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Article

Comparison of agri-environmental phosphorus tests for boreal agricultural and natural Podzols

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Abstract

Over a dozen soil phosphorus (P) extraction procedures have been designed for agri-environmental purposes (P-tests). Sustainable expansion of agriculture into boreal regions dominated by Podzols requires further insights into P extractability. We extracted P from Podzol samples ($n = 96$) using nine P-tests followed by both colorimetric (P_{Col}) and inductively coupled plasma (P_{ICP}) quantifications and assessed the relationships between P-tests. Samples were collected by depth or horizon from agricultural fields and reference sites in eastern, central, and western Newfoundland, Canada. The soil P was extracted with water, citric acid, ammonium bicarbonate diethylenetriaminepentaacetic acid (AB-DTPA), Morgan, Olsen, Bray-1, Bray-2, Mehlich-1, and Mehlich-3 solutions, thus targeting a wide range of extractable P pools in managed and natural Podzols. The soils had a pH of 3.4–6.9, organic matter of 0.5%–47.2%, and Al-M3 of 977–2561 mg kg^{-1}. On average, water extracted the lowest P_{Col} (1.0) and P_{ICP} (5.7) mg kg^{-1}, while citric acid extracted the highest P_{Col} (151) and P_{ICP} (290) mg kg^{-1}. For the managed podzolic soils, the extractability of P followed the sequence water < Morgan < AB-DTPA < Mehlich-1 < Bray-1 < Mehlich-3 $\leq$ Olsen $\leq$ Bray-2 < citric acid; this varied slightly by quantification techniques and soil groups. The differences between P_{ICP} and P_{Col} were most significant for the citric acid extracts. Most P-tests measurements were moderately to strongly correlated to P-$M3_{ICP}$ measurements ($r^2 > 0.50$) but variable with quantification techniques and soil depths. Given the diversity in extractable P pools across management-induced soil conditions, it is evident that a fully informed P management for the Newfoundland Podzols will require calibration of P-tests against crop P uptake.

Key words: Podzols, soil phosphorus, extractable phosphorus, colorimetric quantification, ICP quantification

Introduction

Phosphorus (P) is commonly applied to crops either as mineral fertilizer or through organic materials such as livestock manures (Shen et al. 2011). The availability of P to plants depends on numerous factors, including its amount, soil pH, soil organic matter (SOM), soil moisture, the mineral profile of the soil, and the root structure (Fixen and Grove 1990; Kochian 2012; Baker et al. 2015). Repeated applications of P fertilizers led to excessive P accumulation in soils, that is, legacy P (Sharpley et al. 2013). An easily discernible consequence is the delivery of P to water bodies contributing to algal blooms, primarily through the surface and subsurface runoff (Hart et al. 2004; McDowell et al. 2021).

Soil tests have been employed since the early 1940s to inform soil fertility and support nutrient management recommendations (Peck 1990). Agri-environmental soil P extraction methods (P-tests) were developed to gauge the availability of P across soil types under the assumption that results mimic the soil P, which is available for uptake in the rhizosphere (Peck 1990; Watson and Mullen 2007) or could be potentially released to water bodies (Hart et al. 2004). Globally, at least 17 extraction procedures were developed for assessing soil P thought to be bioavailable over short to medium terms, and several more targeting slowly available or unavailable P (Wuenscher et al. 2015; Nawara et al. 2017; Weihrauch and Opp 2018). The diversity arises because methods have been developed for various soil types and purposes. It was recognized very early on that no single extractant could accurately assess plant-available P across the range of soil conditions (Rost 1917).

The selection of suitable P-*tests* is based on soil properties, precisely pH (soil reaction), which regulate the solubility and availability of P and of other elements in the soil solution and thus the microbial activities (Fixen and Grove 1990; Jones 2001). The P in acidic soils is mainly present as crystalline or amorphous metal oxides, that is, aluminum and iron oxides, and chelated compounds, whereas calcium phosphates are the dominant P sink in alkaline soils (Pierzynski et al. 2005;

Baker et al. 2015). The mechanisms of extracting soil P involve acidic reactions (increased solubility), desorption (anion replacement), complexation, and hydrolysis of cations fixing P (Bray and Kurtz 1945; Fixen and Grove 1990; Jones 2001). However, water can extract readily available P in all soil types and can be employed to assess the risk of loss of soluble P beyond the boundaries of agricultural fields (Messiga et al. 2021). Other P-tests, like Mehlich-3 (M3), have been used to calculate soil P saturation or P sorption capacity using the molar ratio of P-M3 to Al-M3 and Fe-M3 for both agronomic and environmental purposes (Benjannet et al. 2018).

Our classical understanding of soil P availability and management is derived from studies conducted on soils traditionally considered of high agricultural value, that is, loamy to fine texture and near-neutral pH (Penn and Camberato 2019). However, the P availability in Podzols might not conform to the classical applied understanding of agricultural soil chemistry due to its distinct physicochemical properties (Grand and Lavkulich 2013). Podzols typically have a coarse-sandy texture and a pH of 4.0–4.5, which favors the leaching of basic cations from the surface soil; their high Al and Fe contents in the subsurface horizons strongly fix soil P (Sauer et al. 2007), indicating a poor overall plant nutrient supply potential. Expanding agriculture onto Podzols requires careful investigation of soil fertility determinants, including P availability.

Podzolic soils occur across Canada. The regional distribution of Podzolic groups varies: for example, both Humo-Ferric (56%) and Ferro-Humic (44%) are common in Newfoundland, while Humo-Ferric is largely the dominant group in the other provinces (Sanborn et al. 2011). The Podzol properties are related to the regional ecosystem (vegetation, climate, and parent material). Newfoundland Podzols have higher Al-M3 and lower Fe-M3 (Kedir 2020; Kedir et al. 2021*a*, 2021*b*) than in the Maritime provinces (Benjannet et al. 2018).

The northward expansion of agricultural climate into the boreal regions (King et al. 2018) has spurred support for agricultural development by converting natural lands to farmlands (e.g., Government of Newfoundland and Labrador 2017). As this trend accelerates, there is an urgent need to develop our fundamental and applied understanding of P in converted Podzols to ensure that management techniques are adapted to allow environmentally and economically sustainable farming systems.

Soil P-tests that might be suitable for Podzols have been evaluated for forest nutrition (Kalra and Maynard 1991). Given the impact of the land-use conversion on SOM and on the redistribution of soil minerals (i.e., converted topsoils are more representative of deeper horizons than for natural Podzols), we hypothesized that the P extractability and quantification profiles as obtained with the employed P-tests vary across different podzolic soil management and properties. Specifically, we aimed to (*i*) assess the extractability of P in natural and managed Podzols using nine standard P-tests and evaluate the differences between P quantified with colorimetric (molybdate reactive P) and inductively coupled plasma (ICP; total extractable P), and (*ii*) assess the correlation between P-tests and with the soil properties and evaluate the utility of P-M3$_{\mathrm{ICP}}$ based linear regression models for estimating extractable P with other P-tests.

Materials and methods

Site description

Ninety-six soil samples representing three locations, three management types, and different soil depths and horizons were used for the P determination. Sample types reflect the diversity in soil management on the island of Newfoundland (Nfld), part of the Province of Newfoundland and Labrador (NL), Canada, across a series of soil fertility trials carried out in parallel.

The study locations are managed for agriculture, as natural grassland or forest. Sampling was carried out in August 2016 on a dairy farm located in Cormack (CR), western Nfld (49.19°N, 57.24°W), in August 2017 at the provincial Centre for Agriculture and Forestry Development (CA), located in Wooddale, central Nfld (49.03°N, 55.55°W), and in November 2017 at the St. John's Research and Development Centre of Agriculture and Agri-Food Canada (SJ) in eastern Nfld (47.56°N, 52.71°W).

The CR site has an average altitude of 154 m above sea level (asl), average total annual precipitation of 1264 mm and an annual mean temperature of 3.2 °C (Environment Canada 2019). The field has been under various annual crop rotations (mainly centered around potatoes) since the 1950 s and receives regular mineral fertilizers and manure and irregular lime applications. The manure P additions are variable as the NL manure recommendations are based on manure-nitrogen concentrations; according to the provincial recommendations, the amount of P in fertilizers varies between 13 and 109 kg ha^{-1} (Kedir et al. 2021*b*). The natural grassland bordering the CR managed field is well drained but with a water table within 1 m from the surface and is dominated by *Festuca* spp. The CR site is located on a well-drained Humo-Ferric Podzol developed over a loam to sandy loam substratum, originating from shale and soft sandstone parent materials (South 1983).

The CA site has an altitude of ~46 m asl, an annual mean rainfall of 1108 mm, and an annual mean temperature of 4.4 °C (Environment Canada 2019). The CA managed field was used as a tree nursery (>30 years) with annual fertilizer application history of 250 kg ha^{-1} of 13-07-34 in May and 250 kg ha^{-1} of 18-09-18 in July and August, and has no history of lime and manure application (R. Linehan 2017, personal communication). The forested CA soil has well-developed podzolic soil horizons (LFH, E, B, BC, and C). The CA soil is a Ferro-Humic Podzol developed on glaciofluvial deposits (Sanborn et al. 2011).

The SJ site has an elevation ~114 m asl with an annual mean total rainfall of 1534 mm and an annual mean temperature of 5 °C. The SJ managed fields have been in agriculture for >100 years. Historically, most SJ fields are managed under a mix of timothy (*Phleum pratense*), red clover (*Trifolium pratense*), and alsike clover (*Trifolium hybridum*) in rotation with crop research experiments. These fields received 227 kg ha^{-1} of 6-12-12, an unknown amount of manure, as often as 2–3 times per year, and 3 applications of limestone at the rate of 4 Mg ha^{-1} (D. McKenzie 2018, personal communication). The forested SJ soil is relatively young and lacks an E horizon, a residual effect of the relatively recent disturbance (about 50 years ago), which did not allow for significant repodzolization after replantation with black spruce (*Picea mariana*). The SJ soil is an Orthic Humo-Ferric Podzol developed on a glacial till materials (Heringa 1981).

Soil sampling

Soil samples were collected as follows: CR, 8 samples each from 0 to 10 cm (CR-D1) and from 10 to 20 cm (CR-D2) from a managed field ($\mathrm{CR_{managed}}$), and 4 samples each from 0 to 10 cm (CR-D11) and from 10 to 20 cm (CR-D22) from the surrounding buffer zones covered with natural grassland ($\mathrm{CR_{grassland}}$) (archived samples, A. Unc); CA, 20 total samples collected from the managed Ap and E ($\mathrm{CA_{managed}}$), and the forested LFH (O layer), E, and B horizons ($\mathrm{CA_{forested}}$); SJ, 23 samples each from 0 to 20 cm (SJ-D1) and from 20 to 40 cm (SJ-D2) from farmed plots ($\mathrm{SJ_{managed}}$), and 3 samples of LFH and B horizons each from the adjacent forested area ($\mathrm{SJ_{forested}}$).

Soil properties and phosphorus extractions and quantifications

Soils were air dried and passed through a 2 mm sieve. They were analyzed for SOM by loss-on-ignition at 430 °C for 6 h (Jones 2001); pH and electrical conductivity (EC) in 1:2 or 1:5 soil to water for soils with high SOM (Hendershot et al. 2008), particle size distribution with the hydrometer method (Kroetsch and Wang 2008), and exchangeable cations with Mehlich-3 in a 1:10 soil to solution (Mehlich 1984) (Table 1). The P was extracted using nine methods: water (P-Wa), citric acid (P-CA), Olsen (P-Ol), ammonium bicarbonate diethylenetriaminepentaacetic acid (P-AB), Morgan (P-Mo), Bray-1 (P-B1), Bray-2 (P-B2), Mehlich-1 (P-M1), and Mehlich-3 (P-M3). The summary of P extraction parameters is provided in Table 2.

Soil solutions filtered through 0.45 μm filter paper were quantified using spectrophotometry ($\mathrm{P_{Col}}$) at 882 nm (Murphy and Riley 1962), and inductively coupled plasma mass spectroscopy ($\mathrm{P_{ICP}}$) (ICP-MS, i-Cap Q, Thermo Scientific™, Burlington, ON, Canada). The matrix-matched standard solutions were used for the calibration curve ($r^2 > 99.5\%$, data not shown). Based on the preliminary assessment, samples with a concentration beyond the calibration range were diluted to match the calibration range. The colorimetric method measures inorganic P (molybdate reactive), while the ICP measures inorganic and organic P (total extractable P) in the extract (Young et al. 2017). Olsen extracts were not analyzed by ICP as preliminary investigations indicated poor calibration curves for P, Al, Fe, and K.

Statistical analysis

Descriptive and inferential statistics were carried out using OriginPro (Version 2021. OriginLab Corporation, Northampton, MA, USA). The data set was log-transformed and tested for normality using the Shapiro–Wilk test. The residuals were examined for homogeneity of variance using Levene's test before inferential analyses.

Multiple pairwise mean comparisons of P-tests were carried out with a one-way ANOVA (Tukey's test) for managed soil groups having a sample size greater than five ($\mathrm{SJ_{managed}}$: 0–20 and 20–40 cm, and $\mathrm{CR_{managed}}$: 0–10 and 10–20 cm). The mean values and standard error of mean for untransformed data set are summarised in Tables 3 and 4. Using log transformed data set, the Pearson correlation between P-tests was assessed using selected managed soils (SJ-D1 and SJ-D2, $n = 23$ for each soil depth). Similarly, the linear regression analyses between $\mathrm{P\text{-}M3_{ICP}}$ (as predictor variable) and other P-tests analyzed with both colorimetry and ICP were carried out for selected managed soils (SJ and CR). These soils (0–20, 0–10 or 10–20 cm) were selected because they represent environmental and agronomic soil sampling depths, while the SJ-D2 (20–40 cm) represents the subsurface soils. The $\mathrm{P\text{-}M3_{ICP}}$ is the standard fertility test used by the NL soil laboratory (Kedir et al. 2021*b*). Thus, we established a linear equation to convert $\mathrm{P\text{-}M3_{ICP}}$ to other P-tests quantified by colorimetric and ICP, including $\mathrm{P\text{-}M3_{Col}}$. The significance of slope (lesser or greater than zero) was tested using ANOVA (F-test). The significance level was set at $P = 0.05$ throughout this study. Extreme outliers (assessed by Grubbs's test) were excluded from correlation, means comparison and linear regression analyses.

Results and discussion

Physicochemical characteristics of the studied soils

The descriptive summary of soil properties and P-tests is presented in Table 1 and Fig. 1 for all soils and soil groups, respectively. The sand, clay, and silt contents ranged from 20% to 64%, 6% to 38%, and 29% to 64%, respectively; 38% of the soils are loams and 56% of the soils have clay contents between 12.5% and 25.0% (data not shown). The soil pH ranged from 3.4 to 6.9; 56% of samples had a pH between 5.5 and 6.9. The SOM varied between 0.5% and 47% and was >5% for 50% of the samples. The SJ forested organic layer had the highest SOM (47%). Mehlich-3 Al and Fe in all samples ranged from 977 to 2561 and 1 to 369 mg kg^{-1}, respectively. The $\mathrm{P\text{-}M3_{ICP}}$, as measured in all soils, ranged from 2.6 to 156 mg kg^{-1} (Fig. 1*b*). The highest P concentration of 662 mg kg^{-1} was measured as $\mathrm{P\text{-}CA_{ICP}}$ in $\mathrm{CR_{managed}}$ soils. The soil properties (SOM, pH, Mehlich-3 extracted cations, and P) of the managed sites are within ranges previously reported for Newfoundland farms (Kedir et al. 2021*a*, 2021*b*) but higher than those reported for Maritime fields managed under potato crop (Benjannet et al. 2018). This might be related to variations in climate, soil, and management types (Fixen and Grove 1990).

The $\mathrm{CR_{managed}}$ soils were slightly more acidic than $\mathrm{CR_{grassland}}$ soils, possibly an effect due to nitrogen mineralization (Campbell and Zentner 1984), and slightly more Al-M3 content (Table 1). This relatively high Al level in $\mathrm{CR_{managed}}$ soils might be associated with deep ploughing, which brings up the B-horizon rich in amorphous Al silicate or organic Al complexes. This might favor the fixation of P in unavailable forms in the plough layer (Kedir et al. 2021*a*). Conversely, $\mathrm{SJ_{managed}}$ soils have an agronomically favorable pH of ∼6.25 regardless of sampling depth, likely reflecting the long-term (>100 years) soil management involving limestone and manure application and cropping. The relatively young, sandier, and enriched in Al-M3 Ap horizon of the $\mathrm{CA_{managed}}$ was more acidic than $\mathrm{SJ_{managed}}$ and $\mathrm{CR_{managed}}$ soils.

Table 1. Studied soil properties for the studied soils grouped by location, management, and depth/horizon (mean ± standard error of the mean). The "All samples" column sums pooled means, and with minimum and maximum values in parenthesis. The sample size (*n*) varies across the soil groups.

	$\mathrm{SJ}_{\mathrm{managed}}$		$\mathrm{SJ}_{\mathrm{forested}}$		$\mathrm{CR}_{\mathrm{managed}}$		$\mathrm{CR}_{\mathrm{grassland}}$		$\mathrm{CA}_{\mathrm{managed}}$		$\mathrm{CA}_{\mathrm{forested}}$			
Soil properties	0–20 cm ($n = 23$)	20–40 cm ($n = 23$)	LFH ($n = 3$)	B ($n = 3$)	0–10 cm ($n = 8$)	10–20 cm ($n = 8$)	0–10 cm ($n = 4$)	10–20 cm ($n = 4$)	Ap ($n = 5$)	E ($n = 3$)	LFH ($n = 4$)	E ($n = 4$)	B ($n = 4$)	All samples ($n = 96^*$)
Sand (%)	32.44 (±1.14)	41.71 (±1.45)	NA	43.85 (±2.90)	31.57 (±1.09)	29.74 (±1.25)	33.26 (±2.55)	28.24 (±2.30)	56.80 (±1.20)	48.93 (±1.33)	NA	61.60 (±1.16)	35.60 (±0.00)	38.3 (19.8–63.6)
Clay (%)	17.98 (±0.47)	15.63 (±0.40)	NA	17.00 (±0.00)	31.06 (±1.63)	35.05 (±0.47)	29.50 (±3.36)	32.08 (±2.93)	8.36 (±0.75)	6.96 (±1.00)	NA	6.96 (±0.00)	9.46 (±0.29)	19.6 (6.0–37.5)
Silt (%)	49.59 (±1.05)	42.66 (±1.21)	NA	39.15 (±2.90)	37.37 (±0.84)	35.21 (±1.35)	37.24 (±2.90)	39.68 (±3.67)	34.84 (±0.75)	44.11 (±2.33)	NA	31.44 (±1.16)	54.94 (±0.29)	42.1 (29.2–63.6)
pH	6.28 (±0.09)	6.25 (±0.08)	5.05 (±0.09)	5.03 (±0.17)	5.93 (±0.13)	5.88 (±0.12)	6.27 (±0.04)	6.07 (±0.21)	4.80 (±0.02)	5.36 (±0.02)	3.47 (±0.07)	5.23 (±0.03)	3.74 (±0.01)	5.6 (3.4–6.9)
EC (μS cm^{-1})	239.27 (±15.58)	145.97 (±12.59)	192.90 (±12.43)	99.73 (±22.19)	5.43 (±0.14)	5.38 (±0.13)	5.80 (±0.04)	5.59 (±0.23)	171.80 (±0.41)	21.65 (±0.17)	91.00 (±2.66)	82.02 (±9.39)	25.00 (±0.18)	120.0 (4.7–419)
SOM (%)	12.57 (±0.54)	9.31 (±0.43)	47.23 (±0.00)	12.97 (±0.00)	7.30 (±1.10)	6.44 (±1.15)	8.35 (±2.97)	4.81 (±0.80)	3.90 (±0.27)	0.74 (±0.04)	21.50 (±0.72)	4.23 (±0.53)	3.24 (±0.03)	9.5 (0.5–47.2)
Mehlich-3-Al (mg kg^{-1})	1240 (±49)	1748 (±48)	1551 (±17)	2131 (±216)	1725 (±48)	1723 (±49)	1651 (±224)	1480 (±100)	2135 (±16)	2110 (±142)	1109 (±76)	1927 (±194)	1553 (±171)	1615 (977–2561)
Mehlich-3-Fe (mg kg^{-1})	189.82 (±9.66)	159.95 (±9.44)	85.05 (±14.54)	32.02 (±9.83)	15.85 (±1.21)	19.84 (±2.03)	27.70 (±11.82)	16.20 (±5.44)	8.82 (±0.49)	9.60 (±0.20)	71.35 (±16.93)	7.24 (±0.01)	4.71 (±2.15)	98.0 (1.0–369.0)
Mehlich-3-K (mg kg^{-1})	190.95 (±15.86)	76.49 (±10.19)	48.17 (±6.98)	14.42 (±4.51)	103.06 (±8.26)	79.37 (±16.15)	78.19 (±29.05)	49.31 (±24.13)	54.56 (±5.97)	20.08 (±2.17)	74.75 (±5.53)	20.86 (±10.39)	24.30 (±)5.63	95.0 (2.6–342.0)
Mehlich-3-Ca (mg kg^{-1})	195.93 (±10.78)	122.46 (±9.97)	291.96 (±24.57)	80.23 (±20.76)	380.21 (±34.92)	345.59 (±39.71)	325.64 (±109.24)	239.62 (±91.55)	105.15 (±15.72)	57.14 (±8.01)	390.73 (±10.83)	196.23 (±102.47)	154.29 (±70.03)	207.0 (8.3–566.0)

Note: CA, Centre for Agriculture and Forestry Development; CR, Cormack; EC, electrical conductivity; NA, not analyzed; SOM, soil organic matter; SJ, St. John's Research and Development Centre.
*Last column sample size (*n*) for sand, clay, and silt are 89, for Mehlich-3-Al, -Fe, -K, and -Ca are 94.

Table 2. Summary of soil P extraction methods (solution strength, pH, soil to solution ratio, and extraction time). The P concentration in all tests was analyzed with colorimetry and ICP except for the Olsen test due to a poor calibration curve for P, Al, Fe, and K.

		Extraction solution				
P-tests	Extractants	Concentrations	pH	Soil: Solution (*w*/*v*)	Extraction time	Reference
Water	H_2O	NA	6.5–7.0	1:10	1 h	Wang et al. 2015
Citric acid	$C_6H_8O_7$, 99.5%	1% (10.00 g L^{-1})	3.75	1:10	1 h	Thompson 1995
Olsen	$NaHCO_3$	0.5 N (42.00 g L^{-1})	8.5	1:20	30 min	Olsen et al. 1954
	NaOH	0.01 N (0.50 g L^{-1})				
AB-DTPA*,†	DTPA	0.005 M (1.97 g L^{-1})	7.6	1:2	15 min	Soltanpour 1985
	NH_4HCO_3	1 M (79.06 g L^{-1})				
Morgan‡	$NaC_2H_3O_2.3H_2O$	0.74 M (100.00 g L^{-1})	4.8	1:5	5 min	Jones 2001
	Glacial (CH_3COOH)	0.52 M (31.00 mL L^{-1})				
Bray-1	HCl conc	0.025 N (2.04 mL L^{-1})	2.6	1:10	5 min	Bray and Kurtz 1945
	NH_4F	0.03 N (1.11 g L^{-1})				
Bray-2	HCl conc	0.10 N (8.16 mL L^{-1})	2.6	1:10	5 min	Bray and Kurtz 1945
	NH_4F	0.03 N (1.11 g L^{-1})				
Mehlich-1	H_2SO_4 conc	0.025 N (0.70 mL L^{-1})	1.25	1:5	5 min	Jones 2001
	HCl conc	0.05 N (4.00 mL L^{-1})				
Mehlich-3	NH_4F	0.015 N (0.56 g L^{-1})	2.5	1:10	5 min	Mehlich 1984
	EDTA	0.001 M (0.29 g L^{-1})				
	NH_4NO_3	0.25 N (20 g L^{-1})				
	CH_3COOH	0.2 N (11.50 mL L^{-1})				
	HNO_3	0.013 N (0.82 mL L^{-1})				

Note: ICP, inductively coupled plasma; NA, not applicable.
*Ammonium bicarbonate diethylenetriaminepentaacetic acid.
†LFH soil samples were 5 g in 20 mL (1:4 *w*/*v*). ‡LFH soil samples were 3 g in 30 mL (1:10 *w*/*v*).

The $SJ_{managed}$ fields also had a higher SOM than $CR_{managed}$ and $CA_{managed}$ (Table 1), likely a legacy of the high carbon and nitrogen inputs during the century-long farming (Doran et al. 1996). The average SOM of all managed soils in this study is above the critical level of 3.4% SOM (2% C) proposed by the European Soil Strategy Commission for sustainable crop production (Hanegraaf et al. 2009). The SOM in the tested samples varied by depth or horizon, soil and management type, and soil texture similar to other mineral soils, including Podzols (Broadbent 1974).

Comparison of P-tests quantified by colorimetry and ICP

Multiple pairwise comparisons of soil P extracted with nine P-tests and analyzed by colorimetry and ICP were evaluated using SJ-D1, SJ-D2, CR-D1, and CR-D2 managed soils for agronomic and environmental P management purposes (Tables 3 and 4).

The results of the nine P-tests were statistically grouped into three to seven groups (denoted by the letter “a” to “g”); this varied with land-use type and soil depth, likely a function of the distinct relationships between selected soil properties and P extractability and quantification techniques (Table 5). For example, the means of colorimetric P-tests for SJ-D1 soils were statistically grouped into (a) P-CA, (b) P-B2 and P-Ol, (c) P-Ol and P-M3, (d) P-M3 and P-B1, (e) P-M1, (f) P-AB and P-Mo, and (g) P-Wa, in decreasing order (Table 3). This grouping can be linked to the extractable inorganic P that may include (I) mobile orthophosphate ions, (II) labile, easily soluble P, (III) moderately labile and soluble, (IV) stable, slightly soluble, and (V) “fixed,” least soluble P (Weihrauch and Opp 2018). We speculate that for the tested soils in this study, $P\text{-}Wa_{Col}$ might reflect pool I; $P\text{-}AB_{Col}$ and $P\text{-}Mo_{Col}$ might indicate pools I and II; $P\text{-}M1_{Col}$, $P\text{-}B1_{Col}$, $P\text{-}M3_{Col}$ and $P\text{-}Ol_{Col}$ might extract pools I to III; and $P\text{-}B2_{Col}$ and $P\text{-}CA_{Col}$ might partly reflect pools I–IV. However, our speculation on P extractability might not be uniformly applicable for all soils and management types, an observation also reported in other studies (Wang et al. 2004; Wuenscher et al. 2015; Weihrauch and Opp 2018). Thus, targeted assessments are a prerequisite for understanding the detailed P dynamics for particular soils and land uses.

Citric acid extraction

Citric acid extracted more P than other P-tests for most managed soils regardless of quantification techniques and soil depth (Fig. 1). Most likely, the higher P extractability with citric acid might be related to the effect of heating (70 °C for 1 hr) of soil solution during the extraction procedure (Thompson 1995) and minimal re-precipitation of the extracted P (Penn et al. 2018; Penn and Camberato 2019). Also

Table 3. Extracted P (mg P kg^{-1}) in nine P-tests analyzed by the colorimetric method (Tukey's test mean ± standard error of the mean by soil group).

	SJ$_{\text{managed}}$		SJ$_{\text{forested}}$		CR$_{\text{managed}}$		CR$_{\text{grassland}}$		CA$_{\text{managed}}$		CA$_{\text{forested}}$		
P-tests (mg P kg^{-1})	0–20 cm ($n = 22$)	20–40 cm ($n = 22$)	LFH ($n = 3$)	B ($n = 3$)	0–10 cm ($n = 8$)	10–20 cm ($n = 8$)	0–10 cm ($n = 4$)	10–20 cm ($n = 4$)	Ap ($n = 5$)	E ($n = 3$)	LFH ($n = 4$)	E ($n = 4$)	B ($n = 4$)
Citric acid	173.07 (±22.56)a	120.53 (±17.25)a	96.80 (±25.80)	65.23 (±21.27)	314.52 (±30.59)a	269.77 (±41.05)a	234.79 (±61.96)c	210.03 (±60.84)a	121.56 (±21.15)	16.61 (±1.89)	78.74 (±7.89)	7.89 (±1.64)	11.58 (±2.00)
Bray-2	85.98 (±6.26)b	63.28 (±7.03)b	74.67 (±3.60)	37.66 (±12.83)	98.45 (±4.79)b	89.55 (±6.77)b	90.78 (±9.69)ab	79.85 (±10.52)ab	113.73 (±6.29)	55.83 (±7.08)	62.64 (±3.54)	7.60 (±1.75)	18.75 (±2.78)
Olsen	59.65 (±6.04)bc	33.63 (±5.29)c	38.63 (±11.29)	15.13 (±8.01)	85.04 (±8.74)b	67.03 (±8.64)bc	62.68 (±15.18)ab	47.92 (±16.28)bc	66.84 (±6.49)	5.51 (±0.10)	39.56 (±6.69)	2.20 (±0.18)	10.88 (±0.90)
Mehlich-3	44.12 (±6.68)cd	22.76 (±4.69)d	29.86 (±5.26)	6.77 (±3.45)	94.79 (±8.89)b	78.59 (±11.91)bc	73.10 (±22.42)ab	43.73 (±22.92)c	47.47 (±5.43)	17.27 (±1.65)	44.45 (±4.00)	17.38 (±9.91)	18.19 (±5.99)
Bray-1	31.43 (±4.53)d	15.52 (±3.55)d	9.38	10.42 (±4.98)	65.59 (±4.13)b	54.83 (±6.61)bc	58.02 (±9.95)ab	39.09 (±14.79)bc	38.39 (±5.26)	10.93 (±1.60)	48.26 (±1.55)	2.12 (±0.40)	11.66 (±1.85)
Mehlich-1	18.28 (±3.36)e	13.96 (±2.63)d	27.76 (±4.02)	9.19 (±3.92)	57.34 (±7.34)b	46.37 (±7.65)c	32.83 (±8.14)b	31.34 (±5.52)bc	44.75 (±5.84)	16.40 (±2.01)	49.66 (±3.32)	0.99 (±0.18)	4.92 (±0.55)
AB-DTPA	5.59 (±0.68)f	3.83 (±0.62)e	10.13 (±1.62)	2.14 (±0.58)	45.08 (±16.70)c	39.58 (±14.73)d	3.12 (±0.98)c	1.79 (±0.40)d	8.01 (±0.58)	1.20 (±0.02)	15.02 (±1.67)	0.62 (±0.08)	2.02 (±0.12)
Morgan	4.17 (±0.52)f	2.42 (±0.45)f	7.34 (±3.37)	2.14 (±0.58)	3.65 (±0.39)d	2.26 (±0.43)e	1.66 (±0.98)c	1.79 (±0.40)d	6.20 (±1.55)	1.20 (±0.02)	20.55 (±4.86)	0.62 (±0.08)	2.02 (±0.12)
Water	0.96 (±0.07)g	0.60 (±0.11)g	2.12 (±1.41)	0.31 (±0.10)	1.48 (±0.21)e	1.34 (±0.24)e	1.27 (±0.54)c	0.67 (±0.17)d	0.20 (±0.04)	0.10 (±0.02)	bdl	0.32 (±0.05)	1.27 (±0.03)

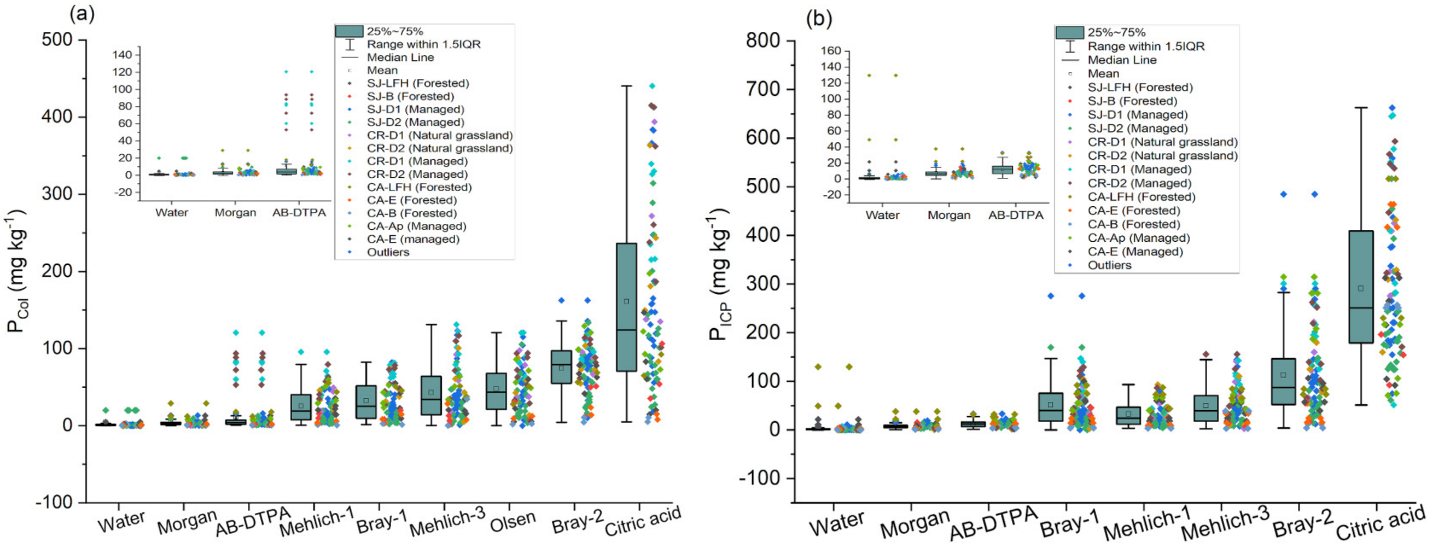
Note: Analysis carried out on log-transformed data for soil groups with a sample size greater than five. Means in the same column that do not share the same letter are significantly different at a significance level of 0.05. AB-DTPA, ammonium bicarbonate diethylenetriaminepentaacetic acid; bdl, below detection limit; CA, Centre for Agriculture and Forestry Development; CR, Cormack; NA, not analyzed; SOM, soil organic matter; SJ, St. John's Research and Development Centre.

Table 4. Extracted P (mg P kg^{-1}) by eight P-tests analyzed by ICP (Tukey's test mean ± standard error of the mean by soil group).

P-tests (mg P kg^{-1})	SJ$_{\text{managed}}$		SJ$_{\text{forested}}$		CR$_{\text{managed}}$		CR$_{\text{grassland}}$		CA$_{\text{managed}}$		CA$_{\text{forested}}$		
	0–20 cm ($n = 22$)	20–40 cm ($n = 22$)	LFH ($n = 3$)	B ($n = 3$)	0–10 cm ($n = 8$)	10–20 cm ($n = 8$)	0–10 cm ($n = 4$)	10–20 cm ($n = 4$)	Ap ($n = 5$)	E ($n = 3$)	LFH ($n = 4$)	E ($n = 4$)	B ($n = 4$)
Citric acid	293.83 (±30.92)a	220.67 (±23.83)a	137.44 (±39.38)	147.67 (±30.24)	433.16 (±74.60)a	438.30 (±53.68)a	358.72 (±35.32)	307.54 (±56.09)	137.14 (±33.07)	296.79 (±15.78)	373.26 (±82.66)	254.13 (±82.66)	440.48 (±13.62)
Bray-2	132.50 (±22.57)b	81.10 (±14.58)b	96.30 (±5.62)	43.14 (±13.58)	195.16 (±21.82)b	157.73 (±27.14)b	142.45 (±32.64)	109.04 (±27.66)	254.47 (±24.21)	51.50 (±5.89)	78.69 (±3.30)	8.04 (±2.29)	19.84 (±2.57)
Bray-1	55.02 (±12.36)c	28.18 (±7.61)c	79.21 (±12.08)	30.56 (±8.29)	95.66 (±11.79)b	76.82 (±13.47)bc	80.02 (±19.85)	48.95 (±21.34)	67.81 (±8.87)	15.86 (±2.21)	83.23 (±4.97)	5.14 (±0.83)	18.81 (±2.73)
Mehlich-3	55.76 (±7.10)c	28.14 (±4.69)c	48.17 (±6.98)	14.42 (±4.51)	103.06 (±8.26)b	79.37 (±16.15)bc	78.19 (±29.05)	49.31 (±24.13)	54.56 (±5.97)	20.08 (±2.17)	74.75 (±5.53)	20.86 (±10.39)	24.30 (±5.63)
Mehlich-1	27.36 (±4.07)d	18.81 (±2.90)c	61.63 (±2.21)	17.32 (±4.81)	46.96 (±6.77)b	56.34 (±7.71)c	40.40 (±9.16)	51.04 (±14.69)	56.94 (±6.96)	20.40 (±2.06)	69.19 (±9.17)	3.81 (±0.31)	9.36 (±0.77)
AB-DTPA	15.68 (±1.06)e	10.79 (±0.77)d	20.00 (±0.51)	19.08 (±3.67)	6.07 (±0.31)c	4.08 (±0.38)d	6.15 (±1.14)	4.80 (±1.20)	18.39 (±1.71)	2.22 (±0.06)	29.81 (±1.35)	4.64 (±0.63)	12.60 (±0.07)
Morgan	9.84 (±0.68)e	6.63 (±0.57)e	12.48 (±0.43)	10.87 (±2.46)	6.48 (±0.44)d	5.28 (±0.56)e	5.71 (±1.13)	4.09 (±1.30)	7.00 (±1.11)	8.75 (±0.00)	29.86 (±4.53)	1.57 (±0.12)	3.39 (±0.21)
Water	2.54 (±0.47)f	1.03 (±0.25)f	12.60 (±4.64)	2.32 (±1.09)	1.60 (±0.79)e	0.99 (±0.32)e	2.18 (±1.21)	1.13 (±0.55)	0.15 (±0.05)	bdl	89.41 (±23.26)	0.13 (±0.04)	1.84 (±0.48)

Note: Analysis carried out on log-transformed data for soil groups with a sample size greater than five. Means in the same column that do not share the same letter are significantly different at a significance level of 0.05. AB-DTPA, ammonium bicarbonate diethylenetriaminepentaacetic acid; bdl, below detection limit; CA, Centre for Agriculture and Forestry Development; CR, Cormack; NA, not analyzed; SOM, soil organic matter; SJ, St. John's Research and Development Centre.

Fig. 1. Summary of P-tests analysed by colorimetry (*a*) and ICP (*b*). Each data point was color coded to represent the soil group (location, depth or horizon, and management type).



the citric acid solution has chemical properties similar to low molecular weight organic acids secreted by plant roots which can facilitate the release of P from clay or organic complexes via anion replacement and acidic reaction (Wuenscher et al. 2015; Zhu et al. 2018; Fäth et al. 2019). The trend was slightly different for P-CA$_{Col}$ in soils with lower available P and SOM (CA$_{forested}$: E and B horizons; Table 3). This might be due to the precipitation of inorganic P or higher molybdate unreactive P in the soil solution (Darch et al. 2016), as higher P-CA$_{ICP}$ was observed for the same soil (Table 4). This could also be an artifact due to the smaller sample size.

The citric acid solution can extract 46 to 79% hydrolysable organic P, significantly more than the Olsen solution at <10% (Hayes et al. 2000; Darch et al. 2016). In this study, the organic P, calculated from the difference between P-CA$_{ICP}$ and P-CA$_{Col}$, accounted for 11%–46% of the extracted total P (P-CA$_{ICP}$) in managed soils (data not shown). The organic P in the soils might be mineralizable and available for plant uptake in medium to long term; the choice of P-tests might thus affect fertility recommendations (Jørgensen et al. 2015; Margalef et al. 2017). The citric acid solution can also extract soluble P from clay minerals and organometallic complexes (DeLuca et al. 2015), more common in acid soils. For example, P-CA$_{ICP}$ was higher in E and B horizons rich in Al minerals than other P-*tests* (Table 4).

Even though the 1% citric acid extraction was suggested for agronomic P recommendations as early as 1894 (Truog 1930), it is not as widely used as the Olsen or M3 tests despite reports of its ability to mimic the organic acid exudates in the rhizosphere (Darch et al. 2016; Menezes-Blackburn et al. 2016; Schneider et al. 2019). Citric acid extraction has been recommended to replace other tests for forest soil inventories (Fäth et al. 2019). The 1% citric acid solution has no or very minimal health risk when handled in the laboratory, and its wastes are more environmentally safe than those of other acidic and alkaline P-tests. A well-calibrated citric acid-based P testing might thus be an excellent alternative for assessing total available P (in the form of orthophosphate and some organic P) in natural and agricultural soils.

Bray-2 extraction

The P-B2 was the second highest in long-term managed fields (SJ$_{managed}$ and CR$_{managed}$ soils) after P-CA, regardless of P quantification techniques and depths (Tables 3 and 4). The P-B2 trends as measured by colorimetry versus ICP were inconsistent across soil management types and properties. This can be partly explained by the diversity in the amount and solubility of legacy P pools (mineral, organic, and complexed P accumulated over time due to continued fertilizer application) across variable histories of soil management and the related variability in SOM and Al (Sherrell 1970; Giroux and Tran 1985; Kedir et al. 2021*b*). Wang et al. (2004) reported a higher amount of P-B2 than P-M3 for acid soils such as Ultisols and Alfisols in Louisiana, likely related to the acid strength of the Bray-2 solution (pH = 2.6) that mainly reflects the P bound to Al and Fe minerals and to some extent, organic compounds but affected by soil texture. Thus, by design, Bray-2 extracts both labile and a portion of nonlabile fixed P pools (Jones 2001) and is a common test for agronomic purposes for various soil types (Ziadi et al. 2013) including acidic soils (Sherrell 1970). In NL, Bray-2 was replaced by Mehlich-3 in 2013 (T. Fagner 2019, personal communication), but there is no documented agronomic evidence for the decision. A suggested reason for preferring Mehlich-3 is the option for ICP quantification of multiple elements within a single extract. This method might be useful to measure total extractable P by accounting for strongly fixed P in long-term managed and forest mineral soils.

Mehlich-3, Bray-1 and Olsen extractions

The mean of P-M3$_{Col}$, P-B1$_{Col}$ and P-Ol$_{Col}$ was statistically not different in long-term managed soils (SJ-D1 and CR-D1;

Table 5. Pearson correlations of P-tests analyzed by colorimetry (Col) and ICP with selected soil properties of SJ (0–20 and 20–40 cm) managed soils.

P-tests (mg P kg^{-1})	Soil depth (cm)	Sand (%)	Clay (%)	Silt (%)	pH	EC (µS cm^{-1})	SOM (%)	M3-Al (mg kg^{-1})	M3-Fe (mg kg^{-1})	M3-Ca (mg kg^{-1})	M3-K (mg kg^{-1})
Water-Col	0–20	0.75*	−0.53*	−0.59*	−0.22	0.45	0.56*	0.12	−0.69*	0.17	0.51*
	20–40	−0.38	0.71*	0.20	0.33	0.78*	0.76*	0.37	−0.52	0.40	0.37
Citric acid-Col	0–20	0.41	0.09	−0.47	−0.61*	−0.17	0.08	0.62*	−0.06	−0.41	0.22
	20–40	0.22	0.16	−0.26	−0.11	0.33	0.28	0.07	−0.10	0.49*	0.67*
Olsen-Col	0–20	0.50	0.09	−0.52*	−0.31	−0.14	−0.01	0.37	−0.30	−0.07	0.40
	20–40	0.07	0.27	−0.11	−0.02	0.41	0.2775	−0.06	0.01	0.56*	0.73*
AB-DTPA-Col	0–20	0.30	−0.32	−0.23	−0.50*	−0.00	0.01	0.17	0.04	−0.24	−0.03
	20–40	0.17	0.18	−0.24	0.14	0.18	0.17	−0.02	−0.00	0.32	0.44*
Morgan-Col	0–20	−0.41	0.47	0.33	−0.25	−0.35	−0.11	0.16	0.12	−0.37	−0.07
	20–40	−0.16	0.05	0.16	0.25	0.19	0.12	−0.24	−0.01	0.40	0.27
Bray-1-Col	0–20	0.32	−0.27	−0.31	−0.74*	−0.21	−0.06	0.38	0.27	−0.31	0.05
	20–40	−0.11	0.22	0.08	−0.35	0.24	−0.07	−0.43*	0.15	0.15	0.65*
Bray-2-Col	0–20	0.37	−0.17	−0.35	−0.78*	−0.13	0.12	0.46	−0.00	−0.47	0.19
	20–40	0.08	0.11	−0.10	−0.16	0.33	0.01	−0.24	−0.02	0.33	0.71*
Mehlich-1-Col	0–20	0.27	−0.02	−0.34	−0.65*	−0.32	−0.24	0.27	0.19	−0.21	0.19
	20–40	0.03	0.06	−0.03	−0.39	0.10	−0.19	−0.37	0.22	0.11	0.60*
Mehlich-3-Col	0–20	0.40	−0.15	−0.42	−0.73*	−0.16	−0.03	0.45	0.11	−0.31	0.19
	20–40	−0.07	0.26	0.03	−0.17	0.33	−0.05	−0.40	0.14	0.29	0.71*
Water-ICP	0–20	0.31	−0.20	−0.8	−0.42	0.11	−0.13	0.01	0.13	0.12	0.231
	20–40	−0.19	0.30	0.11	−0.48*	0.01	0.14	−0.30	−0.03	0.21	0.43*
Citric acid-ICP	0–20	0.55*	−0.10	−0.52*	−0.59*	0.17	0.34	0.76*	−0.28	−0.40	0.29
	20–40	0.11	0.27	−0.20	−0.19	0.38	0.49*	0.11	−0.21	0.49*	0.71*
AB-DTPA-ICP	0–20	0.65*	−0.47	−0.60*	−0.82*	0.16	0.42	0.48	−0.10	−0.40	0.12
	20–40	−0.16	0.39	0.08	−0.54*	0.17	0.25	−0.21	−0.09	0.09	0.55*
Morgan-ICP	0–20	0.59*	−0.16	−0.63*	−0.65*	−0.16	0.21	0.37	−0.09	−0.23	0.17
	20–40	0.04	0.21	−0.08	−0.30	0.21	0.47*	0.03	−0.15	0.40	0.66*
Bray-1-ICP	0–20	0.41	−0.41	−0.37	−0.85*	−0.01	0.14	0.50*	0.19	−0.40	0.05
	20–40	−0.09	0.18	0.07	−0.52*	0.11	0.01	−0.38	0.04	0.04	0.67*
Bray-2-ICP	0–20	0.39	−0.22	−0.38	−0.86*	−0.01	0.22	0.67*	0.08	−0.57*	0.05
	20–40	0.08	0.07	−0.09	−0.26	0.23	0.07	−0.22	−0.00	0.26	0.79*
Mehlich-1-ICP	0–20	0.34	−0.18	−0.35	−0.85*	−0.14	0.17	0.66*	0.19	−0.60*	−0.08
	20–40	−0.05	0.12	0.07	−0.38	0.13	−0.02	−0.28	0.17	0.02	0.64*
Mehlich-3-ICP	0–20	0.37	−0.24	−0.37	−0.78*	−0.12	−0.00	0.46	0.19	−0.34	0.15
	20–40	−0.05	0.16	0.05	−0.21	0.20	0.00	−0.38	0.16	0.29	0.80*

*Significant correlation ($p < 0.05$). **Note:** AB-DTPA, ammonium bicarbonate diethylenetriaminepentaacetic acid; bdl, below detection limit; CA, Centre for Agriculture and Forestry Development; CR, Cormack; EC, electrical conductivity; ICP, inductively coupled plasma; NA, not analyzed; SOM, soil organic matter; SJ, St. John's Research and Development Centre.

Table 3). An equivalent amount of P or a slight difference between P-B1$_{Col}$ and P-M3$_{Col}$ was reported in previous studies for different soils ($n = 2659$) collected from across Ohio and Indiana, USA, representing a range of fertility status (Culman et al. 2020), for Mollisols ($n = 72$) from Pampean Argentina (Gutierrez Boem et al. 2011), and for a 17 soil series (n = 78 site-year) from Iowa, USA (Mallarino 2003). Similarly, P-M3$_{ICP}$ was statistically similar to P-B1$_{ICP}$ for long-term managed soils (SJ$_{managed}$; Table 4), likely due to their propensity to extract similar P pools (Ketterings and Flock 2005). For soils higher in extractable P (CR soils), P-M3 was not significantly different from P-B2, P-Ol, P-B1, and P-M1, regardless of quantification methods, which might be related to lower SOM in *CR* soils (Table 1) and both methods favoured to extract the adsorbed mineral P pool (Jones 2001). In selected soils with <5% SOM (CA$_{managed}$: E, and CA$_{forested}$: E and B), Mehlich-3 extracted slightly more P than Olsen, while for soils with >5% SOM (in both SJ$_{managed}$ and SJ$_{forested}$) Olsen extracted slightly more P than Mehlich-3 (Table 3). This might reflect lower hydrolysis rates of organic P in the Mehlich-3 versus the Olsen, 1% citric acid and Bray-2 solutions (Hayes et al. 2000; Adesanwo et al. 2013; Darch et al. 2016). Similarly, Kedir (2020) reported relatively higher P-M3 than P-Ol and P-CA in unmanaged surface and subsurface Podzols. However, three months after adding inorganic or organic fertilizers and biochar to similar soils under greenhouse conditions, P-Ol and P-CA were higher than P-M3, confirming the effect of soil management on P dynamic (Kedir 2020).

The differences in the soil properties (pH, Al, Fe, and SOM) and the type of fertilizer (mineral and organic) could explain such variations. While the Olsen method was initially designed for calcareous soils (Olsen et al. 1954), it has also been used for acidic soils (Kulhánek et al. 2007). For example, the provinces of Ontario and Manitoba (Canada) use the Olsen method for both agronomic and environmental P management across a range of soil types (Kumaragamage et al. 2007, 2011; Wang et al. 2015).

Morgan and Ammonium bicarbonate-DTPA extractions

The P-Mo and P-AB had similar trends as measured by both analytical methods (Tables 3 and 4), but their relationship was slightly affected by soil properties (Table 5). For most soil samples, both tests yielded lower extractable P than Mehlich-3 but significantly more than P-Wa. This might be due to the capacity of Morgan's solution to solubilize some of the strongly fixed P in Podzols (Young et al. 2017; Kedir et al. 2021*a*). The P-Mo is used for agri-environmental purposes on acidic soils (Daly and Casey 2005; Young et al. 2017). The AB-DTPA method, initially developed as a universal extractant for multiple elements (Soltanpour 1985; van Raij 1994), correlated well with the Olsen method (Jones 2001). These two methods might help to assess actual plant-available P (low concentration) in managed podzolic soils.

Water extraction

Overall, P-Wa was the lowest in the studied soils, with few exceptions for soils having higher P content (CR$_{managed}$ and CR$_{grassland}$) and organic matter-rich layer (SJ$_{forested}$) (Tables 3 and 4). The P-Wa reflects readily available and environmentally labile P (Glæsner et al. 2013), describing dissolved reactive P that may be easily leached (Maguire and Sims 2002). Despite low P mobility in Podzols rich in reactive Al and Fe minerals, the loss of particulate P from acidic sandy soils cannot be discounted (Glæsner et al. 2013). The smaller amounts of water-extractable P in highly reactive mineral horizons of Podzols might exclude organic and particulate P and not reflect the actual risks of P loss. In our study, P-Wa in all managed soils was below the recommended environmental critical P level (9.70 mg P kg^{-1} P-Wa, Khiari et al. 2000). While P-Wa in NL soils indicated minor risks of P loss, it may nevertheless suggest the reality of slow, long-term P transfer from sandy surface Podzols and accumulation in the subsurface where it is stabilized with Al and organic carbon as unavailable P chemical species (Ohno and Amirbahman 2010): a standard podzolization mechanism that removes P from the available pool. However, it may be thus be argued that for Podzols, it might be misleading to rely on P-Wa to monitor environmental quality as it does not account for the potential loss of particulate P (Batjes 2011; Kedir et al. 2021*b*). Alternatively, the P saturation index calculated from the molar ratios of P-M3 to Al-M3 and Fe-M3 could be an option for advising for environmentally sustainable P management (Wang et al. 2012; Szara et al. 2018).

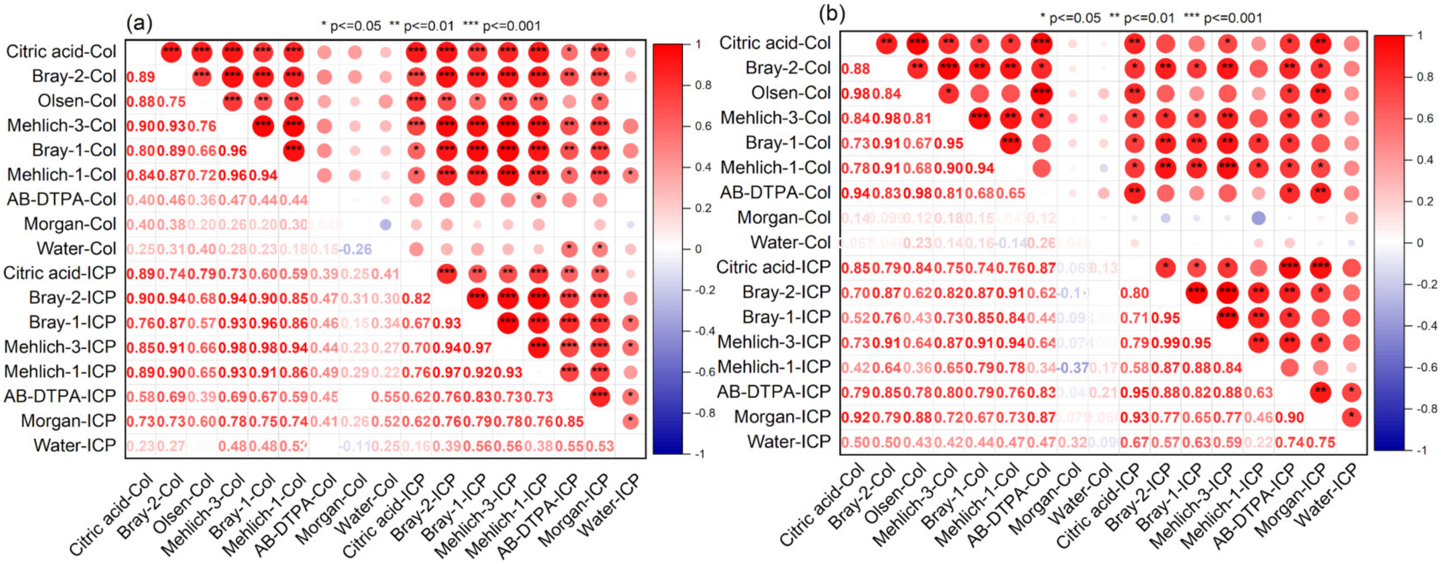
Colorimetric-P and ICP-P comparisons

Except for the P-Wa, all P$_{ICP}$ measurements were significantly higher than P$_{Col}$, confirming the contribution of organic P and possibly nonorthophosphate inorganic P to the total P (P$_{ICP}$) in the tested Nfld Podzol samples (data not shown). The difference of P$_{ICP}$ and P$_{Col}$ can be used to assess extractable organic P in these soils (Adesanwo et al. 2013; Ziadi et al. 2009). For example, the highest mean differences (likely representing organic P) between P$_{ICP}$ and P$_{Col}$ were found for the citric acid (139 mg kg^{-1}), Bray-2 (41 mg kg^{-1}), and Bray-1 (20 mg kg^{-1}). We did not verify the species of organic P; however, Cade-Menun et al. (2018) identified that the myo-inositol hexaphosphate was the dominant organic P species in Mehlich-3 extract for a range of mineral acidic soils (pH$_{H2O}$ = 4.7–6.3; Fayetteville, AR, USA, Saskatchewan, and Prince Edward Island, Canada). In this study, the mean differences between P$_{ICP}$ and P$_{Col}$ for Mehlich-3 and water were slightly lower in managed mineral soils of eastern Canada (Ziadi et al. 2009) and various soils collected across Manitoba either treated with or without manure (Adesanwo et al. 2013). Further investigations are required to identify and confirm the organic P species extracted by citric acid solution and their potential availability for plant uptake in Podzols converted from forest to agriculture.

Summary of P-tests comparisons

The Mehlich-3 method, recognized as a universal extractant, is widely used in North America, including NL and Maritime Canada, to analyze multiple elements alongside P using ICP (Cade-Menun et al. 2018). Olsen, Bray-1, and Mehlich-1 extracted P amounts similar to Mehlich-3 with slight differ-

Fig. 2. Pearson correlations between P-tests for SJ-D1 (*a*) and SJ-D2 (*b*) managed soils ($n = 22$ for each); correlation was performed using log-transformed data sets, for soil groups with larger sample size ($n = 22$). Col, colorimetric; ICP, inductively coupled plasma; SJ, St. John's Research and Development Centre of Agriculture and Agri-Food Canada.



ences related to quantification techniques, soil management types and depths. Citric acid extracted the largest P concentrations in all cases. For unique soils like Podzols converted from forest to agriculture, selecting the most informative P-test for environmentally sustainable P management requires the calibration of selected P-tests against crop yields and uptake rates. Further investigations are also necessary to better understand the availability of organic P in Podzols (Ziadi et al. 2009). This might result in adjustments to the P fertilizer recommendation and support sustainable P management.

Relationships between agri-environmental P-tests quantified by colorimetry or ICP

Pearson correlations

We found significant correlations between P-tests ($r = 0.45$ to 0.98) for selected managed soils (SJ-D1 and SJ-D2, Fig. 2). Ketterings and Flock (2005) and Dari et al. (2019) reported a strong correlation between P_{Col} and P_{ICP} for both P-B1 and P-M3 in various soil types. In our samples, moderate to strong correlations ($r > 0.60$) were found between P-CA, P-Ol, P-B1, P-B2, P-M1, and P-M3 regardless of quantification methods or soil depths. Also, strong correlations between P-B1$_{Col}$ and P-M3$_{Col}$, and P-B1$_{Col}$ and P-Ol$_{Col}$ were reported for various soils across the USA and Canada (Culman et al. 2020) and for agricultural soils in New Zealand (Sherrell 1970), respectively. We found relatively stronger correlations between P-Ol$_{Col}$ and P-CA$_{Col}$ ($r = 0.88$–0.98) in managed soils but aligned with the correlation ($r = 0.75$) reported by DeLuca et al. (2015) calculated across landscapes. Further evaluations are needed to understand the extraction mechanism of the Olsen test (alkaline solution), which resulted in comparable or higher P in Podzols than acidic extractants (Bray-1, Mehlich-1, and Mehlich-3).

The P-Wa had weak to moderate correlations with P-AB and P-Mo for the selected managed soils (Fig. 2). This can be explained by the significant differences in P extraction capacity of the studied P-tests (Tables 3 and 4) and could underplay the risk of soluble P loss. A recent soil test-based survey suggested that agricultural soils in NL have a very wide range of P concentrations (P-M3$_{ICP}$: 1.00–1486 mg kg^{-1}; Kedir et al. 2021*b*) with a significant proportion exceeding the soils' adsorption capacity. Thus, P-Wa might not help to identify podzolic soils with the P loss risk.

Variations in reported correlations for the same analytical methods might be assigned to soil depth, management and properties such as SOM, pH, soil texture, Al-M3, and Fe-M3 (Dari et al. 2019). Note that in the NL boreal region, the differences between soil depths in non-managed soils are important as different soil layers are variably mixed when land is converted to agricultural uses. Overall and in agreement with the previous studies, while it is possible to estimate equivalent extractable P for other environmental and agronomic P-tests from the P-M3$_{ICP}$, variability due to soil conditions requires that this should be carefully assessed and recommended.

Linear regressions

Linear regression fits were determined for all P-tests (both P_{Col} and P_{ICP}) vs. P-M3$_{ICP}$, the standard agronomic soil test in NL and across portions of North America (Dari et al. 2019). For example, the slopes vs. P-M3$_{ICP}$ for SJ-D1 soils were calculated at 1.40, 1.17, 1.15, 0.95, 0.69, 0.68, 0.64, and 0.62 ($0.31 < r^2 < 0.98$, $P < 0.05$) for P-M1$_{Col}$, P-B1$_{Col}$, P-M3$_{Col}$, P-CA$_{Col}$, P-Mo$_{Col}$, P-Ol$_{Col}$, P-AB$_{Col}$, and P-B2$_{Col}$, respectively (Fig. 3). For managed CR-D1 soils, the same slopes were 1.20, 0.83, 1.10, 1.14, not significant, 1.29, not significant, and 0.57, respectively (same as the order reported for SJ-D1; Fig. 3). This vari-

Fig. 3. Linear regression model established between P-M3$_{ICP}$ and other P-tests analyzed by colorimetry (*a*, *c*, *e*, *g*) or ICP (*b*, *d*, *f*, *h*) for managed soil groups collected from 0 to 20 cm (SJ), 20 to 40 cm (SJ), 0 to 10 cm (CR), and 10 to 20 cm (CR), respectively; log-transformed data set; equations with nonsignificant slopes (i.e., not different from zero) are not presented; P-tests with less than five samples were excluded. CR, Cormack; ICP, ICP, inductively coupled plasma; SJ, St. John's Research and Development Centre of Agriculture and Agri-Food Canada.

ability supports the need for P-test calibration for local soil and management types (Mattila and Rajala 2022). Linear regressions of varying strengths have been reported between P-tests and P-M3 in the literature (Steinfurth et al. 2021). For example, Wang et al. (2004) found $r^2 = 0.71$ between P-B2$_{ICP}$ and P-M3$_{ICP}$ for various soils from Louisiana parishes, USA ($r^2 = 0.75$ to 0.98 in this study); Culman et al. (2020) reported $r^2 = 0.71$–0.99 between P-B1$_{Col}$ and P-M3$_{ICP}$ for agricultural soils from North America ($r^2 = 0.67$ to 0.95 in this study); Kumaragamage et al. (2007) reported $r^2 = 0.42$ to 0.91 (non-manured soils) and 0.60 to 0.98 (manured soils) for nine agri-environmental P-tests (colorimetric) vs. P-Ol$_{Col}$ ($r^2 = 0.20$–0.98 in this study for 8 P-tests) (Fig. 2).

Generally, P-Wa, P-AB, and P-Mo had relatively weaker relationships with P-M3$_{ICP}$. This could be due to the difference in extractants capacity to solubilise soil P and variable soil properties such as SOM, Al, and Fe affecting the solubility of organic and inorganic P (Weihrauch and Opp 2018).

The stronger regression coefficients reported in previous studies might be explained by the larger sample size ($n > 2000$), greater consistency in surface soil samples and level of soil P. Our soil samples were collected from fields with contrasting management histories, depths, and soil properties, and relatively small sample sizes (8 to 23 for soil groups) which explain this high variability in regression slopes and coefficients.

Slopes larger than 1 suggest overestimation versus P-M3$_{ICP}$. A combination of a slope >1 with an intercept significantly lower than 0 would suggest that the respective test would underestimate the P-M3$_{ICP}$ at lower concentrations while it would overestimate it at higher concentrations. Such a scenario was noted for the P-B1$_{ICP}$ versus P-M3$_{ICP}$ and for the P-M3$_{Col}$ versus P-M3$_{ICP}$, except for the CR-D2 soil group. The soil groups did have a distinct effect on the relationship between P-M3$_{ICP}$ and P-B1$_{Col}$ (i.e., the latter overestimated P-M3$_{ICP}$ for SJ-D1 soils and underestimated it for CR soils) (Fig. 3).

Nevertheless, the general consistency in trends between our results and previous studies suggests that P-M3$_{ICP}$ might be calibrated and used to inform extractable P from Podzols to support various decisions, that is, agricultural and environmental topics, but this supposes local calibration.

Conclusion

For the first time, extractable P in Nfld boreal Podzols with heterogeneous characteristics was evaluated using nine P extractions (P-tests) quantified with colorimetry and ICP. The sequence of extractable P was P-Wa $\leq$ P-Mo < P-AB < P-M1 < P-B1 < P-M3 $\leq$ P-Ol « P-B2 «< P-CA for both colorimetric and ICP quantifications; for ICP, the series varied slightly such that P-M3 $\leq$ B-P1. The variable results obtained with different test protocols confirmed the existence of different extractable P pools in the Nfld Podzols converted from forest to agriculture. Olsen, Bray-1, and Mehlich-1 extracted P amounts similar to Mehlich-3 with slight differences related to quantification techniques, soil management types and depths. Bray-2 and citric acid extracted 2-folds and 4- to 6-folds more P than Mehlich-3, respectively. Most P-*tests* correlated well with each other ($r \geq 0.70$) except for water, AB-DTPA, and Morgan. The soil conditions had variable but notable effects on the slopes and intercepts of the linear relationships between P-tests. This points to the need for local calibration of P-tests with yield and nutrient uptake data that account for the diverse soil conditions encountered in the boreal regions. It is critical to test methods that are not well correlated with each other to understand the applicability to recommendations of diverse extractable P pools. Multiple options might be possibly available and necessary for most accurate decisions for agronomic and environmental needs in Nfld Podzols and in other boreal regions.

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Competing interests

We declare no competing interest

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