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Phosphorus Sorption Capacity and Its Relationships With Soil Properties Under Podzolic Soils of Atlantic Canada

Amana Jemal Kedir[1,2*], *Judith Nyiraneza*[3], *Kelly Anne Hawboldt*[4], *David Bruce McKenzie*[5] and *Adrian Unc*[1,2,6*]

[1] School of Science and the Environment, Memorial University of Newfoundland, Corner Brook, NL, Canada, [2] Environmental Science Program, Memorial University of Newfoundland, St. John's, NL, Canada, [3] Charlottetown Research and Development Centre, Agriculture and Agri-Food Canada, Charlottetown, PE, Canada, [4] Faculty of Engineering and Applied Science, Memorial University, St. John's, NL, Canada, [5] St. John's Research and Development Centre, Agriculture and Agri-Food Canada, St. John's, NL, Canada, [6] Department of Natural Resource Sciences, McGill University, Montreal, QC, Canada

Repetitive long-term fertilizer application leads to phosphorus (P) accumulation in agricultural soils. This can pose environmental risks if the soil's phosphorus storage capacity is not well understood and considered when planning nutrient management. We investigated the P sorption capacity (PSC) in the surface (0-20 cm, n = 23) and subsurface (20-40 cm, n = 23) of long-term managed podzolic soils in Newfoundland (Nfld), Canada, through batch adsorption using two P concentrations of 150 and 500 mg P L^{-1}, and developed pedotransfer functions to estimate PSC using selected soil properties. Also, the correlation between actual PSC, soil properties, and estimated Phosphorus saturation index (PSI) and soil P sorption capacity (SPSC) both from standard soil test were evaluated. The surface and subsurface soils provided similar median PSC (1.34 and 1.32 mg g^{-1}, respectively, $p = 0.16$) when examined with the 150 mg P L^{-1} solution. With 500 mg P L^{-1} solution, the subsurface soils had significantly higher median PSC than the surface soils of the same fields (2.74 and 2.27 mg g^{-1}, respectively, $p = 0.02$); and had a better linear relationship ($R^2 > 0.40$, $p < 0.05$) with SPSC than at the lower P concentration. The surface soils had significantly higher extractable median P in water, citric acid, and Mehlich-3, higher soil organic matter (SOM), moisture content, *Mehlich-3-Fe*, *-Ca*, and *-K*, PSI, electrical conductivity, silt, and clay contents, while *Mehlich-3-Al*, *Mehlich-3-Al : Fe* ratio, SPSC, and sand were lower than those in the subsurface soils. All soils had comparable pH (~6.3). Pedotransfer function revealed that the PSC could be predicted using SOM, *Mehlich-3-Al*, and *Mehlich-3-P_{ICP}* and thus may be employed for developing testable hypotheses relevant to environmentally and economically viable P management strategies for acidic soils in boreal regions.

Keywords: soil phosphorus sorption capacity, phosphorus saturation index, boreal agriculture, managed podzolic soils, point phosphorus adsorption capacity

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Xiaogang Yin,
China Agricultural University, China

Reviewed by:
Shamsollah Ayoubi,
Isfahan University of Technology, Iran
Tangyuan Ning,
Shandong Agricultural University, China

***Correspondence:**
Amana Jemal Kedir
ajkedir@mun.ca
Adrian Unc
aunc@grenfell.mun.ca

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INTRODUCTION

Phosphorus (P), a critical element for metabolic regulation of all living cells, is a non-renewable and depleted resource (1). Following World War II, and with increased access to fossil fuel (2, 3), P has been heavily mined with ~82% used as fertilizer. This increased the soils' legacy P (4).

During the Green Revolution (5), excessive application of fertilizer led to P accumulation (*i.e.*, legacy P) in agricultural and pasture soils (6). Since then, and with continued P fertilizer applications, soil P build-up has become a major agronomic and environmental concern (7–9). For example, excessive and repetitive manure application to Dutch fields in the 1980s led to an average legacy P of 2,050 kg P ha^{-1} (10, 11). Also, in Germany, an average of 1,100 kg P ha^{-1} was reported in 2010 (12). In Newfoundland (Nfld), Canada, lands converted from boreal forests to agricultural use in the early and mid-20th century were continually manured to maintain fertility. In podzolic soils the large application of manure, calculated to satisfy crop requirements for N, might result in P accumulation (13). There is a lack of information on the long-term managed podzolic soil's P sorption capacity and its relationships with soil properties in Nfld, a region undergoing agricultural expansion through land-use conversion on podzolic soils. The region is similar to other locations in the circumboreal that might undergo similar transformations (14).

The P accumulated in agricultural soils is either strongly fixed by clay minerals and sesquioxides of Al, Fe and Ca and organometallic chelate (6, 15) or loosely adsorbed on the soil surface. The weakly attached P (labile P) can be easily desorbed to maintain the P equilibrium in the soil-solution (16). Based on the soil properties, and mainly to the soil pH, the non-labile P could be transformed to labile and then to available P and vice-versa (17). The legacy P can be brought into the available pool to reduce the need for further P inputs by adjusting the soil pH.

The accumulation of P in soils is thus related to soil buffering capacity in the context of the management history (6, 15, 18). In Denmark, century-old managed arable soils, including Podzols, have higher annual P accumulations (up to 25 kg P ha^{-1}) in surface soils (0-25 cm) and a higher total P mobility to depths of up to 75 cm than adjacent deciduous forest soils (19, 20). Long term (30 years) intensely fertilized Oxisols in Mato Grosso, Brazil, release 14 kg of legacy P ha^{-1} annually. However, 75% of the legacy P may be inaccessible to plants despite the decline of P sorption by the soils; this might be related to the presence of high content of reactive Al and Fe oxides (6). For example, the Ap horizons (plough layer) of long-term managed Podzols in eastern Nfld have a high P sorption capacity, strongly correlated with the soil's high Al content (21). It is thus necessary to understand P dynamics in long-term managed agricultural podzolic soils to ensure efficient utilization of P resources and provide environmental stewardship while satisfying crop requirements (6).

For agronomic or environmental management of P, several soil P extraction protocols (P-*tests*), adsorption tests, and indices were developed to assess the status of P in soils under different management regimes. Among these, soil P storage capacity (SPSC) is used as a proximate parameter for assessing and predicting the P storage and release capacities of soils over short- or long-term after receiving P fertilizers (10). *P-tests* such as Mehlich-1, Mehlich-3, or others, initially developed for agronomic purposes, have recently been also employed for environmental risk assessments (22–25). Phosphorus saturation index (PSI) is calculated from the molar ratio of P to Al or Al plus Fe which can be used as an alternative tool to monitor P status relevant to environmental protection (26–28). The soil's P sorption capacity has thus been well studied to determine soil fertility and assess environmental risks for various soils (29–32). However, site-specific P sorption studies are required to account for regional specificity of soil and environmental variations (33). Phosphorus sorption in long-term managed podzolic soils, particularly the variability in sorption by the depth, has not yet been thoroughly investigated for Nfld podzolic soils, representative of circumboreal podzolic soils.

We aimed to (1) determine and calculate the residual P sorption capacity (PSC) of long-term managed surface (0-20 cm) and subsurface (20-40 cm) podzolic soils using point adsorption technique, i.e., 150 and 500 mg P L^{-1}, and (2) assess the relationships between point P sorption capacities and soil properties and P indices. This information is critical for the development of sustainable P management plans and a data-informed decision support system for the planned agricultural expansion in eastern Canada and elsewhere in the boreal regions with similar soil types and management.

MATERIALS AND METHODS

Site Description

Soils were sampled at the St. John's Research and Development Centre, Agriculture and Agri-Food Canada, (47.56° N, 52.71° W). The site has an elevation ~114 m above sea level with an annual mean rainfall of 1534 mm and temperature of 5° C (34). The sampled fields have been farmed for ~150 to 160 years, mainly for perennial forage production followed, in the last 50 to 80 years, by field crop experiments (35–38). The site covers an area of ~28 hectares divided into 23 unequally partitioned fields, which had been under deep plough farming, mainly for perennial forage production for dairy farms in the Avalon Peninsula (35), since the 1860s. These fields received 227 kg ha^{-1} of 6-12-12 fertilizer and an unknown amount of manure, as often as 2 to 3 times per year, for the first 30 years. During the same period, the fields received three applications of limestone at the rate of 4 Mg ha^{-1} (39, 40). Since 1949, the fields have been used for field trials for forage, annual crops, and vegetables. Most fields were managed under timothy (*Phleum pratense*), red clover (*Trifolium pratense*) and alsike clover (*Trifolium hybridum*)

Abbreviations: Ca, Mehlich-3 extractable calcium; Fe, iron; Al, aluminum; K, potassium; Nfld, Newfoundland; P, Phosphorus; PSC, batch phosphorus sorption capacity; PSI, Phosphorus Saturation Index; SOM, Soil Organic Matter; SPSC, Soil P Sorption Capacity.

mixtures in rotation with research crops and have received various rates of manure, amended with mineral fertilizer, and with intermittent lime applications. The forage fields yielded 1 to 2 cuts annually; silage production and earlier harvesting has allowed for 2 to 3 cuts per year in recent years. Another field, rocky and with poor drainage due to shallow hardpans, was allowed to naturally revert to forest in the 1970s to early 1980s and today is covered by black spruce (*Picea mariana*), mountain ash (*Sorbus americana*), and serviceberry (*Amelanchier bartramiana*) (David McKenzie, Personal Communication, 2018). The at the site is an Humo-Ferric Podzol developed on a glacial till materials (41).

Soil Sampling

Soil samples were collected from 23 managed fields in November 2017, with a stainless-steel sand auger. Proportional to the field size, 3 to 5 sampling locations per field were randomly selected. From each sampling location, triplicated cores were collected at 1-metre intervals from 0-20 cm (surface) and 20-40 cm (subsurface) depths. Thus, for each field a variable number of 9 to 15 same-size samples of about 300 g each were collected in clean bucket for each depth and composited to produce one sample per depth for each field (46 samples). Eventually an aliquot of about 1 L of fresh soil was transferred into 1.5 L polyethylene Ziploc bags and transported to the laboratory.

Sample Handling, Processing, and Analysis

The soils were air-dried for 3 to 5 d in a temperature-controlled room (~35°C with air movement) and then passed through a 2 mm sieve. Samples were analyzed for: soil organic matter (SOM) based on the loss-on-ignition method at 430°C heated for 6 h (42, 43); moisture content (MC) determined by drying field-fresh sample in the forced-air oven at 105°C for 24 hr (43); pH and electrical conductivity (EC) measured in 1:2 soil to water ratio (44); particle size distribution was determined using hydrometer method (45); selected samples were used for mineralogical analysis using a Rigaku Ultima-IV Powder X-Ray Diffractometer (XRD) (Rigaku Corporation, Tokyo, Japan) at 2Theta $theta^{-1}$, 40kV and 44mA. The mineralogical analysis was conducted for selected samples to identify the dominant mineral phases in long term managed podzolic soils. The extractable (potentially available) P was determined in Mehlich-3 (46) 1% citric acid (CA) (47), and deionized water (48, 49) extracts (1:10 soil to solution ratio) using the ascorbic acid method as described by Murphy and Riley (50) and modified by Watanabe and Olsen (51). Mehlich-3 extractable total P and micro- and macro-nutrients were determined using a Prodigy High Dispersion ICP-OES (Teledyne Leeman Labs, Manson, USA).

Point Sorption Test

For all 46 samples, representing surface and subsurface soils, two-point P sorption capacity tests were performed in triplicate (52) using initial concentrations of 150 and 500 mg P L^{-1}. These initial P concentrations were identified from the calibrated sorption isotherm experiment employed in our previous work (21). Briefly, a 2 ± 0.01 g sample of air-dried soil was added to a 125 mL Erlenmeyer flask and saturated with 20 mL of 0.01M KCl solution containing either 150 or 500 mg P L^{-1}. The soil-solution mixture was agitated for 1 h on an end-to-end shaker followed by equilibration at room temperature (~20°C) for 22 h and eventually re-agitated for another 1 h (53). The soil-solution was filtered through 0.45 μm filter paper to collect the filtrate (30, 54–56). The equilibrium P in the filtrate was determined using the ascorbic acid method as described by Murphy and Riley (1962) (50) and modified by Watanabe and Olsen (51).

The point P sorption protocol used in this study is similar to that employed in other studies (30, 54–57) except that microbial inhibitors like toluene or chloroform were not used as they might increase dissolved P in solution through lysis of microbial cells (58). The amount of phosphate sorbed at equilibrium (qe) was calculated using Equation (1):

$$q_e = \frac{(C_i - (C_e - C_o) * V}{m} \dots \quad \dots \quad \dots \quad \dots \qquad \text{Eq. 1}$$

where: q_e (mg g^{-1} of soil) is the amount of P adsorbed at equilibrium; C_i, C_e, and C_o are the initial, equilibrium, and labile P concentrations (mg L^{-1}), respectively; V is the volume of the solution in L and m is the oven-dry soil mass (g) (59).

Estimation of Soil P Sorption Capacity From Mehlich-3 Test

Additionally, we calculated PSI and SPSC indices (9, 26, 60–62) from Equation (2) and (3).

$$PSI = \frac{\frac{M3-P}{31}\left(mmol\ kg^{-1}\right)}{\frac{(M3-Al}{27} + \frac{M3-Fe}{56}\left(mmol\ kg^{-1}\right)} \dots \quad \dots \quad \dots \qquad \text{Eq.2}$$

$$\begin{aligned} SPSC \quad & \left(mg\ kg^{-1}\right) \\ & = (critical\ PSI - soil\ PSI) \\ & \quad \times \left(\frac{M3-Al}{27} + \frac{M3-Fe}{56}\right) \quad \left(mmol\ kg^{-1}\right) \\ & \quad \times 31 \quad mg\ mmol^{-1} \dots \quad \dots \quad \dots \quad \dots \qquad \text{Eq.3} \end{aligned}$$

Critical PSI's of 0.10 for agronomic (SPSC-1) and 0.14 for environmental (SPSC-2) purposes were adopted from the Canadian Maritime provinces (26, 60) and a NL soil fertility survey that was based on standard farmers' soil tests (63). An SPSC value less than zero indicates that the soil serves as a source of P for the plant or environmental contamination (64). Both PSI and SPSC can inform the soil P status related to management history and properties of the specific soil types.

Statistical Analysis

Descriptive and explanatory statistics were carried out using PAST3 (65) and Origin (Pro) version 2019 (OriginLab Corporation, Northampton, MA, USA., 2019). The data distribution was tested using Shapiro-Wilk test before inferential analysis. The P sorption capacity and soil properties, for the surface and subsurface soils, were compared using the Kruskal Wallis test. Pearson correlation (r) was performed to identify the relationship between point P and calculated sorption capacities and soil properties. Additionally, stepwise multiple linear regressions were employed to assess the statistical relationship between point P sorption capacity and selected soil properties. The established relationship can be used to estimate the P sorption capacities of managed podzolic soils from routine soil tests. Tests are considered statistically significant at $P_{H0} < 0.05$.

RESULTS AND DISCUSSION

Soil Characteristics

The surface soils had either silty loam or loamy texture, whereas the subsurface soils had mainly loamy texture. The median contents of clay, silt, and SOM in surface soils were significantly greater than for subsurface soils ($p < 0.001$) while the reverse was observed for Al and sand content (**Table 1**). Surface soils had a median pH of 6.3, EC of 239 µS cm^{-1}, and SOM of 12% (**Table S1**). Subsurface soils have a median pH of 6.3, EC of 148 µS cm^{-1}, and SOM of 9% (**Table S2**). The soil texture and SOM of surface soils are comparable with reference samples collected from the B horizon of adjacent land covered with natural vegetation while the subsurface soils have higher clay and SOM, and lower sand content compared to non-managed BC horizon (21)Click or tap here to enter text.

Nevertheless, the XRD mineralogical analysis showed similar mineral phases in both surface and subsurface soils except for Berlinite ($AlPO_4$), which was only detected in the surface soils (**Table S3**). Differences in soil characteristics between the surface and subsurface could be attributed to the management history as most of the soil-plant interactions and tillage and manure input happened in the top 15-20 cm of the soil. Additionally, the surface soils may have an accelerated biomass turnover resulting in higher SOM in addition to long-term manure application which also increases moisture retention and EC. The surface soils, with higher SOM, had significantly higher EC than subsurface soils (**Table 1**). The SOM is the source of carboxyl and phenolic acids, the largest contributors to cations exchange capacity in the soil (66, 67). Remarkably, the median pH of the surface and subsurface soils was not significantly different. The minor pH increases in the subsurface could be due to cumulative calcium leaching from surface into the subsurface over several years (68) and lower SOM in the subsurface compared to surface soils (**Table 1**). Both surface and subsurface soils have relatively higher SOM compared to other podzolic soils sampled in the western NL, managed for about 60 years (21), or the nearby Canadian Maritime provinces (60). This could be attributed to higher organic carbon input in the Hummo-Ferric podzol through repeated application of manure.

Median molybdate reactive P concentrations in the Mehlich-3, citric acid, and water extract were 36.5, 131.2, and 0.9 mg P kg^{-1} in surface soils and 12.8, 90.1, and 0.7 mg P kg^{-1} in subsurface soils, respectively (**Table S1**). The soluble reactive P measured in water, citric acid, and Mehlich-3 solutions were

TABLE 1 | Comparison of median values of soil's P sorption capacities and soil characteristics between surface (0-20 cm, n = 23) and subsurface (20-40 cm, n = 23) of long term managed podzolic soils.

Soil Variables	Unit	Median Value		Kruskal-Wallis test
		0-20 cm	20-40 cm	P-value
Clay	%	17.96	15.68	<0.001
Silt	%	50.44	41.72	<0.001
Sand	%	31.60	42.88	<0.001
MC	%	44.94	35.61	<0.001
SOM	%	12.24	9.05	<0.001
pH	–	6.29	6.33	0.660
EC	µScm^{-1}	238.58	147.78	<0.001
H_2O-P	mgkg^{-1}	0.85	0.70	<0.001
CA-SrP	mgkg^{-1}	131.24	90.10	<0.001
M3-SrP	mgkg^{-1}	36.49	12.81	<0.001
M3-Ca	mgkg^{-1}	2584.22	1584.17	<0.001
M3-K	mgkg^{-1}	176.89	65.99	<0.001
M3-P	mgkg^{-1}	40.59	15.65	<0.001
M3-Fe	mgkg^{-1}	196.71	150.70	<0.001
M3-Al	mgkg^{-1}	1395.79	1612.77	<0.001
Al : Fe	mmol ratio	14.75	21.28	<0.001
PSI	%	2.85	1.29	<0.001
SPSC-1	mg kg^{-1}	129.93	175.51	<0.001
SPSC-2	mg kg^{-1}	197.06	252.22	<0.001
PAC-150	mgg^{-1}	1.34	1.32	0.162
PAC-500	mgg^{-1}	2.27	2.74	0.020

Moisture content (MC), soil organic matters (SOM), electrical conductivity (EC); H_2O-SrP, CA-SrP, and M3-SrP represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis; M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al are calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminum (Al) analysed by ICP-OES in Mehlich-3 (M3) extract, P saturation index (PSI), soil P sorption capacity (SPSC1 and SPSC2) at 0.10 and 0.14 critical PSI, below the detection limit (BDL) of 0.01 mg P kg^{-1} which varies for the different tests. PAC-150 and PAC-500 represented a P sorption capacity of soils treated with 150 mg P L^{-1} and 500 mg P L^{-1}, respectively.

significantly higher in surface than subsurface soils (**Table 1**). The higher P extractability in citric acid solution for both surface and subsurface soils compared to water and Mehlich-3 solution might be due to the ability of the 1% citric acid solution to extract more organic and inorganic P (69). The significant amount of P extracted by the citric acid from subsurface soils might suggest the vertical mobility of P due to long-term fertilizer input (20, 70, 71), combined with the natural podzolization mechanisms under the boreal climate (72).

The median of total P, potassium (K), calcium (Ca), and iron (Fe) extracted by Mehlich-3 from surface soils were significantly greater than for subsurface soils while for aluminum (Al) the trend was reversed (**Table 1**). The differences between surface and subsurface soils properties can be also attributed to the long-term recurring application of manure or mineral fertilizers, liming, and cropping (68, 73, 74). Previous studies (75–78) reported increased available or total P in surface soils of long-term managed fields. Different P-*tests* can be useful to assess the effect of long-term management on P pools (75). Furthermore, long term manure application leads to P build-up in surface (0-15 cm) soils but also to vertical mobility of available and total P (e.g., Whalen & Chang, 2001; 16 years of manure application).

The P build-up in the soil could occur due to various factors, including (i) nutrient-unbalanced over application of fertilizer, (ii) excessive application of manure targeting only the N requirements (13), and (iii) nature of the soil properties such as high Al and Fe content or low fertilizer responses (high P fixation) (21, 79). However, there is limited knowledge on the P sorption or storage capacity of the long-term managed podzolic soils. Thus, a single point P sorption test, the calculated P indexes based on Mehlich-3 test, and the measured soil properties were used to describe the P sorption capacity of the long-term managed podzolic soils.

Phosphorus Sorption Capacities Determined From a Point Sorption Test

The point P sorption capacity of 23 surface and 23 subsurface soils were significantly increased with increasing the initial P concentration from 150 to 500 mg P L^{-1} (**Tables 1** and **S4**). When the soils were treated with an initial concentration of 150 mg P L^{-1}, the median P sorption capacities of surface and subsurface were 1.34 and 1.32 mg P g^{-1}, respectively, and not significantly different (**Table 1**). Nevertheless, when treated with 500 mg P L^{-1}, the sorption capacity of subsurface soils (median: 2.74 mg P g^{-1}) was significantly greater than for surface soils (median: 2.27 mg P g^{-1}; **Tables 1** and **S4**).

Surface and subsurface soils retained 89% and 88% of P applied at dose of 1.50 g P kg^{-1} dry soil or 150 mg P L^{-1}, and 45% and 55% of P applied at dose of 5.00 g P kg^{-1} dry soil or 500 mg P L^{-1}, respectively, after 24 hrs of contact time at ~20°C. The P retention characteristics can be explained by higher SOM, Ca, and Fe in surface soils and by the higher Al in the subsurface soils, as observed in this study and in our previous work (21). The higher P retention at lower P treatment shows that most P supplied was retained by the soils in forms likely not available for plant uptake. The higher fixation property of the studied soil at lower P concentration suggests adjusting the P recommendation based on soil's sorption capacity in addition to standard P test. For the tested managed podzolic soils, and soils elsewhere with similar characteristics, rapid point P sorption test may be carried out with solution concentrations between 150 and 500 mg P L^{-1}. The decline in proportional P retention capacity observed when the solution with the higher P concentration was used indicates the soils could be saturated in the future, and thus increases the risk of P losses. Börling et al. (2001) (52) also recommended that point P sorption testing should be carried out with a solution of 600 mg P kg^{-1}.

A higher P sorption in the subsurface soils may be environmentally advantageous for reducing the leaching of P from the surface soil towards groundwater. The risk of particulate P losses cannot be ruled out. The P absorbed by the surface soils can be a source of labile P to replenish depleted P in the soil-solution. The long-term managed podzolic surface soils might thus serve as both source and sink while the subsurface soils mainly serve more as a sink for P. In the long-term, some deep-rooted crops might be able to access P accumulated in the subsurface soils depending on the chemical strength of fixed P species and soil management (80).

Previous reports for non-calcareous soils (grassland soils in Ireland) have also suggested Al as the dominant P fixing agent and have reported maximum P sorption capacities of 0.63 mg P g^{-1} (33). Values ranging from 0.19 to 0.38 mg P g^{-1} were reported for long-term managed (35-40 years) topsoil in central and southern Sweden (52). A maximum P sorption capacity of 8.23 and 3.12 mg P g^{-1} for a plough layer (Ap) and B horizon of managed field, and 5.08 and 5.35 mg P g^{-1} for unmanaged B and BC horizon were reported for the same study sites, respectively (21). The tested podzolic soils had several folds higher P sorption capacities than these other soils.

The mechanism of P sorption in the soil is linked to SOM, and mineral content (mainly Al), and possibly organometallic complexes (53, 57, 81). High level of calcium as result of long-term limestone application was also measured in surface soils (**Table S1**); Ca might precipitate P and contribute to the higher P sorption observed in our study (82), in addition to Al and Fe oxides (83–85). Nevertheless, the evidence for whether the SOM has negative or positive effect on P sorption in the soil is inconsistent (86). The SOM is a source of carboxyl anions (ROO−) that attract P-retaining cations in addition to Al and Fe oxyhydroxides (87). In our study, the SOM had a good Pearson correlation ($r = 0.49$ to 0.71, $p < 0.05$) and linear relationships ($r^2 = 0.22$ to 0.50, $p < 0.05$) with the P sorption capacity for surface and subsurface soils (**Figure 1**). In the absence of detailed carbon chemical speciation, we cannot speculate on the mechanisms relating SOM to P sorption capacities. Phosphorus adsorbed on SOM and metal-organic surfaces may easily be mineralized to available P forms depending on the soil pH and microbial activities (82).

Despite the studied soils had long-term (>100 years) management history, the tested soils had lower labile P (colorimetric Mehlich-3-P), a function of a higher P sorption capacity (**Tables 1** and **S4**), compared to some long-term managed podzolic soils in western Nfld, tropical sulfic soils in Brazil, or even alkaline soils in Manitoba and Ontario soils (6, 56, 63, 88). On the other hand, tropical acidic clay soils that received P fertilizers for three decades (6) had similar P retention trends regardless of the status of residual P. As often described, the Al and Fe levels in clay and Podzols are responsible for soil's P sorption capacity (6, 33, 88, 89).

Citric acid-P and water-extracted P were also negatively correlated with P sorption capacity which confirmed the surface and subsurface soils to have a higher P retention capacity than reported elsewhere, with reactive Al oxides the most obvious driver (6, 78, 89).

Phosphorus Sorption Indices Calculated From Mehlich-3 Test

Surface soils had a significantly higher median PSI (2.85 ± 1.73%) than subsurface soils (1.29 ± 1.15%) (**Tables 1**, **S1** and **S2**). The difference could be assigned by significantly lower aluminum to iron ratio and higher extractable P in surface than subsurface soils. The calculated P indices in this study are three to eight-fold lower than agronomically recommended PSI (10%) in the Canadian Maritime provinces (26, 60) or PSI values reported for farms in Nfld (63). The subsurface soils had a significant higher agronomic and environmental SPSC than surface soils due to higher *Mehlich-3-Al* and *-Fe* content (**Table 1**). The positive SPSCs indicates the studied soils can serve as P sink and this lower the risk of P loss. The estimated soil's P sorption capacity is >20-folds lower compared to point P sorption in this study or maximum P sorption capacity measured in Nfld podzolic soils (21). The smaller SPSC might be attributed to the soil management conditions such as P sources, intensity, and history of fertiliser application, cropping systems, and crop types, and extractability of the Al and Fe in Mehlich-3 solution. Despite the huge difference observed, the P indices calculated from Mehlich-3 extractable P, Al, and Fe support the results obtained from the point P sorption capacity assessment. This implies that P sorption status of managed podzolic soils can be easily estimated either from standard soil test or point P sorption test.

Correlation of Point Phosphorus Sorption Capacity With Soil Properties

The point P sorption capacity assessed in this study had a significant positive correlation with *Mehlich-3-Al*, and SOM irrespective of the initial P concentrations (**Figure 1**). Aluminum and SOM were previously reported to be the main contributing factors for higher soil's P sorption capacity (33, 90, 91). The dominant role of Al in controlling P sorption in podzolic soil was supported by the positive relationships between the point P sorption test with the *Mehlich-3-Al* to *-Fe* ratio and calculated SPSC (**Figure 1**). Furthermore, the point P sorption capacities of the tested soils had a significant positive linear correlation with the soil moisture content, which might reflect the significant correlation of moisture content with SOM (r = 0.51 and 0.77 for surface and subsurface, respectively, p <0.05; data not shown).

On the other hand, *Mehlich-3-Fe* and P extracted by Mehlich-3, 1% citric acid, and water, and calculated PSI were negatively correlated with P sorption capacities, confirming that soils with higher extractable P had lower P retention capacity and vice versa. Remarkably, the proportion of the silt fraction had a significant negative linear correlation with P sorption capacity of subsurface soil (**Figure 1B**). In agreement with Villapando and Graetz (2001) (91), there was a significant negative correlation between P sorption and *Mehlich-3-Fe* (**Figure 1**), which strengthens the argument that the Al oxides and possibly organic-Al chelates are the major players in P sorption, above iron, in podzolic soils.

The point P sorption capacities were not significantly correlated with clay content or pH (**Figure 1**). Previous studies reported both lower P mobility in soils with high clay (92), no impact of clays (52) or positive correlation of P sorption parameters with clay content (90). This suggests that the soil's mineral composition have a role beyond the simple textural classification. Furthermore, long-term liming may mask the relation between P sorption capacity with clay and pH by modifying the clay surface charges. The pH range (6.3 ± 0.4) was near the ideal range for P availability and was likely not wide enough to allow for sufficient impact on the analysis. The significant linear correlations of P sorption with the extractable *Mehlich-3-P*, *-Al*, and *-Fe*, and SOM, obtained from standard farmers' soil tests, widely employed in North America, suggest that these parameters can be used as input variables in pedotransfer functions for rapid estimation of the tested podzolic soils' P sorption capacity. This could support the P fertilizer recommendation process.

Multiple Regression Analyses to Assess Relationships Between Phosphorus Sorption Capacity and Selected Soil Properties

Soil variables identified to have a significant correlation with the point P sorption capacity, based on simple linear correlations were used as independent variables for predictive multiple linear regressions. Collinear independent variables that were weakly correlated with dependent variables were excluded from the pedotransfer function.

The SOM alone explained about 20-50% of the variability of the P sorption capacity in both surface and subsurface soils (**Table 2**). The negative correlation between SOM and Fe (r = 0.48 and 0.59, p <0.05, data not shown), and Al and Fe (r = 0.31 and 0.63, p <0.05, data not shown) for surface and subsurface soils, respectively, demonstrated the dominant role of SOM and Al in P sorption capacity, an observation supported by other studies (78, 87). The SOM of surface and subsurface soils was greater than for soils in the nearby Canadian Maritime provinces (26, 60), likely due to long-term management or organic matter supplied from long-term manure application (93), and differences in cropping systems. For example, forage fields experience no or minimal soil disturbance or ploughing, while the potato fields common in Maritime provinces that require extensive soil preparation which might affect the SOM content (94, 95).

Another important predictor of the soil's P sorption capacity was the Al content of the soil, which explained up to 37% of the soil's P sorption variability. Furthermore, Al was a better predictor in surface soils (**Table 2**). Villapando and Graetz (2001) concluded that copper chloride-extracted Al (organic matter-bound Al) was the major single factor controlling over

TABLE 2 | Stepwise multivariate regression results for the relationships between P sorption parameters and selected soil variables.

Dependent Variable[£]	Independent Variable	Coefficient	Standard Error	p-value	Partial R^2
q1	Constant	1.16	0.039	<0.001	–
	M3-P	-2.00×10^{-3}	0.27×10^{-3}	0.267	0.26
	M3-Fe	-0.89×10^{-4}	0.79×10^{-4}	<0.001	0.28
	M3-Al	1.13×10^{-4}	1.94×10^{-5}	<0.001	0.37
	CA-P	4.16×10^{-4}	7.78×10^{-5}	<0.001	0.08
	SOM	5.72×10^{-3}	1.25×10^{-3}	0.110	0.22
q2	Constant	4.63×10^{-1}	1.24×10^{-1}	<0.001	–
	M3-Fe	6.13×10^{-4}	1.59×10^{-4}	<0.001	0.25
	M3-Al	2.20×10^{-4}	2.88×10^{-5}	<0.001	0.35
	CA-P	-2.89×10^{-4}	4.96×10^{-5}	<0.001	0.08
	Silt	-2.74×10^{-3}	9.75×10^{-4}	0.007	0.11
	SOM	2.05×10^{-2}	2.79×10^{-3}	<0.001	0.32
	pH	5.82×10^{-2}	1.22×10^{-2}	<0.001	0.03
q3	Constant	-3.68	1.63	0.027	–
	M3-P	3.02×10^{-2}	1.76×10^{-2}	<0.001	0.26
	M3-Fe	2.42×10^{-3}	1.15×10^{-3}	0.039	0.08
	M3-Al	1.29×10^{-3}	4.08×10^{-4}	0.002	0.10
	H_2O-P	2.96×10^{-1}	2.60×10^{-1}	0.260	0.07
	CA-P	4.98×10^{-3}	2.31×10^{-3}	0.035	0.17
	M3-srP	-5.25×10^{-2}	2.41×10^{-2}	0.033	0.28
	SOM	6.08×10^{-2}	2.55×10^{-2}	0.020	0.32
q4	Constant	-5.54	9.54×10^{-1}	<0.001	–
	M3-P	-6.73×10^{-2}	2.76×10^{-2}	0.018	0.10
	M3-Al	1.82×10^{-3}	2.27×10^{-4}	<0.001	0.26
	CA-P	-3.05×10^{-3}	1.08×10^{-3}	0.006	0.03
	M3-srP	7.05×10^{-2}	2.82×10^{-2}	0.015	0.09
	SOM	1.51×10^{-1}	1.67E-02	<0.001	0.47
	pH	6.62×10^{-1}	1.13×10^{-1}	<0.001	0.06

[£] *q1 and q2 represent the point P sorption capacity of surface (0-20 cm) soils treated with 150 and 500 mg P L^{-1} initial concentrations, and q3 and q4 represent the point P sorption capacity of subsurface (20-40 cm) soils treated with 150 and 500 mg P L^{-1} initial concentrations, respectively.*

Only the variable with R^2 >0.05 are presented.

R^2 is the coefficient of determination or proportion of variance explained by the model.

60% of the variability in the sorption of P in the Bh horizon of podzolic soils (91). The *Mehlich-3-Al* in this study might not fully account for the organic bound Al portion, similar to lower extractability of organic P (96).

The total P extracted by Mehlich-3 explained ~26% of the variability in the P sorption capacity when the soils are treated with lower initial P concentration (**Table 2**). The long-term fertilized soils expected to decrease the soil's P sorption capacity

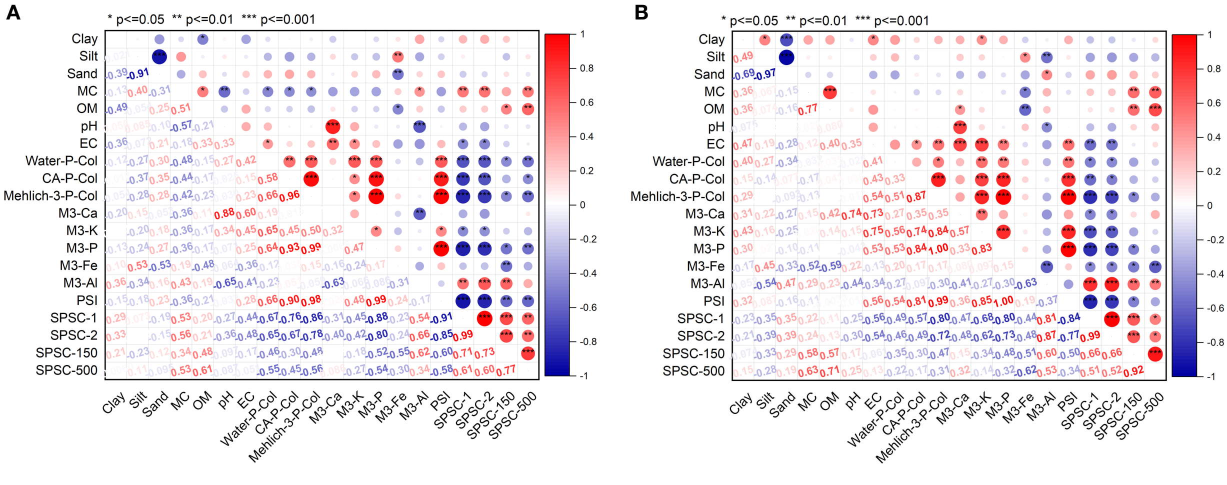

FIGURE 1 | Pearson correlation between soil's P sorption capacity and soil properties for managed SJRDC soils collected from **(A)** 0-20 cm (n = 23) and **(B)** 20-40 cm (n = 23). M3-Ca, M3-K, M3-P, M3-Fe, and M3-Al represent calcium (Ca), potassium (K), phosphorus (P), iron (Fe), and aluminum (Al)measured by ICP-OES in Mehlich-3 (M3) extract, respectively. Water-P-$_{Col}$, CA-P$_{Col}$, and M3-P$_{Col}$ represent soluble reactive P determined in deionized water, 1% citric acid, and Mehlich-3 extract using ascorbic acid colorimetry analysis, respectively; P saturation index (PSI), soil P sorption capacity (SPSC-1 and SPSC-2) at 0.10 and 0.14 critical PSI; PAC-150 and PAC-500 represented a P sorption capacity of soils treated with 150 mg P L^{-1} and 500 mg P L^{-1}, respectively.

(88) but the tested soils had not reached their maximum P sorption capacity (21). The models presented here could be used to predict the P sorption index of the long-term managed fields in similar settings, by using data available from routine farmer's soil tests. However, the use of the P sorption capacity or soil test P for environmental risk assessments must be verified under field conditions (97, 98).

CONCLUSIONS

The long-term managed surface layer of podzolic soils had higher extractable *Mehlich-3-P*, *-K*, and *-Fe*, SOM, and EC, than the subsurface soils. The reverse was true for Al. The effect of long-term liming was reflected in the increased pH of both soil layers. The P accumulation in the surface soil and potential vertical P mobility to the subsurface soil layers signals the need for proper management of P in such soils. Thus, the tested surface soil likely acts as both source and sink for P while the subsurface soil might mainly serve as a P sink.

The measured P sorption capacities were comparable for both soil layers at the low P concentration(150 mg P L^{-1}); however, a significantly higher P sorption capacity was observed in the subsurface than surface soils at the higher P concentration (500 mg P L^{-1}), a phenomenon attributable to higher Al content. Therefore, a higher initial P concentration of 500 mg P L^{-1} is recommended for assessing the point P sorption capacity of similar podzolic soils. Alternatively, the P sorption capacity could be estimated from SOM, *Mehlich-3-P*, and *-Al*; related pedotransfer functions may be employed to develop testable hypotheses for the development of environmentally and economically viable P management strategies for acidic soils in boreal regions.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

Conceptualization and methodology, AK, AU, and DM. Data analysis and interpretation, AK and AU. Investigation, AK. Writing – original draft, AK and AU. Writing – review and editing, AK, AU, JN, DM, and KH. Funding acquisition, AU. Resources, AU and DM. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fsoil.2022.931266/full#supplementary-material

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