https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Intensive agricultural management-induced subsurface accumulation of water extractable colloidal P in lime concretion black soil

Shouhao Li[a,b], Shuiqing Chen[a], Shanshan Bai[a], Jinfang Tan[a,b*], Xiaoqian Jiang[a,b*]

[a] School of Agriculture, Sun Yat-sen University, Guangzhou, Guangdong 510275, PR China

[b]Modern Agricultural Innovation Center, Henan Institute of Sun Yat-sen University, PR China

Corresponding to: jiangxq7@mail.sysu.edu.cn and tanjf7@mail.sysu.edu.cn

ABSTRACT:

Long-term excessive application of mineral fertilizer leads to accumulation of phosphorus (P) in lime concretion black soil, which increases the risk of P migration and loss from soil profile. The colloids in the profile are important carriers for P migration due to high P adsorption and transport capacity. In this study, water extractable colloids (WECs) were obtained from 0 ~ 120 cm soil profile by soil fractionation method, and their physicochemical properties were analyzed. Solution ^{31}P nuclear magnetic resonance (NMR) and P K-edge XANES were used to characterize the species and distribution of colloidal P in fertilized farmland soil profile. Total and available P in bulk soil and colloids decreased with soil depth. The organic P (OP) contained ~97 to 344 mg kg^{-1} per bulk soil and 110-630 mg/kg per WECs in soil profile with composition of orthophosphate monoesters and diesters according to NMR results. It suggested that OP in WECs from subsoils might be affected by the translocation of colloidal P (CP) from surface soils probably due to soil acidification and preferential flow caused by swelling-shrinkage clays including montmorillonite and nontronite. Additionally, the more negative zeta potential of surface soil colloids suggests the high mobility of colloidal P to the subsoils. The CP concentrations for <2 μm was about 38-

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

93 mg/kg per bulk soil, which is 6-37 folds of dissolved reactive P (DRP) concentrations, suggesting that the role of CP for P transport in the soil profile is dominated. This study showed that inorganic and organic P migrated from surface to deeper layer along the lime concretion black soil profile, with soil colloids having a significant effect on P migration from both surface and subsurface layers. The results have an important significance for soil P migration evaluation and agricultural non-point source pollution control in lime concretion black soil.

Keywords: Subsurface soil; Water extractable colloids, Organic P, Solution 31P-NMR, P K-edge XANES

INTRODUCTION:

Phosphorus (P) as one of essential macronutrients for crops is strongly immobilized with inorganic and organic soil components (Arai and Sparks, 2007). The lime concretion black soil is characterized by low water-air permeability, poor fertility, and strong swelling-shrinkage properties (Chen *et al.*, 2020). Therefore, high-intensity agriculture practices such as excessive fertilization have been applied for decades to maintain grain yields. Additionally, artificial ditches (~1-1.5 m depth) are usually dug out in the edge of field to facilitate drainage. However, long-term excessive input of mineral fertilizers may result in considerable P accumulation in agricultural soils and the artificial ditches bring increasing risk of P losses into surface water and ground water, causing serious environmental issues such as outbreaks of cyanobacteria and eutrophication (Whalen and Chang, 2001; Koopmans *et al.*, 2003; Hansen *et al.*, 2004). In addition to the transport of soil surface P (Pote *et al.*, 1996), transport of soil subsurface P has also been considered as a crucial pathway to waterways (Jorgensen and Fredericia, 1992; Kronvang *et al.*, 1997; Xue *et al.*, 1998; Hens and Merckx, 2001; Williams *et al.*, 2016; Jiang *et al.*, 2021). Some researchers have reported that high rainfall events promote the losses of P from tile drainage (1.0-1.4 m depth) (Royer *et al.*, 2006). In previous study in USA, colloidal P was the dominant P fraction of total P in tile water during high rainfall events (Jiang *et al.*, 2021). The colloids were found to carry over 1000 mg of P kg^{-1}, which was dominated in the transported P from subsurface

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

soil (Jiang *et al.*, 2021).

Currently, only a few papers have investigated dissolved and colloidal P distribution in subsoils which involved forest soils and Mollisols (Gentry *et al.*, 2007; Wang *et al.*, 2020; Li *et al.*, 2022). However, it is still not clear about the distribution of mobile colloidal P as well as their speciation in the soil profile of lime concretion black soil. Furthermore, whether the transport of colloidal P from topsoils to subsoils occurs and contributes to total P in subsurface flow is not clearly understood. Considering that the presence of shrink and swell clays in lime concretion black soil, the translocation of dissolved and colloidal P from surface soil to subsoils by preferential flow is expected as an important P transport pathway and leads to spatial redistribution within soil profiles. Additionally, the artificial ditches could also facilitate the transport of dissolved and colloidal P from both surface and subsurface soil, which is an important non-point source of eutrophication. Furthermore, the intensive input of fertilizer in lime concretion black soil (~600 kg/hm^2 compound fertilizer, N-P-K: 28-6-6) was also expected to facilitate the release of colloidal P (Liang *et al.*, 2016).

It is accepted that colloidal P could be derived from surface soils if the mobile colloids in subsurface soil contains organic P (Li *et al.*, 2022). The aim of this research was to explore (1) the dispersion of water-extractable colloids (WECs) in the soil profile for intensively managed lime concretions black soil and (2) physicochemical properties and P speciation of WECs with different depths. This information is the first for the assessment of colloidal P release potential from subsoils in lime concretion black soil and is valuable for the construction of sustainable strategies to control agricultural P loss.

2. MATERIALS AND METHODS

2.1 Site description and soil sampling

The selected site was located at the agricultural study site in Pingyu County, Henan Provinces, China with precipitation of 904.3 mm and annual mean temperature of 15 °C, respectively. According to the World Reference Base for soil resources (WRB, 2014), the soil type found in this region is lime concretion black soil. Soil samples defined as

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

A, B, C, and D were collected from four sites: Chenji Village (33°00'N and 114°51'E), Dingying Village (33°09'N and 114°49'E), Xinggang Village (32°99'N and 114°84'E), and Hanqiao Village (32°56'N and 114°49'E). Samples were taken along four vertical profiles at five or six different depths, i.e., 0-20, 20-40, 40-60, 60-80, 8-120 cm (or 80-100 and 100-120 cm), which are denoted as depth 1, 2, 3, 4, 5 (or 5 and 6), respectively. The cultivation system in the region involved rotating winter wheat and summer maize crops. The fertilizers for winter wheat contained 750 kg/hm^2 compound fertilizer (N-P-K: 15-15-15) and 300 kg/hm^2 urea. Those for summer maize included 600 kg/hm^2 compound fertilizer and 225 kg/hm^2 urea. The samples were air-dried, ground, and passed through 2-mm sieve before analysis.

2.2 Physicochemical characterization of the soils

Soil pH was assessed by using a pH meter with a soil-to-water ratio of 1:2.5. Soil total carbon (C) and nitrogen (N) levels were analyzed with an elemental analyzer (Jin *et al.*, 2016). Oxalate extracted P (i.e. OA-P) was extracted by ammonium oxalate and oxalic acid (Jiang *et al.*, 2015) and considered as the P bonded to amorphous, poorly crystalline and organo-Fe/Al (hydr)oxides (Masiello *et al.*, 2004; Kleber *et al.*, 2005; Neubauer *et al.*, 2013). The dithionite-citrate-bicarbonate (i.e. DCB) extracted P was extracted by sodium citrate solution, sodium hydrogen carbonate solution and sodium dithionite (Jiang *et al.*, 2015) and considered as P associated with organically bound, amorphous and crystalline Fe oxides. The activities of acid and alkaline phosphatase, denoted as ACP and ALP respectively, were determined by performing *p*-nitrophenyl phosphate assays on moist soil samples at two pH conditions, 6.5 and 11 respectively (Tabatabai *et al.*, 1969). Soil available P was extracted with 0.5 M $NaHCO_3$ at pH 8.5 (Van Lierop, 1988) and measured by molybdate blue colorimetry (Murphy and Riley, 1962). Total inorganic P (TIP) was extracted by sulfuric acid and dilute sodium hydroxide solution separately via the sequential extraction method by Kronvang et al.(1997) and measured by molybdate blue colorimetry. For the total P (TP), the extracts that were acquired from the acid and base treatments were treated with potassium persulfate and sulfuric

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

acid before molybdate blue colorimetry and the sum of digested extracts was defined as TP. The total organic P (TOP) was the difference between TP and TIP.

2.3 Soil particle separations and characterization of water extractable colloids

The soil samples of A and B with different depths were fractionated by the method described by Séquaris et al. (2003). Briefly, 100 g of soil was dispersed in 200 mL Milli-Q water in a 1 L Duren bottle and shaken for 6 h at 150 rpm. Then 600 mL Milli-Q water was added and mixed to settle. The particles >20 µm and 2-20 µm were obtained by removing the supernatant after settling for 6 min and 12 h, respectively. The supernatant was subsequently spun at 3500×g for 5 min to obtain the water extractable colloids with size of 0.35-2 µm (calculated based on stokes' law). The final supernatant is defined as "dissolved fraction" although a small quality of nanoparticles might be present. The dissolved reactive P (DRP) and dissolved total P (DTP) were measured by molybdate blue colorimetry (Murphy and Riley, 1962) before and after the digestion of potassium persulfate and sulfuric acid for the "dissolved fraction".

To elucidate the inorganic and organic P species, the extracted colloidal samples from sample A and B with different depths were selected for the NMR analysis. The colloid samples (1 g) were mixed with 10 mL of solution containing 0.25 M NaOH and 0.05 M Na_2EDTA for 4 h (Jiang *et al.*, 2017) . After that, extracts were centrifuged at 10000 ×*g* for 30 minutes. The P, Fe, and Mn contents in the supernatant were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The rest supernatant was freeze-dried and then 100 mg freeze-dried extracts were dissolved in 0.1 mL D_2O and 0.9 mL of a solution containing 1.0 M NaOH and 0.1 M Na_2EDTA. After being prepared, the samples underwent centrifugation for 20 minutes at 10000 ×*g*. The resulting supernatant was subsequently analyzed using a Bruker 500-MHz spectrometer with a 5 mm NMR tube. The NMR parameters contained 0.68 s acquisition time, 90° pulse width, 8000 scans, and proton decoupling. The relaxation time, which fell within the range of 3-6 seconds, was estimated by correlating

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

P/(Mn+Fe) with spin-lattice relaxation times (McDowell *et al.*, 2006). The spiking samples with myo-inositol hexakisphosphate (myo-IHP), α- and β- glycerophosphate, and adenosine monophosphate were cited to facilitate peak identification (Bai *et al.*, 2023). The α-, β-glycerophosphates and mononucleotides (Glyc+nucl) were classified as orthophosphate diesters rather than to monoesters (Young *et al.*, 2013; Liu *et al.*, 2018). The area under each peak was determined by integrating spectra that were processed with a line broadening of 2 and 7 Hz. Mestrenova 10.0.2 software was used to process all spectra. Additionally, zeta potential of colloids from sample A and B with different depths were measured using a Zetasizer (Malvern). The X-ray powder diffractometer (XRD, Empyrean) was selected to identify mineral compositions for soil colloids in the 2θ range from 3° to 90° with the scan step size of 0.026° and the scan rate of 10° min^{-1}.

To elucidate the P bonding fractions in the WEC fractions, the P K-edge X-ray absorptions near-edge structure (XANES) measurements were performed at Beamline 4B7A of the Beijing Synchrotron Radiation Facility, Beijing, China. The following standard samples were chosen: aluminum phosphate (Al-P, $AlPO_4$), iron phosphate dihydrate (Fe-P, $FePO_4 \cdot 2H_2O$), inositol hexakisphosphate (IHP), and hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$). The soil spectra were collected using a SiLi detector in PFY mode, providing detailed information about the fluorescence yield. The spectra of P standard samples were measured in total electron mode without self-absorption. Multiple spectra (three repetitions for soil samples) were collected and averaged. All XANES spectra were measured by Athena (0.9.26). The absolute energy scale was calibrated to 2149 eV (E0) as the maximum energy of the first peak in the first derivative spectrum of $AlPO_4$ (Beauchemin *et al.*, 2003). Linear combination fitting (LCF) of the soil P spectra was conducted in the relative energy range between -10 and 30 eV. The goodness of fit was judged by the chi-squared values and R values, and P standard samples yielding the best fit were considered as the most possible P species in the investigated soil samples.

2.4 Statistical analysis

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

One way ANOVA and single factor analysis of variance were used to test significant differences of soil indicators with different soil profiles. Tukey's honesty significance difference (HSD) test was used, and the significance level was 0.05. SPSS 25.0 and Excel software were used for statistical analysis. These data were created using OriginPro 2021 (OriginLab Corp., Northampton, MA, USA).

3. RESULTS AND DISCUSSION

3.1 Physicochemical characterization and P distribution of Soil profile

As the depth increased in all soil samples, the soil pH exhibited a significant overall increase from acidic to alkaline conditions, ranging from 4.88 to 8.37 (Table 1). The serious acidity of the topsoil (0-20 cm) is probably due to increasing release of protons by nitrification processes after excessive application of nitrogen fertilizers (750 kg/hm^2 compound fertilizer and 300 kg/hm^2 urea per year in the studied area) and the continuous removal of base cations by crop harvest (Guo *et al.*, 2010). The calcareous nature of lime concretion black soil at the study site contributed to subsoils with pH values of slight alkalinity. The contents of total carbon (from 1.17 to 0.25%) and total nitrogen (from 0.14 to 0.03%) decreased significantly from topsoil to subsoil (Table 1). The accumulation of total C and N in surface soil (0-20 cm) could be related to the increased organic matter contents by biomass inputs from crop residue and N fertilization. The deepest layer soil (80-120 cm) contained the highest pH values and lowest total C and N contents, suggesting that the subsurface soil (20-80 cm) was also influenced by these intensive agricultural managements to some extent. The activities of acid phosphatase (ACP) was as high as 1177 μg/(g*h) in topsoil and decreased with the depth of soil layer as low as 96.2 μg/(g*h) in subsoil (Table 1). The activities of both acid and alkaline (ALP) phosphatase decreased significantly with depth for all the samples. The ACP was higher in the surface soil (0-20 cm) but was lower in the subsurface soil (20-120 cm) compared to ALP. Acid phosphatase activity, mainly released by plant roots and fungi, is predominant in acidic soils (Eivazi *et al.*, 1977; Juma and Tabatabai, 1977; Arenberg *et al.*, 2020). Alkaline phosphatase activity, primarily produced by soil microbes, is optimized in neutral and alkaline conditions

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

(Juma and Tabatabai, 1988; Dick *et al.*, 2000; Krämer and Green, 2000). The higher acid phosphatase activity in surface soil may be attributed to acidic pH and the rhizosphere effect, where plant roots and fungi are easily concentrated (Häussling *et al.*, 1989). Thus, lower acid phosphatase activity in the subsurface soil (< 20 cm) was due to increasing pH with depth.

Oxalate extractable P concentration ranged from ~30-162 mg kg^{-1} (~7-45% of TP) in all soils (Table 1). The oxalate extractable P concentration in the surface soils was ~127 to 162 mg/kg and it accounted for 19-27% of TP and ~76 to 98 % of DCB extractable P, suggesting that amorphous Fe/Al oxides bounded P was dominated for the Fe-P in the surface soils compared to crystalline Fe/Al oxides. Many studies have reported that the majority of P was associated with amorphous Fe /Al oxides fractions in many soil types (Rick and Arai, 2011; Jiang *et al.*, 2015). It has been reported that specific anion adsorption such as P suppressed the transformation of amorphous Fe oxides to crystalline Fe oxides (Biber *et al.*, 1994), supporting the lower amount of P associated with crystalline Fe oxides.

The concentrations for TIP, TOP, and TP are included in Fig.1. The total P concentrations in all soil samples were observed to range from approximately 230 to 670 mg kg^{-1}, and exhibited a generally decreasing trend with increasing soil depth. (Fig. 1). Total inorganic P accounted for ~48 to 65% of TP and TOP accounted for ~35 to 52% of TP in all soil samples. Organic P accumulation (~97 to 344 mg kg^{-1}) was measured in all soil depths. The C/P ratio of > 200:1 is favorable for P immobilization (Dalal and Hallsworth, 1977; Sanyal and De Datta, 1991). The C/P ratio of soil samples in this study was about 9.5 to 22.1, which promoted P mineralization. Thus, the accumulation of organic P in the surface soil would be due to the increasing organic matter contents, rather than the biological immobilization of P. Gradual transport of OP from surface to subsoils could contribute to the accumulation of OP in the subsoils. Available P was very high with ~20 to 40 mg kg^{-1} in the surface soils but decreased dramatically with increasing depth in all samples (Fig. 1). The available P content in the topsoil has been classified as "high", and a threshold of 20 mg/kg has been regarded as optimal growth

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

level for crops (Li *et al.*, 2015). This implies that the surface soils (0-20 cm) contained enough available P for the growth of winter wheat and corn.

3.2 Physicochemical properties of water extracted colloids (WECs)

Considering that all four samples showed similar physicochemical properties and P distribution, we further investigated the colloids of samples A and B with different depth. It is crucial to mention that the WECs are colloids that are well-defined with size of 0.35-2 µm operationally. The major soil series are sandy loam and loam, with the colloidal mass of 5.3 to 8.3% (Table 2). The colloidal mass increased with depths for both samples and previous researcher has reported a similar tendency for the recovery rate of WECs in dark-colored Mollisols (Li *et al.*, 2022). Notably, no colloids exited in the depth > 60 cm for sample B, suggesting that the generation of colloids from weathered minerals in subsoils was limited. It suggested that the colloids in the depth >60 cm for sample A originated from the transport of upper soil colloids.

The XRD results further verified it considering that the colloids of sample A and B with all depths contained the same mineral composition (Fig. 3). The minerals in all the colloids included montmorillonite, nontronite, and illite, indicating the existence of swelling-shrinkage clays. These secondary minerals all have a significant adsorption capacity for P (Gérard, 2016; Chen *et al.*, 2020). Values of zeta potential for WECs were approximately -20 mV at the surface soil, but the values increased with depth (Table 2). A higher P concentration in surface soils could facilitate P special adsorption to minerals of WECs such as iron oxyhydroxide (e.g. hematite, goethite, and ferrihydrite) and aluminosilicate minerals (Arai and Sparks, 2001; Celi *et al.*, 2001; Jiang *et al.*, 2015), causing the surface charge lower compared to that of WECs in subsurface soils. The more negative values of zeta potential at surface soil suggests the higher mobility of colloidal P from the surface soil to the subsoils. It is important to note that DRP accounted for only 29-51% of DTP (Table 2). Furthermore, the sum of colloidal P concentration for <0.35 µm (i.e. the difference between DTP and DRP) and 0.35-2 µm was about 38-93 mg/kg soil, which is 6-37 folds of DRP. It suggested that the contribution of CP to transport P in both surface and subsurface soil environment is

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

important and should not be overlooked.

3.3 Inorganic and organic P distribution in WECs with soil depth

At each sampling site, the concentration of TP in WECs was found to be the highest in the topsoil layer (0-20 cm), with a range of 1150 to 1300 mg kg^{-1}. (Fig. 3). The amounts were significantly higher than the TP in bulk soils (~600-700 mg kg^{-1}). The soil colloids enriched in secondary clays such as montmorillonite, nontronite, and illite as shown in XRD results could readily immobilize P. Generally, the TP of colloids at each site was found to decrease with increasing soil depth. Most colloidal P at the surface soil was from fertilizers and plant residues. The concentration of total IP in WECs was found to be high (ranging from 680 to 730 mg kg^{-1}) in the topsoil and displayed a decreasing trend with increasing soil depth across all sites. As predicted, total OP concentration was high (430-630 mg kg^{-1}) in the colloids of surface soil. This is associated with the high OC concentration in the surface soil, and P was probably immobilized in the organic matter of soil. The decline in tendency of OP concentrations with soil depth was probably due to the decreasing OM contents. It is noteworthy that OP was still presented in the WECs of subsoils where the C/P is less than 300 that could not support immobilization for the accumulation of OP (Table 1 and 3). This finding implies that colloidal-bound OP has the potential to be transported from topsoil to subsoil layers.

3.4 Solution 31P NMR analysis and P K-edge XANES analysis

The ^{31}P NMR spectroscopy spectra of WECs were presented in Table 3. It is worth mentioning that NaOH-EDTA extracted P in the NMR analysis was below 100 %. Therefore, the concentrations of OP and IP did not correspond with the chemical digestion data presented in Fig. 2. For inorganic P, orthophosphate was found in all samples but pyrophosphate was only found in the surface soil. Pyrophosphate was present in live fungal tissue and was easily decomposed (Koukol *et al.*, 2008). In addition to inorganic P, the OP in the WECs of all depths for sample A and B contained similar species including orthophosphate monoesters (36-128 mg kg^{-1}) and diesters (0-89 mg kg^{-1}) according to NMR results (Table 3). It was clear that OP existed in mobile colloids for both surface and subsoils, suggesting that OP in WECs from subsoils was

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

affected by the translocation of CP from surface soils (Li *et al.*, 2022). Colloids containing clay minerals in the soil profile could retain orthophosphate monoesters and diesters. Inositol phosphate has also been found to be adsorbed on amorphous metal oxides and clay minerals (e.g. montmorillonite, illite, and kaolinite) (Barka and Anderson, 1962; Celi et al., 1999).

The normalized XANES spectra of WECs in sample A and B with soil profile are shown in Table 4 and Fig. 4. Aluminum phosphate (Al-P), iron phosphate dihydrate (Fe-P), hydroxyapatite (HAP), and inositol hexakisphosphate (IHP) were detected in WECs for all the samples. The XANES results of WECs showed that the proportions of Al-P, Fe-P, and IHP of WECs decreased but HAP increased with soil depth. As a typical alkaline soil containing carbonate concretions, the lime concretions black soil facilitated the formation of Ca-P minerals, thus causing low P availability for crops (Westermann, 1992; Iyamuremye et al., 1996; Li et al., 2011). The decrease of soil pH in the surface soils accelerated the dissolution of Ca mineral phases, the release of associated colloidal P, and the transformation of Ca-P to Al-P and Fe-P, thus increasing the concentrations and proportions of higher activity inorganic P fractions (Zhao *et al.*, 2019). The proportions of IHP decreased with soil depth but IHP still existed as certain amounts in the subsoil, which further confirmed the results of NMR.

4. CONCLUSIONS

In this study, the distribution of WECs with soil profiles (0-120 cm) was investigated in lime concretion black soil with high intensity agricultural management. The P-rich WECs (0.35-2 μm) was dispersed from surface soils to subsoils with the proportion of 5.3-8.3% of bulk soil. The TP concentration in the WECs was as high as 1150-1300 mg kg^{-1}. It is noteworthy that OP associated with WECs were found in subsurface soils, indicating the colloidal P was transported from surface soils to subsoils, resulting in the distribution of P-rich WECs throughout the entire soil profile. Soil colloids with a greater negative charge resulting from P adsorption may be repulsed by negatively charged soil mineral surfaces, leading to the transportation of these colloidal P to the subsoil. The soil acidification in lime concretion black soil could facilitate deterioration

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

of Ca-stabilized aggregates, accelerated the release of associated colloidal P and furthermore shifted the composition from Ca dominated colloids to Fe/Al oxides enrich ones. The existence of swelling-shrinkage minerals such as montmorillonite and nontronite promoted preferential flow and the transport of colloidal P. Furthermore, the artificial ditches could also facilitate the transport of WECs from surface soil to subsoils. The sum of colloidal P <2 μm was 6-37 folds of DRP, suggesting that the contribution of CP to P transport in the whole soil profile is predominant. Thus, it is crucial to take into account the impact of colloidal P when predicting P loss from surface to subsurface flow.

References:

Arai, Yuji, and DL Sparks. "Phosphate Reaction Dynamics in Soils and Soil Components: A Multiscale Approach."ADVANCES IN AGrONOMY,94, 135-79. https://doi.org/doi.org/10.1016/S0065-2113(06)94003-6.2007.

Arai, Yuji, and Donald L Sparks. "Atr–Ftir Spectroscopic Investigation on Phosphate Adsorption Mechanisms at the Ferrihydrite–Water Interface." JOURNAlL OF COLLOIDINTERFACE SCIENCE241, no. 2 317-26. http://doi.org/org10.1006/jcis.2001.7773.2021

Arenberg, Mary R, Xinqiang Liang, and Yuji Arai. "Immobilization of Agricultural Phosphorus in Temperate Floodplain Soils of Illinois, USA." BIOGENCHEMISTRY,150, no. 3, 257-78. https://doi.org/10.1007/s10533-020-00696-1.2020.

Beauchemin, Suzanne, Dean Hesterberg, Jeff Chou, Mario Beauchemin, Régis R Simard, and Dale E Sayers. "Speciation of Phosphorus in Phosphorus-Enriched Agricultural Soils Using X-Ray Absorption near-Edge Structure Spectroscopy and Chemical Fractionation." JOURNAL OF ENVIORNMENTAL QUAlITY,32, 1809-19. https://doi.org/10.2134/jeq2003.1809.2003.

Biber, Madeleine V, and Werner Stumm. "An in-Situ Atr-Ftir Study: The Surface Coordination of Salicylic Acid on Aluminum and Iron (Iii) Oxides." ENVIOONMENTALSCIENCETECHNOLOGY,28,763-68. https://doi.org/10.1021/es00054a004.1994.

Celi, L, M Presta, F Ajmore-Marsan, and Elisabetta Barberis. "Effects of Ph and Electrolytes on Inositol Hexaphosphate Interaction with Goethite." SOIL SCIENCE SOCIECT OF AMERICA JOURNAL,65,753-60. https://doi.org/10.2136/sssaj2001.653753x.2001.

Chen, Lin, Fang Li, Wei Li, Qi Ning, Jingwang Li, Jiabao Zhang, Donghao Ma, and Congzhi Zhang. "Organic Amendment Mitigates the Negative Impacts of Mineral Fertilization on Bacterial Communities in Shajiang Black Soil."APPLIED SOIL ECOLOGY,150 ,103457. https://doi.org/10.1016/j.apsoil.2019.103457.2020.

Dalal, RC, and EG Hallsworth. "Measurement of Isotopic Exchangeable Soil Phosphorus and Interrelationship among Parameters of Quantity, Intensity ,and Capacity Factors." SOIL SCIENCE SOCIECTOFAMERICAJOURNAL41,8186https://doi.org/10.2136/sssaj1977.03615995004100010025x2003.

Dick, Warren A, L Cheng, and P Wang. "Soil Acid and Alkaline Phosphatase Activity as Ph Adjustment

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Indicators."SOIL BIOLOGY BIOCHEMISTRY,32, 1915-19. https://doi.org/10.1016/S0038-0717(00)00166-8.2000.

Eivazi, F, and MA Tabatabai. "Phosphatases in Soils." SOIL BIOLOGY BIOCHEMISTRY 9, 167-72. https://doi.org/10.1016/0038-0717(77)90070-0.1977.

Gérard, Frédéric "Clay Minerals, Iron/Aluminum Oxides, and Their Contribution to Phosphate Sorption in Soils—a Myth Revisited."GEODERMA,262,213-26. https://doi.org/10.1016/j.geoderma.2015.08.036.2016.

Guo, JH, XJ Liu, Yong Zhang, JL Shen, WX Han, WF Zhang, P Christie, et al. "Significant Acidification in Major Chinese Croplands." SCIENCE,327, no. 5968,1008-10. https://doi.org/10.1016/j.scitotenv.2017.09.289.2010.

Hansen, Jeremy C, Barbara J Cade-Menun, and Daniel G Strawn. "Phosphorus Speciation in Manure-Amended Alkaline Soils." JOURNAL OF ENVIRONMENTAL QUALITY, 33, no. 4 ,1521-27. https://doi.org/10.2134/jeq2004.1521.2004.

Häussling, M, and H Marschner. "Organic and Inorganic Soil Phosphates and Acid Phosphatase Activity in the Rhizosphere of 80-Year-Old Norway Spruce [Picea Abies (L.) Karst.] Trees." BIOLOGY FERTILITY OF SOILS, 8, no. 2 , 128-33. https://doi.org/10.1007/bf00257756.1989

Hens, Maarten, and Roel Merckx. "Functional Characterization of Colloidal Phosphorus Species in the Soil Solution of Sandy Soils." ENVIRONMENTAL SCIENCE TECHNOLOGY, 35, no. 3 , 493-500. https://doi.org/10.1021/es0013576.2001.

Iyamuremye, F, RP Dick, and J Baham. "Organic Amendments and Phosphorus Dynamics: Ii. Distribution of Soil Phosphorus Fractions." SOIL SCIENCE, 161, no. 7, 436-43. https://doi.org/10.1097/00010694-199607000-00003.1996

Jiang, Xiaoqian, Wulf Amelung, Barbara J Cade-Menun, Roland Bol, Sabine Willbold, Zhihong Cao, and Erwin Klumpp. "Soil Organic Phosphorus Transformations During 2000 Years of Paddy-Rice and Non-Paddy Management in the Yangtze River Delta, China." SCIENTIFIC REPORTS, 7 ,1-12. https://doi.org/10.1016/j.geoderma.2022.116296.2017

Jiang, Xiaoqian, R Bol, S Willbold, H Vereecken, and E Klumpp. "Speciation and Distribution of P Associated with Fe and Al Oxides in Aggregate-Sized Fraction of an Arable Soil." BIOGEOSCIENCES 12, no. 21 , 6443-52. https://doi.org/10.5194/bg-12-6443-2015.2015.

Jiang, Xiaoqian, Kenneth JT Livi, Mary R Arenberg, Ai Chen, Kai-yue Chen, Lowell Gentry, Zhe Li, Suwei Xu, and Yuji Arai. "High Flow Event Induced the Subsurface Transport of Particulate Phosphorus and Its Speciation in Agricultural Tile Drainage System." CHEMOSPHERE 263 , 128147. https://doi.org/10.1016/j.chemosphere.2020.128147.2021

Jin, Yi, Xinqiang Liang, Miaomiao He, Yu Liu, Guangming Tian, and Jiyan Shi. "Manure Biochar Influence Upon Soil Properties, Phosphorus Distribution and Phosphatase Activities: A Microcosm IncubationStudy."CHEMOSPHERE,142,12844https://doi.org/10.1016/j.chemosphere.2015.07.015. 2016

Jorgensen, PR, and Johnny Fredericia. "Migration of Nutrients, Pesticides and Heavy Metals in Fractured." GEOTECHNIQUE, 42, no. 1 ,67-77. https://doi.org/10.1016/0148-9062(92)91738-g.1992.

Juma, NG, and MA Tabatabai. "Effects of Trace Elements on Phosphatase Activity in Soils." SOILSCIENCESOCIETYOFAMERICAJOURNAL,41,343-46https://doi.org/10.2136/sssaj1977.03615995004100020034x.1977

Juma, NG, and MA Tabatabai "Phosphatase Activity in Corn and Soybean Roots: Conditions for Assay

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

and Effects of Metals." PLANT SOIL,107, no. 1 (1988): 39-47.
Kleber, M, R Mikutta, MS Torn, and R Jahn. "Poorly Crystalline Mineral Phases Protect Organic Matter in Acid Subsoil Horizons." EUROPEAN JOURNAL OF SOIL SCIENCE, 56, 717-25. https://doi.org/10.1016/j.geoderma.2004.12.018.2005
Koopmans, GF, WJ Chardon, J Dolfing, O Oenema, P Van der Meer, and WH Van Riemsdijk. "Wet Chemical and Phosphorus-31 Nuclear Magnetic Resonance Analysis of Phosphorus Speciation in a Sandy Soil Receiving Long-Term Fertilizer or Animal Manure Applications." JOURNAL OF ENVIRONMENTAL QUALITY, 32, no. 1 , 287-95. https://doi.org/10.2134/jeq2003.0287.2003
Koukol, Ondřej, Blanka Beňová, Magda Vosmanská, Tomáš Frantík, Miroslav Vosátka, and Marcela Kovářová. "Decomposition of Spruce Litter Needles of Different Quality by Setulipes Androsaceus and Thysanophora Penicillioides." PLANT SOIL 311, no. 1 ,151-59. https://doi.org/10.1007/s11104-008-9666-5.2008.
Krämer, Susanne, and Douglas M Green. "Acid and Alkaline Phosphatase Dynamics and Their Relationship to Soil Microclimate in a Semiarid Woodland." SOIL BIOLOGYBIOCHEMISTRY, 32, no. 2 , 179-88. https://doi.org/10.1016/S0038-0717(99)00140-6.2000
Kronvang, B., R. Grant, and A. L. Laubel. "Sediment and Phosphorus Export from a Lowland Catchment: Quantification of Sources." [In English]. WATER AIR AND SOILl POLLUTION 99, no. 1-4 ,465-76.1997
Kronvang, Brian, Anker Laubel, and Ruth Grant. "Suspended Sediment and Particulate Phosphorus Transport and Delivery Pathways in an Arable Catchment, Gelbaek Stream, Denmark." HYDROLOGICAL PROCESSES,11, no. 6 (1997): 627-42.
Li, Haigang, Jian Liu, Guohua Li, Jianbo Shen, Lars Bergström, and Fusuo Zhang. "Past, Present, and Future Use of Phosphorus in Chinese Agriculture and Its Influence on Phosphorus Losses." AMBIO, 44, 274-85. https://doi.org/10.1007/s13280-015-0633-0.2015
Li, Ying, Kenneth JT Livi, Mary R Arenberg, Suwei Xu, and Yuji Arai. "Depth Sequence Distribution of Water Extractable Colloidal Phosphorus and Its Phosphorus Speciation in Intensively Managed Agricultural Soils." CHEMOSPHERE 286,131665. https://doi.org/10.1016/j.chemosphere.2021.131665.2022
Li, Ying, Kenneth JT Livi, Mary R Arenberg, Suwei Xu, and Yuji %J Chemosphere Arai. "Depth Sequence Distribution of Water Extractable Colloidal Phosphorus and Its Phosphorus Speciation in Intensively Managed Agricultural Soils."CHEMOSPHERE,286,131665. https://doi.org/10.1016/j.chemosphere.2021.131665.2022
Liang, Xinqiang, Yi Jin, Yue Zhao, Zhibo Wang, Rongqiang Yin, and Guangming Tian. "Release and Migration of Colloidal Phosphorus from a Typical Agricultural Field under Long-Term Phosphorus Fertilization in Southeastern China." JOURNAL OF SOILS SEDIMENTS, 16, 842-53. https://doi.org/10.1007/s11368-015-1290-4.2016
Liu, Jin, Barbara J Cade-Menun, Jianjun Yang, Yongfeng Hu, Corey W Liu, Julien Tremblay, Kerry LaForge, et al. "Long-Term Land Use Affects Phosphorus Speciation and the Composition of Phosphorus Cycling Genes in Agricultural Soils." FRONTIERS IN MICROBIOLOGY, 9,1643. https://doi.org/10.3389/fmicb.2018.01643.2018
Masiello, CA, OA Chadwick, J Southon, MS Torn, and JW Harden. "Weathering Controls on Mechanisms of Carbon Storage in Grassland Soils." GLOBAL BIOGEOCHEMICAL CYCLES, 18. https://doi.org/10.1029/2004GB002219.2004
McDowell, RW, I Stewart, and BJ Cade-Menun. "An Examination of Spin–Lattice Relaxation Times

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

for Analysis of Soil and Manure Extracts by Liquid State Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy." JOURNAL OF ENVIRONMENTAL QUALITY 35,293-302. https://doi.org/10.2134/jeq2005.0285.2006

Murphy, JAMES, and John P Riley. "A Modified Single Solution Method for the Determination of Phosphate in Natural Waters." ANALYTICA CHIMICA ACTA, 27, 31-36. https://doi.org/10.1016/s0003-2670(00)88444-5.1962.

Neubauer, Elisabeth, Walter DC Schenkeveld, Kelly L Plathe, Christian Rentenberger, Frank Von Der Kammer, Stephan M Kraemer, and Thilo Hofmann. "The Influence of Ph on Iron Speciation in Podzol Extracts: Iron Complexes with Natural Organic Matter, and Iron Mineral Nanoparticles." SCIENCE OF THTOTALENVIRONMENT 461, 108-16. https://doi.org/10.1016/j.scitotenv.2013.04.076. 2013.

Pote, DH, TC Daniel, PA Moore Jr, DJ Nichols, AN Sharpley, and DR Edwards. "Relating Extractable Soil Phosphorus to Phosphorus Losses in Runoff." Soil Science Society of America Journal60, no. 3 , 855-59. https://doi.org/10.2136/sssaj1996.03615995006000030025x.1996..

Rick, Allison R, and Yuji J Soil Science Society of America Journal Arai. "Role of Natural Nanoparticles in Phosphorus Transport Processes in Ultisols." ,75,335-47. https://doi.org/10.2136/sssaj2010.0124nps.2011.

Royer, Todd V, Mark B David, and Lowell E Gentry. "Timing of Riverine Export of Nitrate and Phosphorus from Agricultural Watersheds in Illinois: Implications for Reducing Nutrient Loading to the Mississippi River." ENVIRONMENTAL SCIENCE TECHNOLOGY,40,4126-31. https://doi.org/10.1021/es052573n.2006.

Sanyal, SK, and SK De Datta. "Chemistry of Phosphorus Transformations in Soil." In Advances in Soil Science, 1-120: Springer, 1991.

Séquaris, J-M, H %J Colloids Lewandowski, Surfaces A: Physicochemical, and Engineering Aspects. "Physicochemical Characterization of Potential Colloids from Agricultural Topsoils." 217,93-99. https://doi.org/10.1016/S0927-7757(02)00563-0.2003.

Shanshan, Bai, TAN Jinfang, Zeyuan ZHANG, WEI Mi, Huimin ZHANG, and Xiaoqian JIANG. "Phosphorus Speciation and Colloidal Phosphorus Response to the Cessation of Fertilization in Lime Concretion Black Soil." PEDOSPHERE, https://doi.org/10.1016/j.pedsph.2023.01.004 .2023.

Tabatabai, M Ali, and John M Bremner. "Use of P-Nitrophenyl Phosphate for Assay of Soil Phosphatase Activity." SOIL BIOLOGY BIOCHEMISTRY 1, 301-07. https://doi.org/10.1016/0038-0717(69)90012-1.1969

Van Lierop, W "Determination of Available Phosphorus in Acid and Calcareous Soils with the KelownaMultiple-ElementExtractant."SOILSCIENCE,146,284 https://doi.org/10.1097/00010694-198810000-00009.1988.

Wang, Liming, Anna Missong, Wulf Amelung, Sabine Willbold, Jörg Prietzel, and Erwin Klumpp. "Dissolved and Colloidal Phosphorus Affect P Cycling in Calcareous Forest Soils." GEODERMA 375 , 114507. https://doi.org/10.1016/j.geoderma.2020.114507.2020

Westermann, DT "Lime Effects on Phosphorus Availability in a Calcareous Soil." Soil Science SOCIETY OF AMERICA JOURNAL 56, 489-94. https://doi.org/10.2136/sssaj1992.03615995005600020024x.1992

Whalen, Joann K, and Chi Chang. "Phosphorus Accumulation in Cultivated Soils from Long-Term Annual Applications of Cattle Feedlot Manure." Journal of environmental quality 30, 229-37. https://doi.org/10.2134/jeq2001.301229x.2001

Williams, Mark R, Kevin W King, William Ford, Anthony R Buda, and Casey D Kennedy. "Effect of

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Tillage on Macropore Flow and Phosphorus Transport to Tile Drains." WATER RESOURCES RESEARCH, 52, 2868-82. https://doi.org/10.1002/2015WR017650.2016

WRB, Iwg. World Reference Base for Soil Resources 2014: International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. World Reference Base for Soil Resources 2014: international soil classification system for naming soils and creating legends for soil maps, 2014.

Xue, Yuan, Mark B David, Lowell E Gentry, and David A Kovacic. "Kinetics and Modeling of Dissolved Phosphorus Export from a Tile-Drained Agricultural Watershed." WILEY ONLINE LIBRARY, . http//doi/10.2134/jeq1999.00472425002800030048x.1998.

Young, Eric O, Donald S Ross, Barbara J Cade-Menun, and Corey W Liu. "Phosphorus Speciation in Riparian Soils: A Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy and Enzyme Hydrolysis Study." SOIL SCIENCE SOCIETY OF AMERICA JOURNAL,77,1636-47. https://doi.org/10.2136/sssaj2012.0313.2013.

Zhao, Fengyan, Yongyong Zhang, Feike A Dijkstra, Zhijun Li, Yueqi Zhang, Tianshi Zhang, Yingqi Lu, Jinwei Shi, and Lijuan Yang. "Effects of Amendments on Phosphorous Status in Soils with Different Phosphorous Levels." CATENA,172,97-103. https://doi.org/10.1016/j.catena.2018.08.016.2019.

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

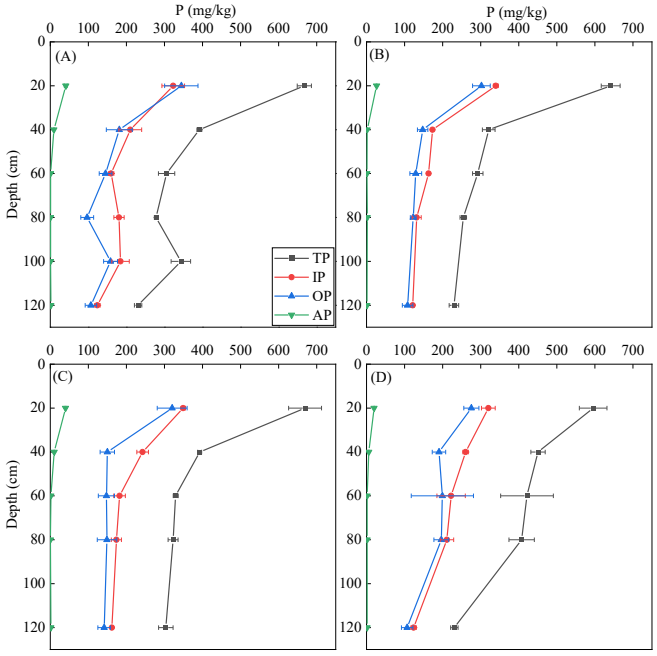

Fig. 1. The concentrations of available phosphorus (AP), total phosphorus (TP), inorganic phosphorus (IP), and organic phosphorus (OP) in soil profiles of sample A, B, C, and D.

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

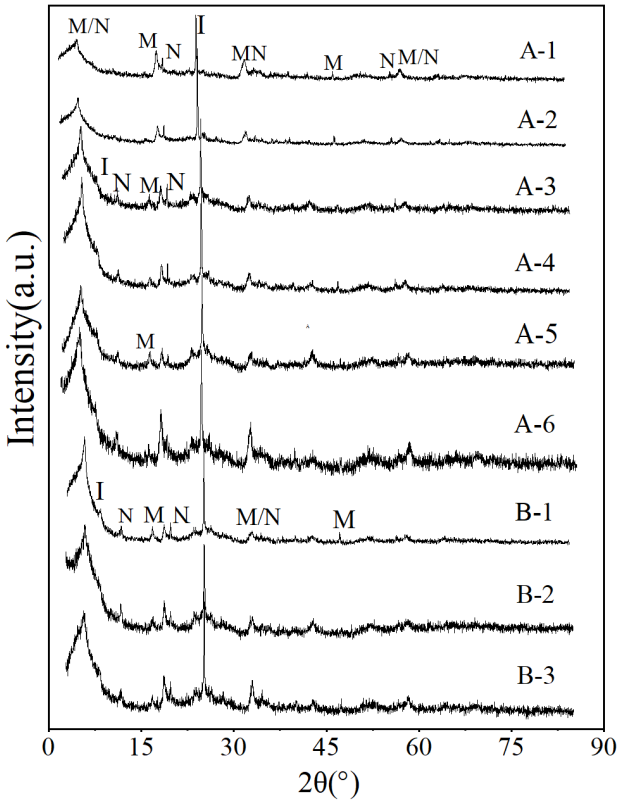

Fig. 2. XRD patterns of water-extractable colloid (WEC) fractions for soil sample A and B with different depths (N: nontronite; M: montmorillonite; I: illite).

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

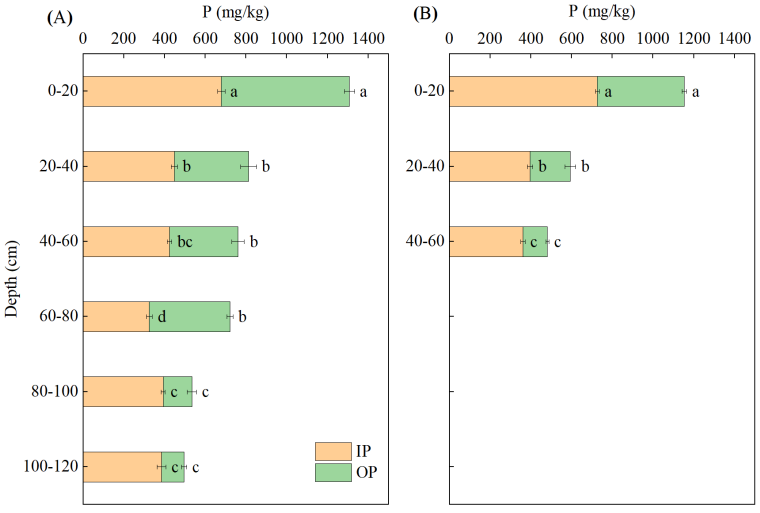

Fig.3 Inorganic (IP) and organic P (OP) concentrations (mg P/kg colloids) for water-extractable colloid (WEC) fractions of sample A and B with different depths.

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

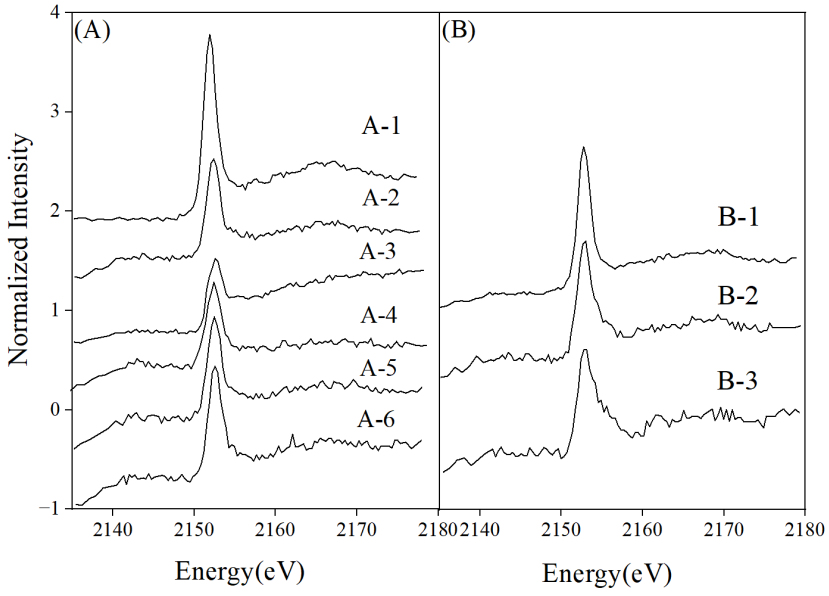

Figure 4. Linear combination fitting of P - K-edge XANES Spectra of water-extractable colloid (WEC) fractions from profile soil (Samples A-1 to A-6 and B-1 to B-3).

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Table 1 Physicochemical characteristics of bulk soils.

Sample	Depth(cm)	pH	%TC	%TN	C/P	ACP (μg/(g*h))	ALP (μg/(g*h))	OA-P (mg/kg)	DCB-P (mg/kg)
A	0-20	5.13±0.04e	0.91±0.00a	0.10±0.00a	15.3±0.9bc	647.8±13.5a	465.5±10.2a	142.9±0.8a	178.3±12.3a
	20-40	6.43±0.10d	0.54±0.01d	0.07±0.01b	12.1±0.6c	280.5±4.1b	305.3±14.1d	121.4±5.5b	121.4±5.5bc
	40-60	7.23±0.02c	0.52±0.00e	0.06±0.01bc	12.6±2.1c	213.3±6.7c	358.6±4.9c	137.6±6.5b	137.6±6.2b
	60-80	7.52±0.02b	0.67±0.01c	0.06±0.01bc	16.4±1.2b	127.8±9.8d	390.3±8.1b	31.9±3.5c	98.8±22.1c
	80-100	7.52±0.02b	0.75±0.01b	0.07±0.00b	22.1±1.9a	122.6±11.7d	414.0±11.1b	67.0±6.2b	103.1±16.7bc
	100-120	7.70±0.02a	0.50±0.01f	0.06±0.01c	22.0±1.1a	96.2±8.2e	346.4±16.6c	75.8±15.3b	100.6±5.5c
B	0-20	4.88±0.07e	1.17±0.01a	0.14±0.00a	17.5±1.2a	997.2±14.6a	701.4±14.7a	141.70±9.5a	185.9±2.8a
	20-40	6.28±0.02d	0.66±0.01b	0.08±0.00b	17.0±0.1a	413.0±4.7b	514.7±5.8b	84.7±1.3b	121.4±7.8b
	40-60	7.41±0.01c	0.48±0.00d	0.06±0.00c	14.6±0.3b	186.6±3.8c	509.3±17.9c	59.7±12.7c	66.6±11.4d
	60-80	8.03±0.01b	0.35±0.01e	0.05±0.00d	10.8±0.59c	147.2±14.3d	392.5±16.6d	73.7±3.2bc	99.8±2.8c
	80-120	8.37±0.01a	0.52±0.01c	0.04±0.00e	17.2±0.4c	100.1±9.3e	326.2±14.3e	60.7±1.9c	79.1±0.9d
C	0-20	5.01±0.02e	0.94±0.00a	0.11±0.00a	14.1±0.4b	1177.6±31.8a	510.6±15.2b	161.7±5.6a	182.3±6.0a
	20-40	6.23±0.03d	0.54±0.00b	0.07±0.00b	13.8±0.2b	332.4±12.8b	377.3±15.3d	33.7±0.7b	70.4±3.90b
	40-60	7.32±0.04c	0.48±0.00c	0.06±0.00c	16.4±1.1a	190.0±4.7c	578.1±7.6a	29.7±13.4b	45.6±8.8c
	60-80	7.60±0.03b	0.39±0.01d	0.04±0.01d	13.9±0.2b	176.6±3.2c	489.5±4.2b	41.7±6.2b	43.8±5.3c
	80-120	7.74±0.03a	0.27±0.00e	0.04±0.00d	9.5±0.4c	126.8±17.9d	448.1±7.4c	48.7±4.81b	50.1±4.3c
D	0-20	5.17±0.04e	0.88±0.01a	0.10±0.01a	13.8±0.4b	749.6±9.6a	502.1±12.9bc	126.7±6.2a	129.2±6.30a
	20-40	6.97±0.06d	0.57±0.02b	0.07±0.00b	18.0±0.3a	435.4±3.2b	557.2±14.6a	33.7±2.7b	51.4±2.07c
	40-60	7.46±0.03c	0.50±0.00c	0.06±0.00c	17.6±0.9a	136.7±5.8c	526.0±16.3b	34.7±7.0b	65.6±2.28b
	60-80	7.78±0.03b	0.36±0.01d	0.04±0.01cd	14.3±0.7b	175.9±6.5d	497.1±1.7c	42.7±5.7b	49.8±49.1c
	80-120	8.04±0.01a	0.25±0.00e	0.03±0.01d	10.9±0.6c	97.9±2.3e	349.4±10.3d	37.7±1.7b	40.1±1.93c

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Table 2 Soil fractionation, physicochemical characteristics and P levels of water extracted colloids.

Sample	Depth (cm)	Soil texture	Soil sand fractions (>20 μm, %)	Soil silt fractions (2-20 μm, %)	Colloidal fraction (0.35-2 μm, %)	Zeta potential (mV)	Colloidal P (0.35-2 μm) (mg/kg soil)	DTP (<0.35μm, mg/kg soil)	DRP (<0.35μm, mg/kg soil)
A	0-20	sandy loam	57.0±4.0ab	34.8±3.8ab	6.2±0.3c	-19.1±2.7	80.7±3.6a	22.1±1.0a	10.0±1.3a
	20-40	sandy loam	55.7±1.4ab	34.2±1.2ab	6.3±0.3bc	-18.5±1.1	51.0±1.7b	15.3±0.9b	7.4±0.4b
	40-60	sandy loam	57.3±4.5 ab	33.6±4.4ab	6.9±0.2bc	-17.9±0.6	52.4±1.9b	12.3±1.2c	4.6±1.1c
	60-80	sandy loam	56.8±2.7ab	33.0±2.5ab	7.3±0.6ab	-17.5±2.9	52.9±4.4b	6.7±1.4d	2.6±0.5cd
	80-100	sandy loam	59.7±2.9 a	30.4±3.3b	7.0±0.5bc	-15.7±2.7	37.3±1.3c	6.0±0.3d	2.0±0.7d
	100-120	loam	50.3±1.6 b	38.8±0.9a	8.3±0.5a	-15.8±0.8	41.2±1.4c	4.1±0.8d	1.2±0.3d
B	0-20	sandy loam	56.3±3.4a	35.9±3.6a	5.3±0.3b	-22.0±1.7	61.3±2.7a	19.5±1.1a	10.0±1.3a
	20-40	sandy loam	56.5±3.2a	34.8±4.1a	5.3±0.4b	-18.9±1.0	31.6±1.5b	14.4±1.2b	6.3±0.4b
	40-60	sandy loam	57.0±1.9a	33.1±1.2a	6.5±0.3a	-9.0±0.6	31.1±1.1b	11.2±0.9c	4.6±0.3b

DTP: total P concentrations of dissolved fractions (<0.35 μm); DRP: reactive P concentrations of dissolved fractions (<0.35 μm).

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Table 3. Concentrations of inorganic and organic P extracted by NaOH-Na_2EDTA (mg /kg^{-1}) in the water-extractable colloid (WEC) fractions of sample A and B by solution ^{31}P-NMR.

		Inorganic P (mg/kg)		Organic P (mg/kg)					
				Orthophosphate Monoesters				Orthophosphate Diesters	
Sample	Depth(cm)	Orth	Pyro	Monoesters*	Myo-IHP	Scyllo-IHP	Other Monoesters	Diesters*	Glyc+nucl
A-1	0-20	202.4	10.1	50.6	8.1	3.5	39	89.1	81.0
A-2	20-40	46.8	5.1	62.0	1.4	0.0	60.6	15.4	1.8
A-3	40-60	14.1	0.14	42.2	0.6	2.0	39.6	11.4	0
A-4	60-80	14.0	0.84	38.5	0.4	0.00	38.1	0.0	0
A-5	80-100	15.3	5.5	39.6	9.2	0.00	30.4	8.1	3.5
A-6	100-120	12.5	0.0	36.3	3.8	0.00	32.5	7.5	3.8
B-1	0-20	427.5	8.6	128.3	4.3	17.6	106.4	21.4	8.5
B-2	20-40	121.0	7.3	128.1	3.7	0.00	124.4	12.2	7.3
B-3	40-60	57.5	10.4	52.9	3.5	0.00	49.4	1.7	1.7

https://doi.org/10.5194/egusphere-2023-709
Preprint. Discussion started: 8 May 2023

Table 4 Phosphorus K-edge XANES fitting results showing the relative percent of each P species in water-extractable colloid (WEC) fractions (%) of sample A and B.

Sample	Depth (cm)	Al-P (%)	Fe-P (%)	HAP (%)	IHP (%)
A-1	0-20	17.0±4.0	33.0±3.0a	10.0±2.0c	32.0±6.0a
A-2	20-40	13.0±2.0	30.0±5.0a	26.0±4.0bc	30.0±0.8ab
A-3	40-60	14.0±7.0	28.0±0.8a	32.0±7.0abc	26.0±5.0abc
A-4	60-80	12.0±1.0	29.0±3.0a	35.0±3.0abc	22.0±7.0abc
A-5	80-100	11.0±3.0	24.0±3.0ab	45.0±2.0ab	10.0±0.8c
A-6	100-120	9.0±7.0	16.0±3.0b	53.0±7.0a	13.0±5.0bc
B-1	0-20	25.0±7.0a	36.0±2.0a	13.0±3.0b	17.0±6.0
B-2	20-40	11.0±0.9b	19.0±6.0a	32.0±4.0ab	9.0±4.0
B-3	40-60	3.0±0.6b	20.0±5.0b	60.0±10.0a	7.0±4.0

Al-P: aluminum phosphate ($AlPO_4$), Fe-P: iron phosphate dihydrate ($FePO_4{\cdot}2H_2O$), HAP: hydroxyapatite ($Ca_5(PO_4)_3OH$), and IHP: inositol hexakisphosphate. Values in each column followed by the different lowercase letters indicate significant differences ($P < 0.05$).