Dominant glacial landforms of the lower Great Lakes region exhibit different soil phosphorus chemistry and potential risk for phosphorus loss

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ABSTRACT

Phosphorus (P) losses from agricultural soils are a growing economic and water-quality concern in the Lake Erie watershed. While recent studies have explored edge-of-field and watershed P losses related to land-use and agricultural management, the potential for soils developed from contrasting parent materials to retain or release P to runoff has not been examined. A field-based study comparing eight agricultural fields in contrasting glacial landscapes (hummocky coarse-textured till-plain, lacustrine and fine-textured till-plain) showed distinct physical and geochemical soil properties influencing inorganic P (P_i) partitioning throughout the soil profile between the two regions. Fields located on the coarse-textured till-plain in mid-western Ontario, Canada had alkaline calcareous soils with the highest Total-P_i concentrations and the majority of soil P_i stored in an acid-soluble pool (up to 91%). In contrast, loosely to moderately soluble P_i concentrations were higher in soils of the lacustrine and fine-textured till-plain in southwestern Ontario, northeast Indiana and northwestern Ohio, US. Overall, soils on the lacustrine and fine-textured till-plain had a greater shrink swell-capacity, likely creating preferential flow to minimize P_i interaction with the more acidic, lower carbonate and lower sorption capacity soils. These differences in soil P_i retention and transport pathways demonstrate that in addition to management, the natural landscape may exert a significant control on how P_i is mobilized throughout the Lake Erie watershed. Further, results indicate that careful consideration of region-specific hydrology and soil biogeochemistry may be required when designing appropriate management strategies to minimize P_i losses across the lower Great Lakes region.

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Introduction

Phosphorus (P) is a fundamental nutrient for crops; yet, it represents a serious environmental threat to receiving aquatic ecosystems. Persistent harmful algal blooms and hypoxia in Lake Erie, similar to many other surface water bodies, are largely driven by excess P loading (*e.g.*, Stumpf et al., 2012). This has led to bi-national targets by the US and Canada to reduce annual and spring P loadings by 40% from 2008 levels (International Joint Commission (IJC), 2014). Non-point sources dominate P loadings into Lake Erie (Maccoux et al., 2016), where agriculture is the major non-point source (Michalak et al., 2013). Phosphorus loadings in river tributaries vary considerably across the Lake Erie watershed, with the majority of P loadings originating from US tributaries (>80%) relative to Canada (Maccoux et al., 2016). To achieve water quality targets, it is critical to understand the factors controlling these regional differences in P loading.

Large landscape variability in topography and texture of glacial deposits exists within the Lake Erie watershed and across the lower Great Lakes region. Hummocky, coarse-textured glacial till characterizes mid-western Ontario, Canada, while lacustrine and fine-textured glacial till dominate southwestern Ontario, northeast Indiana and northwestern Ohio in the US (Government of Canada and U.S. Environmental Protection Agency, 1995). While soluble reactive P (SRP) concentration frequently exceeds water quality guidelines (*i.e.*, 0.02–0.03 mg/L total P, Environment Canada, 2004; Correll, 1998) in agricultural runoff and agricultural-fed tributaries in both regions, differences in SRP export patterns have emerged. Persistent SRP concentrations across a range of discharge volumes in edge-of-field runoff and tributaries in the western Lake Erie basin indicate transport-limitation (*i.e.*, hydrology-driven SRP export, King et al., 2017; Williams et al., 2016). In contrast, more variable SRP concentrations across flow regimes in edge-of-field runoff have been observed in mid-western Ontario, suggesting supply-

limitation (*i.e.*, chemodynamic SRP export, Plach et al., 2018). The observed differences in SRP export patterns across this landscape gradient highlight the potential role of varying soil physical and geochemical properties on regional P loading due to soils originating from contrasting glacial deposits in the Lake Erie watershed and lower Great Lakes region.

Many field and laboratory studies have related surficial soil properties to SRP losses in surface runoff [*e.g.*, soil test P (STP) concentrations (Heckrath et al., 1995; McDowell and Sharpley, 2001; Pote et al., 1996; Wang et al., 2012; Vadas et al., 2005), degree of P saturation (Hooda et al., 2000; Sharpley, 1995), and soil equilibrium concentrations (EPC$_0$) (Fang et al., 2002)]. Surficial soil properties, however, are unable to consistently predict SRP leaching from subsurface drainage (*e.g.*, Andersson et al., 2013; Djodjic et al., 2004). This is largely attributed to differing flow pathways and reactive properties of the soil. For example, fine-textured soils have a greater sorption capacity for P compared to coarse-textured soils (*e.g.*, Ige et al., 2005; Poirier et al., 2012), but they can also be prone to fissures and cracking that facilitate P losses by preferential flow and bypassing of soil sorptive sites (Jarvis, 2007; Kleinman et al., 2009). Elevated SRP loss in subsurface drainage from fields with fine-textured soils compared to medium- to coarse-textured soils within the Lake Erie region have been attributed to differences in soil physical and chemical characteristics (Beauchemin et al., 1998; Eastman et al., 2010; Pease et al., 2017; Van Esbroeck et al., 2016); yet, few studies have directly measured the reactive properties and partitioning of P in soil horizons across the texture gradient found within the watershed.

The abundance and reactivity of differing minerals (*e.g.*, metaloxides, carbonates) and organic matter (*e.g.*, plant residues, soil microorganisms) are also important to soil SRP sorption and storage of P within agricultural soils (Beauchemin et al., 2003; Eriksson et al., 2016; Hesterberg, 2010; Holtan et al., 1988). Establishing soil geochemistry and solid-phase partitioning of inorganic P (P$_i$) can help inform the potential for soil SRP release due to changes in substrate reactivity and mineral solubility under fluctuating soil conditions (*e.g.*, pH, redox conditions), which is essential for predicting the timing of SRP availability to crops and runoff and the fate of P$_i$ associated with eroded soils that become entrained in downstream water-columns or settle to bed sediments. Although solid-phase P$_i$ partitioning has been examined in suspended particulates and bottom sediments in agricultural tributaries of the lower Great Lakes region (*e.g.*, Young et al., 1985; Stone and English, 1993; Mayer and Manning, 1989), characterizing the relative availability of P$_i$ (labile *versus* non-labile forms) of the source material (*i.e.*, agricultural surficial and subsurface soils) is relatively limited across this region (Ribey and O'Halloran, 2016).

To design and plan appropriate cropland management strategies to achieve the targeted SRP reductions to Lake Erie, it is critical that not only P inputs (*e.g.*, fertilizer type and form, application timing) are assessed, but also the stability of P$_i$ stored in the soil. The objectives of this field-based study were therefore to investigate the spatial variation of: 1) P$_i$ distributions between surficial, subsurface, and deep soils; 2) reactive solid-phases for P$_i$ partitioning; and 3) the sorptive properties of soils affecting P$_i$ partitioning in agricultural croplands in contrasting glacial landforms from the hummocky coarse-textured glacial to the lacustrine and fine-textured glacial till-plain across the Lake Erie watershed and the lower Great Lakes region of Canada and the US.

Materials methods

Field soil sampling

Agricultural soils covering the dominant glacial landform types of the lower Great Lakes region (hummocky coarse-textured till-plain and lacustrine and fine-textured till-plain) were collected from eight fields in Ontario (LON, ILD, SM and ESS), Canada, and Ohio (BO and BG) and Indiana (KC1 and KC2) in the US (Fig. 1). All study sites were

within the combined Lake St. Clair-Lake Erie watershed, with the exception of the LON site in mid-western Ontario, which is in the Lake Huron watershed. Across southwestern Ontario, northwestern Ohio and northeastern Indiana, wet forests and marshlands dominated the landscape after the last glacial ice age due to poor drainage of the deposited lacustrine sediments in that region. All fields were under a corn-soy-wheat crop rotation, with no P fertilizer or manure applied during the 6 months prior to soil sampling. Lime amendments were, however, added to a subsection of the Indiana fields 9 months prior to sampling. All study fields contained tile drains, which were located ~0.9 m below the soil surface with the exception of the ESS site, at which the tile depth was ~0.6 m. Detailed descriptions of the Ontario field sites (LON, SM and ILD), as well as concentrations of total P (TP) and SRP in the surface runoff and tile drainage (LON and ILD) have been reported previously (Plach et al., 2018; Van Esbroeck et al., 2016). Similarly, site descriptions and P concentrations and loadings from the Ohio field sites have been reported in Pease et al. (2017) and Williams et al. (2016).

Composite soil samples, made up of three cores, were collected from five depths (0–5, 5–15, 15–30, 30–60 and 60–90 cm) at three locations *i.e.*, three separate composite samples per field in May and June 2016. Soil samples were homogenized, air-dried in triplicate at 30 °C, and passed through a 2-mm sieve prior to analysis. All soil depths were analyzed for composition [organic matter and carbonates], particle size distribution, gravimetric moisture content, soil pH, and STP concentrations. A subset of the three sampling depths *i.e.*, surficial (0–5 cm), subsurface (15–30 cm) and deep (tile depth; 60–90 cm) soils, were analyzed for solid-phase P$_i$ partitioning, reducible iron (Fe) oxides and sorption properties.

Soil phosphorus analysis

STP concentrations were assessed by Olsen (Olsen et al., 1954), Bray-1 (Bray and Kurtz, 1945), and Mehlich-3 (Mehlich, 1984) methods. Extracts were filtered through a Whatman No. 42 filter paper and analyzed for SRP by colorimetric analysis (ammonium-molybdate ascorbic-acid, Bran Luebbe AA3, Seal Analytical Ltd.: Method No. G-175-96 Rev. 13 for SRP). The detection limit for SRP analysis was 1 μg/L. Analytical precision was determined on 10% duplicates and the relative percent difference between duplicates was found to be ≤6%.

Solid-phase P$_i$ partitioning was determined on a subset (surficial, subsurface and deep) of field moist samples (homogenized and passed through a 2-mm mesh screen) using the fractionation procedure summarized in Zhang and Kovar (2009) for calcareous soils. Briefly, P$_i$ was quantified in four operationally defined soil fractions: loosely adsorbed P$_i$ on oxide surfaces (*e.g.*, AlOx and FeOx) and P$_i$ compounds soluble in bases, likely clay bound-P (NaOH + NaCl (*i.e.*, Sol-P$_i$)); reductant soluble P$_i$ (*i.e.*, redox-sensitive metal oxides) (sodium citrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O)-sodium dithionite (Na$_2$S$_2$O$_4$)-sodium bicarbonate (*i.e.*, CDB-P$_i$)); acid-soluble P$_i$ for carbonate and apatite bound-P (HCl (*i.e.*, HCl-P$_i$)). The residual soil was digested in 10% K$_2$S$_2$O$_8$ in an autoclave at 120 °C for 2 h to target refractory organic and mineral associated P$_i$ (*i.e.*, Res-P$_i$). Soil was centrifuged at 10,000 rpm for 5 min (11,180 ×g) and washed with saturated NaCl between each extraction step. The wash was added to the extract in each step prior to analysis. Extracts were analyzed colorimetrically according to Murphy and Riley (1962). Interferences in the CDB-P$_i$ extract and the acid-molybdate reagent (Murphy and Riley, 1962) were corrected by oxidizing excess dithionite by exposing the samples to air and by adding an ammonium molybdate solution to each sample prior to the acid-molybdate reagent to improve color development (Weaver, 1974). Extracts for Sol-P$_i$ and HCl-P$_i$ were neutralized with HCl and NaOH, respectively, prior to analysis.

Soil composition

Soil pH on air-dried samples was measured in 0.01 M CaCl$_2$ at a soil to solution ratio of 1:2 (Hendershot et al., 1993). Bulk organic matter