllo-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

neo-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
D-*chiro*-IHP	2.9 ± 0.8 b	11.6 ± 4.5 b	24.4 ± 11.2 a	11.5 ± 8.4 b	17.1 ± 11.2	8.1 ± 7.7
Total IHP	24 ± 6.8 b	65 ± 24 ab	111 ± 48 a	73 ± 249 ab	91 ± 47 x	46 ± 33 y
α-glycerophosphate	1.6 ± 0.5	3.7 ± 2.3	6.1 ± 2.1	4.7 ± 4.2	5.3 ± 2.9	2.7 ± 23
ß-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 ± 0.3 b	2.7 ± 0.5 a	4.6 ± 2.4 a	4.3 ± 1.7 a	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	44 ± 13 b	122 ± 51 ab	202 ± 87 a	138 ± 82 ab	169 ± 85 x	83 ± 56 y
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	25 ± 7	60 ± 44	50 ± 16	54 ± 39	66 ±	29 ± 13 y

	Diesters					33 x	
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 ± 19 b	187 ± 90 ab	260 ± 106 a	195 ± 123 ab	241 ± 108 x	115 ± 71 y

Note: Means with different letters in the same row within either land use or landscape position are significantly different ($p < 0.10$)

[a] IHP, inositol hexakisphosphate; M:D ratio, ratio of orthophosphate monoesters to orthophosphate diesters, using data corrected for diester degradation.