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Residual phosphorus is a significant pool in soil phosphorus cycling

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Sequential phosphorus (P) fractionation schemes are widely used to characterize soil P pools, yet the most chemically resistant forms are often omitted in modern applications of fractionations. We quantified inorganic and organic P in ten predominantly clayic or fine sandy acidic agricultural soils from SW Finland, paying special attention to the residual P not recovered in the four common extractions of Chang-Jackson scheme (NH_4Cl-, NH_4F-, NaOH-, and H_2SO_4-extractable P). Total P (H_2SO_4-H_2O_2-HF) ranged from 1148 to 2467 mg kg^{-1}, with organic P constituting 15–49%. The four inorganic fractions represented on average 43% of total P. A substantial residual P pool (304–474 mg kg^{-1}) accounted for 25% of total P and 32–42% of inorganic P, exceeding the size of any individual P fraction. Our results suggest that routine fractionation may substantially underestimate soil inorganic P reserves and oversimplify our view on long-term P dynamics. This has implications for long-term P budgets and P availability under fluctuating redox conditions, including erosion-mediated P losses.

Key words: agricultural soils, inorganic P, P fractionation, residual P, total P

Introduction

In characterization of soil phosphorus (P), various sequential extraction procedures are used to separate P pools of different solubilities. The fractions extracted with a given solution are commonly assumed to correlate with plant-availability or with assumed binding constituents (e.g., surfaces of Fe and Al oxides, apatite P). The Hedley (Hedley et al. 1982) sequential fractionation scheme for P is nowadays likely the most used procedure worldwide, but the older Chang and Jackson (1957) scheme is still the one that has been historically applied to Finnish soils more frequently. In most, if not all, contemporary studies involving the Chang-Jackson procedure the extraction stops at H_2SO_4 extraction. The following steps, i.e., reductant soluble P fraction (citrate-dithionite step) and occluded P (by 0.1 M NaOH or 0.5 M NH_4F solution) remain unquantified. Also, the residue was in Chang and Jackson (1957) original procedure further analyzed for P after sodium carbonate fusion, and all extraction steps together likely yielded a good estimate for the total inorganic P in soil.

For studies focusing primarily on the ability of soils to supply P for crops in up to decadal scales the more resistant fractions may be of lesser importance (Tiessen and Moir 1993). For example, in studies on the fate of fertilizer P in soils of Finland, only the four first steps of the Chang and Jackson procedure have commonly been carried out (Hartikainen 1989, Yli-Halla 1989, Jaakkola et al. 1997, Rodriguez-Gonzalez et al. 2018), neglecting the more sparingly soluble P. However, for long-term P budgets, or fate of legacy P, we need to consider that P inputs that are adsorbed on metal hydroxide surfaces undergo solid-state diffusion and co-transformations with metal oxides, with time becoming ever less readily extractable. Where soils undergo annual redox cycles, it is easy to imagine that when Fe hydroxides precipitate on particle surface in aerated zones of soil matrix, adsorbed P no longer resides on particle surface, but underneath these newly formed layers. Upon drying hydroxides are transformed to oxides that are more resistant to dissolution. Repeated redox cycles may form layered Fe oxide concentrations, similar to those that one may observe in old root channels. Then, it is not surprising if a P extraction step such as by 0.1 M NaOH that mainly extracts P through ligand exchange, is not able to specifically target Fe oxide associated P. Inability of the four first Chang and Jackson fractionation steps to extract Fe-associated P is evident by the data of Kaila (1964) in which reductant soluble P, after preceding extractions of the Chang and Jackson procedure, averaged 75 mg kg^{-1} or 12% of inorganic P. If one is interested in the P transformations in the soil system in a geological time scale, the sizes of the sparingly soluble pools are essential knowledge.

In this study, we quantified inorganic and organic P in ten agricultural soils, paying particular attention to the inorganic P not extracted in the four first fractions of the Chang and Jackson procedure the way it is nowadays most conducted. The purpose of the study is to remind the P research community of the recalcitrant P pool that is

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often neglected but its omission may distort our view on long-term P cycling and fate of historical fertilizer inputs. Moreover, residual Fe-associated P is a part of the total P flux mediated, for example, by erosion, and assumptions on its bioavailability in reduced environment directly affect the view of erosion control as the main water protection measure in agriculture (Uusitalo et al. 2003).

Materials and methods

Composite soil samples were collected from private fields in Lake Pyhäjärvi watershed in the municipality of Tammela, southwestern Finland in autumn 2000. The watershed totals 639 km^2 and is a relatively flat area about 100 m above the current sea level. Soils of the area partly consist of glacial till which is predominantly under forest vegetation. Agricultural land, mostly used for growing spring-sown cereals or ley, is composed of fine- and medium-textured soils and some peat soils. The fine-textured soils were formed of the sediment accumulated in small shallow lakes that have been reclaimed for agriculture, e.g. the present Kalliojärvi field opening (included in our sampling) was turned in agricultural use about 70 yrs ago.

At the time of sampling, the fields were either ploughed, covered with stubble or growing perennial ley. Soil samples of 15 litres were taken with a spade from (0–20 cm) plough layer. The soil samples were air dried and crushed to pass a 2-mm sieve. Soil texture was determined by finger assessment. The soil samples were analyzed for pH, measured in a 1:2.5 water suspension, and carbon, determined by dry combustion with LECO628 analyzer (Leco Corp., St. Joseph, MI, USA). The samples were analyzed for soil test P by single extractions 1) with 0.5 M $NaHCO_3$ solution at pH 8.5 for 30 min (Olsen et al. 1954) and 2) using the Finnish national agronomic method of extraction with pH4.65 ammonium acetate - acetic acid solution at 1:10 volumetric soil-to-solution ratio for 1 h (P-Ac, Vuorinen and Mäkitie 1955), resembling the Morgan method extraction. The short-range ordered (hydr)oxides of Al and Fe were determined with the acid (pH 3.0) 0.2 M oxalate extraction method by Schwertmann (1964).

Six out of the 10 soil samples had clayic textures with micaceous mineralogy (Yli-Halla et al. 2009) while three represented medium-textured soils and one with unknown particle size distribution was close to being an organic soil (Table 1). All soils were non-calcareous. According to the WRB classification, the clayic soils were probably Stagnosols and the sandy and silty soils were Regosols (Lilja et al. 2017). The soil highest in carbon was likely a Gleysol because the carbon content was slightly too low for a Histosol. According to the Finnish interpretation of the P-Ac, eight of the soil samples represented the third and fourth class of P-Ac abundance in a seven-step classification, while two were richer in P-Ac. The range of Olsen soil test values from 21 to 84 mg kg^{-1} suggests that the soils contained a substantial amount of legacy P inherited from previous fertilizations mostly accumulated during the last 60 years.

Table 1. Some characteristics of the experimental soil samples

Sample	Crop	Texture	pH(H_2O)	C, %	Al(ox)	Fe(ox)	P-Ac	P-Olsen
					mmol kg^{-1}		mg l^{-1}	mg kg^{-1}
Py 13	Ploughed	SC	n.d.	3.0	95	269	9.0	43.3
Ku 15 /II	Ley	SC	5.7	3.2	86	147	7.2	38.0
Py 07	Ley	SiC	5.5	3.6	100	164	6.2	31.7
Ku 11	Ploughed	SC	6.6	3.7	100	218	29.5	81.1
Ku 14	Ploughed	SC	6.0	3.7	101	209	13.9	52.0
Ku 22	Ploughed	VFS	6.1	6.1	108	56	14.4	83.7
Py 10	Ley	C	n.d.	6.8	129	178	4.2	21.2
Ku 16	Ploughed	CSi	5.3	14.0	207	183	5.9	25.7
Ku 21 /II	Ley	FS	5.7	14.2	112	99	6.6	34.4
Ku 06	Rapeseed stubble	Organic	5.9	18.6	337	142	7.0	35.0
Mean			5.8	7.7	137	167	10.4	44.6

C=Heavy clay; SC=sandy clay; SiC=silty clay; CSi=Coarse silt; VFS=Very fine sand

For this study, inorganic P reserves were analysed with duplicates using the Chang and Jackson (1957) fractionation method as modified by Hartikainen (1979). This method consists of four consecutive extractions (1:50 soil-solution ratio) with 1 M NH_4Cl, 0.5 M NH_4F (pH 8.5), 0.1 M NaOH and 0.25 M H_2SO_4, which are targeted to extract easily soluble P, and originally thought to separate P bound to Al oxides (Al-P), P bound to Fe oxides (Fe-P) and Ca phosphates (Ca-P). The concentration of P in the extracts was determined colorimetrically with the molybdenum blue method using a spectrophotometer. Organic P was determined according to the Saunders and Williams method where soil organic P is calculated as a difference of P extracted with 0.5 M H_2SO_4 before and after ignition at 550 °C (Olsen and Sommers 1982). To determine total P, soil samples were digested with duplicates with concentrated H_2SO_4, H_2O_2, and HF upon 10 min of heating (≃ 423 K) (Bowman 1988) and P was measured with ICP-OES. The difference between total P and the sum of Chang and Jackson fractions plus organic P was regarded as residual P, consisting of occluded P and other forms of very sparingly soluble P.

Results

Total P (TP) ranged from 1148 to 2467 mg kg^{-1}. There was a tendency that low SOC soils were often lower in TP than the soils richer in SOC (r=0.72, *p*=0.019); the soil with the highest SOC content was also richest in TP, being the only one with P content exceeding 2 g kg^{-1}. The soil highest in SOC had also a high content of organic P (1210 mg kg^{-1}, 49%), while in the other soils, the range (239–720 mg kg^{-1}) corresponded 15–40% of TP. The ratio of organic C to organic P (mg mg^{-1}) averaged at 145 (range 76–282 mg mg^{-1}) with some positive correlation with SOC (r=0.66, *p*=0.038).

The sum of the first four inorganic Chang and Jackson P fractions (478–1017 mg kg^{-1}) comprised on average 43% of TP with the range of 32–48%. As usual, the content of NH_4Cl-P was very low and will not be discussed further. As an average, the NH_4F-P, NaOH-P and H_2SO_4-P comprised a rather similar proportion of TP, 12%, 16% and 15% each. In all soils but one, NaOH-P was more abundant (on average 29%) than NH_4F-P. The ratio of NH_4F-P/NaOH-P correlated with the ratio of Al-ox/Fe-ox (r=0.77, *p*=0.0092).

Table 2. Phosphorus fractions of the experimental soils, all expressed in mg kg^{-1}

Sample	NH_4Cl-P	NH_4F-P	NaOH-P	H_2SO_4-P	Org-P	Residual P	Total P
Py 13	0.4	123	289	214	239	419	1296
Ku 15 /II	0.3	91	182	255	336	393	1257
Py 07	0.3	109	197	160	361	309	1148
Ku 11	0.3	250	368	306	257	435	1709
Ku 14	4.9	148	299	268	485	442	1642
Ku 22	5.1	356	137	150	413	321	1382
Py 10	0.4	108	194	190	365	338	1183
Ku 16	3.5	155	299	247	720	400	1823
Ku 21 /II	2.3	120	158	349	503	304	1439
Ku 06	0.1	385	255	140	1210	474	2467
Mean	1.8	185	238	228	489	384	1535

Quantitatively, the range of residual P (304–474 mg kg^{-1}) was quite narrow, but substantial (Table 2). On an average, 25% of TP was not recovered in the four inorganic Chang and Jackson fractions or in the pool of soil organic P. Considering inorganic P only, 37% (32–42%) of soil inorganic P was not included in the first four Chang and Jackson fractions. In the six clayic soils, the residual P amounted to 26–31% of TP while in the other four coarser soils, relative contribution of residual P was less, 19–23%.

Discussion

The average soil test P (P-Ac) of our experimental soils was at the same level as in the entire Finland (11–13 mg l^{-1}; Lemola et al. 2023). The TP was within the range commonly measured in agricultural soils of Finland even though the mean value (1.54 g kg^{-1}) was higher than in the material of 24 soils (1.21 g kg^{-1}) collected 50 years ago

(Saarela et al. 2003), or in 221 soils (1.03 g kg^{-1}) collected more than 60 years ago (Kaila 1963), both from agricultural mineral top soils. Plenty of P has accumulated in agricultural soils of Finland during the last decades, including years of highly positive P balances (annually up to 35 kg ha^{-1}) since 1970s until the mid-1990s (Uusitalo et al. 2007), which likely explains the higher TP level in the present soil material. While our dataset is small (n = 10) and from a geographically restricted area, differences from the older studies are directionally consistent with long-term positive P balances reported for Finland and our material can be regarded as representative of the current agricultural soils of Finland.

The average sum of the first four Chang and Jakson inorganic P fractions (651 mg kg^{-1}) was 39% higher than in 156 clayic, silty and loamy agricultural mineral topsoil samples from early 1960's (470 mg kg^{-1}, Kaila 1964) or 19% higher than in 104 predominantly clayic topsoil samples from late 1970's (547 mg kg^{-1}, Hartikainen 1982). Our small set of soils contained 147% or 62% more NH_4F-P than the materials of Kaila (1964) and Hartikainen (1982), respectively. In the rest of the fractions, there was 34% and 7% more NaOH-P and 5% and 11% more H_2SO_4-P in the present material than in the two older studies. These differences again probably reflect the accumulation of legacy P that has been shown to occur in the NH_4F-P and NaOH-P fractions in the first place (Hartikainen 1989, Rodriguez Gonzalez et al. 2018). Comparing to Kaila (1964), an annual average increase of 7.8 kg ha^{-1}, totalling 470 kg ha^{-1}, has taken place in the NH_4F-P and NaOH-P fractions during the last 60 years, assuming a bulk density of 1.25 kg dm^{-3} and plough layer depth of 22 cm, with practically no coarse fragments (>2 mm) in these soils.

The present results strongly remind that inorganic soil P is not completely extracted in the first four Chang and Jackson fractions (NH_4Cl, NH_4F, NaOH, H_2SO_4) but on average, 384 mg kg^{-1} (mean 37%, range 32–44% of inorganic P) remained as residual P. Quantitatively, the residual P was more abundant than any of the fractions explicitly determined. The proportion of residual P in our small soil material was somewhat like the 30% in Kaila's 156 agricultural clayey, silty and loamy soils even though the average quantity of residual P in our soils was 86% higher than in Kaila's material (206 mg kg^{-1}). This difference of 178 mg kg^{-1} corresponds to 489 kg ha^{-1} (22 cm-plough layer, bulk density 1.25 kg dm^{-3}), or an annual increase of 8.1 kg ha^{-1} over a span of 60 years. We are fully aware of the shortcomings of these comparisons. In terms of P contents and distribution 60 years ago, our soils have not necessarily been similar to Kaila's (1964) soils. However, the substantially larger stock of residual P in our soils combined with the well-known positive P balance in agricultural soils of Finland would suggest that residual P may not be a source of plant-available P but it may be a gradual sink for legacy P.

In this study, the residual P included also the reductant soluble P which was determined separately in Kaila's study (1964), where it amounted to 75 mg kg^{-1} (12% of inorganic P). This pool consists of P that has been released from primary minerals by weathering, or added to soil as fertilizer, and adsorbed by secondary Fe (hydr)oxides and covered by layers of Fe (hydr)oxides precipitated later, ending up occluded into the interiors of Fe (hydr)oxides. Solid state diffusion has also been proposed as a mechanism of P sorption (Barrow 1983, Barrow et al. 2023). After a rapid initial adsorption, a slow process where phosphate diffuses into the adsorbent takes place, making the involved phosphate less extractable. It is feasible that the diffusion and occlusion processes are responsible for a slow increase of the residual P, a topic that requires further research. Even though hardly bioavailable in aerobic conditions, this P may be at least partially released in naturally reducing conditions.

Residual P has also been assumed to contain occluded aluminium-iron phosphates and lattice phosphates (Chang and Jackson 1957) or apatite inside mineral crystals (Kaila 1964), an assumption supported by the abundance of the H_2SO_4-P fraction in soils of Finland. In Kaila's material, the residual fraction (not including the reductant soluble P) on average amounted to 126 mg kg^{-1} (19% of inorganic P). It is likely that this very poorly soluble P fraction may have been largely dissolved away in strongly weathered soils, as shown in the original Chang and Jackson (1957) paper but may be quantitatively more important in less weathered soils like those in Finland.

It has been established that young soils in the early stages of weathering contain less P in the reductant soluble and occluded forms than do old soils in advanced stages of weathering (Yang and Post 2011). Our results recall that the resistant forms of P should not be forgotten in soils of Finland either when doing a comprehensive accounting on soil P reserves and P fluxes. The same risk of underestimating inorganic soil P resources as in the Chang and Jackson procedure applies to the Hedley fractionation procedure if the scheme is stopped at the 1 M HCl stage which is comparable to the 0.25 M H_2SO_4 stage of the Chang and Jackson procedure.

Finally, it is emphasized that the content of organic soil P cannot be calculated as the difference of the TP and the first four Chang and Jackson fractions because the difference contains also residual P. This calculation yields inflated estimates on the size of the organic P pool. For the same reason, the content of TP cannot be calculated as the sum or the first four Chang and Jackson fractions plus organic P.

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