

Sorption and desorption of organic matter in soils as affected by phosphate

Marie Spohn^{a,b,*}, Kateřina Diáková^a, Felipe Aburto^c, Sebastian Doetterl^d, Jakub Borovec^e

^a Soil Biogeochemistry, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Dr.-Hans-Frisch-Straße 1-3, 95448 Bayreuth, Germany

^b Biogeochemistry of Forest Soils, Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), Lennart Hjelm's väg 9, 75007 Uppsala, Sweden

^c Laboratorio de Investigación en Suelos, Aguas y Bosques (LISAB), Facultad de Ciencias Forestales Universidad de Concepción, Victoria 631, Concepción, Chile

^d Department of Environmental Systems Science, Swiss Federal Institute of Technology, ETH Zurich, Zurich, Switzerland

^e SoWa Research Infrastructure, Biology Centre CAS and Faculty of Science, University of South Bohemia, České Budějovice, Czech Republic

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ABSTRACT

The contribution of different adsorption processes to soil organic matter (SOM) stabilization and the consequences of the intensification of land use on the adsorption of SOM are not yet fully understood. Therefore, this study aimed to explore the adsorption of dissolved organic carbon (DOC) in soils as well as desorption of organic carbon (OC) caused by phosphate addition. We conducted desorption and sorption experiments with DOC, phosphate (Na_2HPO_4), and chloride (KCl) in topsoil and subsoil samples from a Ferralsol, an Andosol, and a Podzol. Furthermore, we quantified the size of DOC by size-exclusion chromatography.

We found that phosphate addition caused a strong increase in the DOC concentration in all soils. The DOC concentration was elevated by up to a factor of 4.5 compared to a control (water only) within five minutes after phosphate addition and kept increasing further with time, particularly in the Ferralsol. After 10 days, the DOC concentrations in the P addition treatment were between 5.5 and 18.0 times higher than in the control treatment. In contrast, chloride addition did not lead to increased DOC concentrations compared to the control (water only). Phosphate addition led mostly to desorption of organic matter of medium molecular size (10–100 and 100–1000 kDa) in the Ferralsol and the Andosol and of large molecular size (>1000 kDa) in the Podzol. In contrast, potassium chloride addition shifted the size distribution of DOC in the soil solution towards small compounds (<10 kDa), likely because KCl addition affected the aggregation of DOC compounds, in contrast to Na_2HPO_4 addition. Furthermore, phosphate addition also decreased subsequent sorption of DOC in the Ferralsol and the Andosol by a factor of up to 2.9 and 2.1, respectively.

Our results have far-reaching implications because they show that phosphate addition can lead to desorption, and thus to destabilization of SOM, particularly in Ferralsols, and can also prevent further sorption of organic matter in soils. Our study provides a mechanistic explanation of why phosphate addition can decrease soil organic carbon sequestration and stabilization. This mechanism should be considered in the analysis of land-use and tillage effects on SOM sequestration in the future. Furthermore, our study indicates that also medium and large molecular size organic matter is stabilized through adsorption in soils.

1. Introduction

Organic matter is stabilized in soils against microbial decomposition through several processes (Sollins et al., 1996; Torn et al., 1997; von Lützow et al., 2006). Yet, the relative contributions of different processes to organic matter stabilization are not fully understood. In addition, the consequences of land-use intensification for organic matter stabilization, and specifically for the adsorption of organic matter in

soils with different mineral composition have not been fully explored yet.

Sorption protects organic compounds against decomposition by steric hindrance since it physically prevents enzymes from binding to the compounds and catalyzing their decomposition. Further, sorption impedes that organic compounds are taken up by microorganisms (von Lützow et al., 2006; Kögel-Knabner et al., 2008; Kleber et al., 2015). Thus, the number of sorption sites in a given soil determines to a

* Corresponding author at: Biogeochemistry of Forest Soils, Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), Lennart Hjelm's väg 9, 75007 Uppsala, Sweden.

E-mail address: marie.spohn@slu.se (M. Spohn).

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considerable extent the amount of soil organic matter (SOM) that the soil can store (Mayer, 1994; Sollins et al., 1996; von Lütow et al., 2006; Jackson et al., 2017). Recent synthesis studies claim that adsorption stabilizes mostly small organic substances with a molecular size < 600 kDa against decomposition in soils (Sokol et al., 2019; Basile-Doelsch et al., 2020), but empirical evidence for this is slender.

The primary mechanisms by which organic matter sorbs onto mineral surfaces are electrostatic interaction, commonly referred to as non-specific sorption, and ligand exchange-surface complexation, also called specific sorption. Hydrophobic interaction, hydrogen bonding, and polyvalent cation bridging also contribute to sorption of organic matter in soils (Kaiser and Guggenberger, 2000; Kleber et al., 2015). The energies of electrostatic bonds are much lower than those associated with ligand exchange-surface complexation (Kleber et al., 2015). Ligand exchange surface complexation refers to structural metal cations, mostly iron (Fe) and aluminum (Al), replacing their coordinative OH or OH₂ ligand by another ligand, which can be an organic or inorganic anion (Stumm et al., 1980). Organic matter with a high proportion of carboxyl and hydroxyl moieties preferentially adsorbs through ligand-exchange surface complexation and through polyvalent cation bridging at high pH (Gu et al., 1994). Not only organic matter compounds but also inorganic anions such as sulfate and phosphate can form ligand-exchange surface complexes (Hingston et al., 1967; Goldberg and Spósito, 1985; Arai and Sparks, 2007). In contrast, other anions, such as chloride or nitrate, cannot form ligand-exchange surface complexes and adsorb mostly through energy-poorer, electrostatic interactions to mineral surfaces. These ions cannot exchange with ions that form ligand-exchange surface complexes at a given pH and ionic strength (Hingston et al., 1967). The fact that phosphate but not chloride can replace organic matter that forms ligand-exchange surface complexes has been used to gain insights into the mechanisms by which organic matter sorbs in soils (Mikutta et al., 2007).

Previous studies showed that the concentrations of dissolved organic C (DOC, which is organic C < 0.45 µm) and microbial respiration in soils is increased due to the addition of phosphorus (P), and they attributed this to the alleviation of microbial P limitation that increases microbial activity and organic matter decomposition (Cleveland et al., 2002; Griffiths et al., 2012; Liu et al., 2012; Strickland et al., 2010; Fisk et al., 2015). Yet, increased respiration rates and DOC concentrations in response to P addition might likely be caused by desorption of organic carbon (C) from mineral surfaces (Spohn and Schleuss, 2019).

Phosphate and organic matter compete for binding sites in soils. Thus, changes in the phosphate concentration in the soil solution can strongly affect the sorption and desorption of organic compounds, and thus the destabilization and decomposition of SOM. Phosphate addition can lead to desorption of organic matter causing an increase in the concentration of DOC (Beck et al., 1999; Kaiser and Zech, 1999; Kahle et al., 2004; Zhang and Zhang, 2010; Bonifacio et al., 2013; Scott et al., 2015; Spohn and Schleuss, 2019; Li et al., 2020) and of low molecular weight organic acids, such as oxalate, malate, and phthalic acid in soils (Afif et al., 1995; Liu et al., 1999; Guan et al., 2006). The desorption of organic matter renders these organic compounds available for microbial decomposition. Accordingly, several studies showed that addition of phosphate to soil increased soil respiration (Munevar and Wollum, 1977; Griffiths et al., 2012; Miyazawa et al., 2013; Liu et al., 2012; Cleveland et al., 2006; Strickland et al., 2010; Fisk et al., 2015; Spohn and Schleuss, 2019). Phosphate cannot only lead to desorption of sorbed organic matter, but sorbed phosphate can also prevent sorption of organic matter in soils by keeping the binding sites occupied (Gu et al., 1994; Kaiser and Zech, 1997; Hur and Schlautman, 2004; Kahle et al., 2004; Hunt et al., 2007; Schneider et al., 2010). The amplifying effect of phosphate on DOC desorption and soil respiration has been shown particularly for Andosols in several studies (Munevar and Wollum, 1977; Beck et al., 1999; Miyazawa et al., 2013; Li et al., 2020), which might be due to the high content of allophanes commonly found in silandic Andosols. However, phosphate might also have strong effects on organic

C sorption in other soils with high contents of Fe and Al oxyhydroxides and thus a large, positively charged mineral surface area. Yet, little is known about the effect of P addition on organic C sorption and desorption in other soil orders with high contents of Fe and Al oxyhydroxides, such as Ferralsols.

The aim of this study was to explore adsorption and desorption of SOM as affected by phosphate addition in different soils. This aim is in line with the recent suggestion by Kleber et al. (2021) to explore sorption dynamics not with pure minerals but in soils where the newly offered adsorbate can compete with and induce the release of previously adsorbed organic compounds. We tested the following hypotheses. First, a substantial proportion of SOM can be desorbed by phosphate but not by chloride in Ferralsols, Andosols, and Podzols. Second, the amount of organic C that is stabilized in soils through adsorption and can be desorbed by phosphate addition is particularly high in Andosols due to the high content of Al oxyhydroxides. Third, SOM compounds that desorb due to phosphate addition mostly have a small molecular size (<600 kDa). Fourth, the high saturation of soils with phosphate decreases the adsorption of organic matter, particularly in Andosols due to the high content of Al oxyhydroxides.

To test these hypotheses, we conducted a series of sorption experiments with a Ferralsol, an Andosol, and a Podzol. In the first experiment, we studied the short-term desorption of DOC caused by phosphate addition under conditions that minimize microbial activity. In the second experiment, we examined desorption of organic carbon (OC) caused by phosphate and chloride addition over ten days and analyzed the size of the DOC. Finally, in the third experiment, we quantified DOC sorption after a large proportion of sorption sites had been saturated with phosphate. We choose a Ferralsol, an Andosol, and a Podzol for this study because these soils contain differing concentrations of Fe and Al oxyhydroxides and allophanes whose surfaces are protonated at low pH, and thus can maintain electrostatic interactions with organic and inorganic anions. At the same time, they can also bind inorganic and organic anions through ligand exchange surface complexation.

2. Material and methods

2.1. Soils, sampling, and sample preparation

The three soils selected for this study are forest soils, and there is no indication that they have ever received any P fertilizer. The Ferralsol is located in the Kahuzi-Biega National Park situated in the Democratic Republic of the Congo (2°18'15"S and 28°45'14"E). The soil's parent material consists of mafic alkali-basalts (Schlüter and Trauth, 2006). The soil is located at 2216 m a.s.l, where the mean annual temperature is 15.1 °C, and the mean annual precipitation is 1924 mm. The dominant vegetation is a primary tropical mountain forest. The soil is classified as an Umbric Ferralsol according to the world reference base for soil resources (FAO, 2006). An extensive description on the soil mineralogy as well as the elemental composition of the parent material of the Ferralsol can be found in Doetterl et al. (2021). While no detailed information on clay mineralogy is available for the specific soil studied here, similar sites in the region with a comparably advanced weathering stages have been dominated by low activity clays (kaolinite) and high amounts of pedogenic oxides, controlling soil C storage (Kirsten et al., 2021), making soils enriched in Al and Fe and depleted of Si. The Andosol is located in the Andes in Central Chile (37°04'19"S and 71°42'04"W) and belongs to the Santa Bárbara soil series. The soil is located at 946 m a.s.l. The mean annual temperature is 12.2 °C, and the mean annual precipitation is 1769 mm. The parent material is a deposit of young volcanic ashes, and the dominant vegetation is temperate deciduous *Nothofagus* sp. forest. The soil is classified as a Eutric Amphichernic Follic Epialuandic Andosol (FAO, 2006). The Andosol profile was derived from mafic ash relatively enriched in olivine and iron pyroxene originated from the Chillan and Antuco Volcanos (Besoin, 1985). The parent material of Andosols in this part of Chile generally do not contain crystalline clay minerals

(Bertrand and Fagel, 2008). The Podzol is located in Southern Germany (49°58'49"N and 11°34'58"E). The soil is located 445 m a.s.l., where the mean annual temperature is 8.3 °C, and the mean annual precipitation is 638 mm. The parent material is Guembel sandstone, and the dominant tree species are *Pinus sylvestris* and *Picea abies*. The soil is classified as an Entic Podzol (FAO, 2006). For further details about Podzol properties in the region see Eusterhues et al (2005).

Two samples were collected from three soil profiles (one per each soil). We collected samples from the depth intervals ranging from 0 to 10 cm (topsoil) and 40–50 cm (subsoil) from the Ferralsol and the Podzol. Similarly, we collected samples from the 0–20 cm (topsoil) and the 40–80 cm depth interval (subsoil) from the Andosol. The topsoil sample was taken from the A horizon in all soils and the subsoil samples from the B horizon. Besides, we collected samples from the organic layer of the Andosol and the Podzol. All samples were air-dried and transported to the laboratory at the University of Bayreuth. The mineral soil samples were sieved (<2 mm), and only the <2 mm fraction was used for the analyses.

2.2. Soil characterization

Soil texture was analyzed according to Köhn (1928). For this purpose, samples were pre-treated with H₂O₂ as an oxidant to destroy organic substances. The coarse fractions were separated through wet sieving. The remaining fraction (<63 µm) was dispersed in 25 ml Napyrophosphate and transferred into cylinders, where fine silt and clay content were assessed by sedimentation analysis (DIN ISO 11 277). Soil pH was measured in deionized water in a soil:solution ratio of 1:2.5. Al and Fe were extracted in oxalate (ox) and in dithionite (d) solutions according to Schwertmann (1964) and Mehra and Jackson (1958) and were quantified using an ICP-OES (Vista-Pro radial, Varian, USA). To determine total organic C (TOC), total N (TN), and total P (TP), subsamples of each soil were dried at 105 °C and milled in a ball mill. TOC and TN were measured using an element analyzer (Vario Max Elementar, Hanau, Germany). TP was determined by ICP-OES (Vista-Pro radial, Varian) after pressure digestion in aqua regia (HNO₃ + HCl). Dissolved organic C (DOC), dissolved N (DN), and dissolved inorganic P (DIP) were extracted and determined as described in Section 2.3 for the experimental treatment without P addition. Dissolved inorganic P was determined according to the molybdenum-blue method (Murphy and Riley, 1962) using a multiplate reader (Infinite® M200 PRO, Tecan Austria GmbH, Grödig, Austria). The quantification limit for DIP was 0.08 mg l⁻¹.

2.3. Short desorption experiment

We tested the effect of the addition of several concentrations of phosphate on the fast desorption of OC in a short experiment, similar to the one described by Spohn and Schleuss (2019). To minimize microbial activity, each step of the experiment was conducted, maintaining a constant temperature of 5 °C. Three grams of each soil were shaken in 30 ml deionized water with different concentrations of Na₂HPO₄ on a horizontal shaker for five minutes. Subsequently, the samples were centrifuged at 1500 × g for 15 min, and the supernatant was filtered through a cellulose acetate filter of 0.45 µm pore size (Sartorius Stedim Biotech GmbH, Göttingen, Germany) using a vacuum pump. The dry soil samples were dispersed in the solution. We used five different Na₂HPO₄ concentrations that correspond to 0, 0.25, 0.75, 1.5, and 3.0 mg P g⁻¹ soil (which were added in the form of solution that had the following P concentrations; 0, 8.3, 25, 50 and 100 mg P l⁻¹). The lower concentrations were chosen based on the P concentrations used in similar experiments; 0.100 mg P g⁻¹ soil (Heuck et al., 2015; Nottingham et al., 2015), 0.200–0.250 mg P g⁻¹ soil (Cleveland et al., 2002; Spohn and Schleuss, 2019), 0.330 mg P g⁻¹ soil (Fisk et al. 2015), 0.700 mg P g⁻¹ soil (Neff et al. 2000). The higher concentrations were chosen with the intention to desorb all organic C that can be desorbed by phosphate. It

should be noticed that soil solution P concentrations are normally much lower than the P concentrations applied here (except for the direct vicinity of dissolving P fertilizer particles). Thus, the applied concentrations represent an extreme treatment whose main purpose was to better understand the sorptive stabilization of organic matter in soils. After the centrifugation step and the removal of the supernatant, the same procedure was repeated three times. Thus, the experiment consisted of three consecutive cycles in which the respective P solution was added. All steps of the experiment were conducted in triplicate. Hence, we gained a total of 270 solutions from this experiment (3 soils × 2 depths × 5 P concentrations × 3 replicates × 3 sequential extractions). In addition, four blanks with water were prepared in each of the three cycles that were centrifuged and filtered as the samples. In addition, we conducted a control experiment to elucidate the effect of pH on DOC desorption. For this purpose, we increased the pH of Millipore water to pH 9.3 using NaOH, which corresponds to the pH of the 0.1 mg l⁻¹ Na₂HPO₄ solution. We treated the soil samples with the solution in the same way as detailed above for the Na₂HPO₄ solution and the control (water only).

We determined DOC, DN, total P, and inorganic P in the filtered extracts. DOC and DN were determined using a TOC Analyzer (multi N/C 2100, Jena Analytics, Germany). The quantification limit for DOC was 0.3 mg l⁻¹, all samples were measured two times and a third time if the difference exceeded 5% of the smaller value. A correction for drift was done after every 10 samples. We used certified reference material (ION-96.4 lot 0316). Total dissolved P was determined using an ICP-OES (Vista-Pro radial, Varian Inc., USA). The quantification limit for P was 0.15 mg l⁻¹, all samples were measured three times. A correction for drift was done after every 10 samples. We used certified reference material (SPS-SW2 Batch 136 und SPS-WW2 Batch 114).

2.4. Long desorption experiment

Since the exchange reaction between phosphate and DOC had not come to an end during the short desorption experiment, we conducted a long desorption experiment over ten days with the highest P addition treatment of the short experiment (3.0 mg P g⁻¹ soil). Besides the P addition treatment, we also had a KCl addition treatment in the long experiment to determine the amount of DOC that was adsorbed through electrostatic forces and could be desorbed by KCl. For this purpose, 3 g of soil were shaken in 30 ml of deionized water that either (i) contained no salts (control) or (ii) Na₂HPO₄ in a concentration corresponding to 3.0 mg P per g soil or (iii) or KCl in a concentration corresponding to 3.4 mg Cl per g soil in a gas-tight serum flask on a horizontal shaker at five 5 °C for ten days. The dry soil samples were dispersed in the solution. The experiment was conducted in three replicates. Thus, 54 samples were processed (3 soils × 2 depths × 3 treatments × 3 replicates). After ten days, the CO₂ concentration in all flasks was determined using a gas chromatograph (SRI 8610C, SRI Instruments Europe GmbH, Bad Honnef, Germany) equipped with a flame ionization detector. For this purpose, a gas sample was taken from the headspace using a syringe. After the sample had been taken, flasks were opened, and solutions were filtered through cellulose acetate filters with 0.45 µm pore size (Sartorius Stedim Biotech GmbH, Göttingen, Germany) using a vacuum pump. We determined the pH, DOC, DN, total P, and inorganic P in the filtered samples as described above. Further, we measured the Cl concentration in the control and the Cl treatment using ion chromatography (881 Compact IC pro, Metrohm Ltd., Herisau, Switzerland). Also, we performed size-exclusion chromatography on the filtered extracts (see Section 2.6).

2.5. DOC retention experiment

To determine the effect of P sorption in soil on subsequent DOC sorption and retention, we conducted a third experiment, in which we simulated percolation of DOC through soils to which high amounts of P had been applied. For this purpose, at the end of the long desorption

experiment (Section 2.4), the total mass of each soil sample was added on top of the filter at the end of the filtration processes. Subsequently, 30 ml of a DOC-rich solution were poured over the soil, and the solution was allowed to percolate through the soil and the 0.45 μm pore size filter. DOC concentration was measured using a TOC analyzer (multi N/C 2100, Jena Analytics, Germany) in the solution (i) before it was applied to the soil and (ii) in the 54 samples that were collected after the solution had percolated through the soil. The DOC-rich solution was prepared from the samples of the organic layer of the soils that were thoroughly mixed in equal proportions. The material was shaken in deionized water in a ratio of 1:40 w/v for 2 h on an overhead shaker. Subsequently, the DOC solution was filtered through a cellulose filter (Rotilabo 113P, Carl Roth GmbH + Co., Karlsruhe, Germany) overnight at 2 °C. The DOC concentration of the solution was 296 mg l^{-1} .

2.6. Size-exclusion chromatography

The DOC size distribution in the solutions at the end of the long desorption experiment was analyzed using a size-exclusion chromatograph. The distribution of the DOC across four size classes (>1000 kDa, 100–1000 kDa, 10–100 kDa, and <10 kDa) was quantified. For this purpose, the samples were analyzed on the SEC-PDA-ICP/QQQ system with the following analytical conditions. Chromatographic size exclusion (SEC) separation was done using a 2 mm isocratic Dionex system with Agilent PL aquagel-OH Mixed-H 8 μm column and a flow of 0.9 ml per minute of distilled water. The Dionex photodiode array (PDA) detector and Agilent ICP/QQQ in No gas mode connected in series were used for the online detection of the spectrophotometric properties of analytes and their C concentrations, respectively. The chromatographic parts' calibration was performed using a set of polyethylene glycol (PEG) standards covering the molecular mass from 250 Da to 1000 kDa. Before injection, samples were diluted to 20–30 mg C/L based on the DOC concentrations analyzed previously in the samples. The detection limit of the ICP/QQQ system for C was 0.5 mg g^{-1} , in connection with SEC it was 1 mg l^{-1} for each of the four size classes.

2.7. Calculations

The amount of DOC that desorbed during the short desorption experiment in the different P addition treatments was calculated based on the difference in DOC concentration between the P addition treatments and the control treatment. In the long desorption experiment, the calculation was performed in the same way, but here the total amount of $\text{CO}_2\text{-C}$ was added to the DOC to account for the mineralization of DOC during the experiment. The amount of P that adsorbed to the soil matrix in the different P addition treatments was calculated as the sum of dissolved P in the control treatment plus P added in the P addition treatment minus the P in the P addition treatments. The amount of DOC that was retained (through adsorption) in the DOC retention experiment was calculated as the amount of DOC added to the soil, and the amount of DOC recovered after percolation.

Table 1

Selected physical and chemical properties of the soils, including oxalate and dithionite extractable iron (Fe_{ox} and Fe_{d}) and aluminum (Al_{ox} and Al_{d}), total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP), b.d.l. stands for below detection limit. For details about the soil texture see Table S1.

Soil	Depth	Texture			Fe_{ox} (mg g^{-1})	Fe_{d} (mg g^{-1})	Al_{ox} (mg g^{-1})	Al_{d} (mg g^{-1})	$\text{pH}_{\text{H}_2\text{O}}$	TOC (mg g^{-1})	TN (mg g^{-1})	TP (mg g^{-1})	Molar TOC:TN ratio	Molar TOC:TP ratio
		Clay (%)	Silt (%)	Sand (%)										
Ferralsol	topsoil	61.3	35.9	2.8	23.09	22.18	11.85	3.82	3.70	46.14	5.33	2.85	10.1	41.8
Ferralsol	subsoil	71.9	24.4	3.7	22.85	27.31	10.30	3.87	4.03	19.59	1.59	2.56	14.3	19.7
Andosol	topsoil	9.9	80.3	9.8	6.29	16.23	21.51	13.00	4.85	66.93	5.26	1.46	14.8	118.2
Andosol	subsoil	3.5	46.2	50.3	7.50	35.42	17.81	10.96	5.22	18.52	1.33	0.65	16.3	73.5
Podzol	topsoil	1.5	6.2	92.3	0.56	0.85	0.46	0.09	3.93	6.98	0.28	0.07	28.7	248.1
Podzol	subsoil	4.0	3.6	92.4	1.51	1.39	1.61	0.33	4.37	2.13	b.d.l.	0.14	–	39.8

3. Results

3.1. Soil properties

The soil texture was dominated by clay in the Ferralsol and fine sand in the Podzol both in the top- and subsoil (Table 1 and Table S1). The Andosol was dominated by silt in the topsoil and clay in the subsoil (Table 1). The concentration of oxalate-extractable Fe decreased in the order Ferralsol > Andosol > Podzol. In contrast, the oxalate-extractable Al concentration was highest in the Andosol (Table 1). $\text{pH}_{\text{H}_2\text{O}}$ was in the acidic to very acidic range in all soils, lowest in the topsoil of the Ferralsol, and highest in the Andosol subsoil (Table 1). TOC content was highest in the topsoil of the Andosol and lowest in the topsoil of the Podzol.

The DOC concentration in the soil solution decreased in the following order; Ferralsol topsoil > Andosol topsoil > Podzol topsoil > Ferralsol subsoil > Andosol subsoil > Podzol subsoil (Table 2). DIP concentrations ranged from 1.57 mg g^{-1} in the Ferralsol to 5.40 mg g^{-1} in the Podzol. The DOC:DIP ratios were highest in the top of the Ferralsol and 17–22 times lower in the Podzol's topsoil and the Andosol's subsoil. DOC was differently distributed across the four molecular size classes in the six soil horizons (Table 3). DOC was nearly equally distributed across all four size classes in the Ferralsol, particularly in the topsoil. In the Andosol, 64 and 75% of the DOC were found in the fraction with the largest molecular size (>1000 kDa) in the top- and subsoil, respectively. Also, in both the top- and subsoil of the Podzol, most DOC was found in the fraction with the largest molecular size. However, this fraction only contained 30 and 35% of the DOC of the top- and the subsoil, respectively, and the DOC was more evenly distributed across the four fractions than in the Andosol (Table 3).

3.2. Short desorption experiment

The short-term addition of 0.25 mg P g^{-1} soil led to an increase in the DOC concentration in all soils and soil depths after the first extraction cycle by a factor of 1.3 (in the Podzol topsoil) to 1.8 (in the Ferralsol subsoil) (Fig. 1A), even though the soils were only shaken for 5 min with

Table 2

Chemical properties of the soil solutions in the control treatment in the first cycle in the short desorption experiment, including dissolved organic carbon (DOC), dissolved organic nitrogen (DN), and dissolved inorganic P (DIP). b.d.l. stands for below detection limit. Total P was b.d.l. in all soil solutions.

Soil	Depth	DOC ($\mu\text{g g}^{-1}$)	DN ($\mu\text{g g}^{-1}$)	DIP ($\mu\text{g g}^{-1}$)	Molar DOC:DN ratio	Molar DOC:DIP ratio
Ferralsol	topsoil	379	124	1.6	3.6	1124
Ferralsol	subsoil	126	12	1.6	12.7	230
Andosol	topsoil	146	44	2.4	3.9	490
Andosol	subsoil	43	6	2.4	9.0	50
Podzol	topsoil	113	5	5.4	29.5	64
Podzol	subsoil	103	b.d.l.	2.6	–	113

Table 3
Proportion of DOC in the soil solution of the Ferralsol, the Andosol, and the Podzol in four molecular sizes classes. Shown are means ± standard deviation of 3 independent replicates.

Soil	Depth	Proportion of DOC >1000 kDa (%)	Proportion of DOC 100–1000 kDa (%)	Proportion of DOC 10–100 kDa (%)	Proportion of DOC <10 kDa (%)
Ferralsol	topsoil	22.8 ± 7.6	25.1 ± 4.1	23.6 ± 4.8	28.5 ± 1.4
Ferralsol	subsoil	30.4 ± 10.2	7.4 ± 1.8	28.4 ± 3.9	33.8 ± 8.2
Andosol	topsoil	64.0 ± 18.0	9.9 ± 3.2	10.8 ± 9.1	15.3 ± 11.2
Andosol	subsoil	75.4 ± 7.0	9.7 ± 1.0	5.3 ± 2.0	9.6 ± 5.4
Podzol	topsoil	30.5 ± 7.4	29.5 ± 8.0	18.5 ± 1.2	21.5 ± 2.0
Podzol	subsoil	35.0 ± 6.8	28.1 ± 3.9	27.8 ± 3.2	9.1 ± 1.2

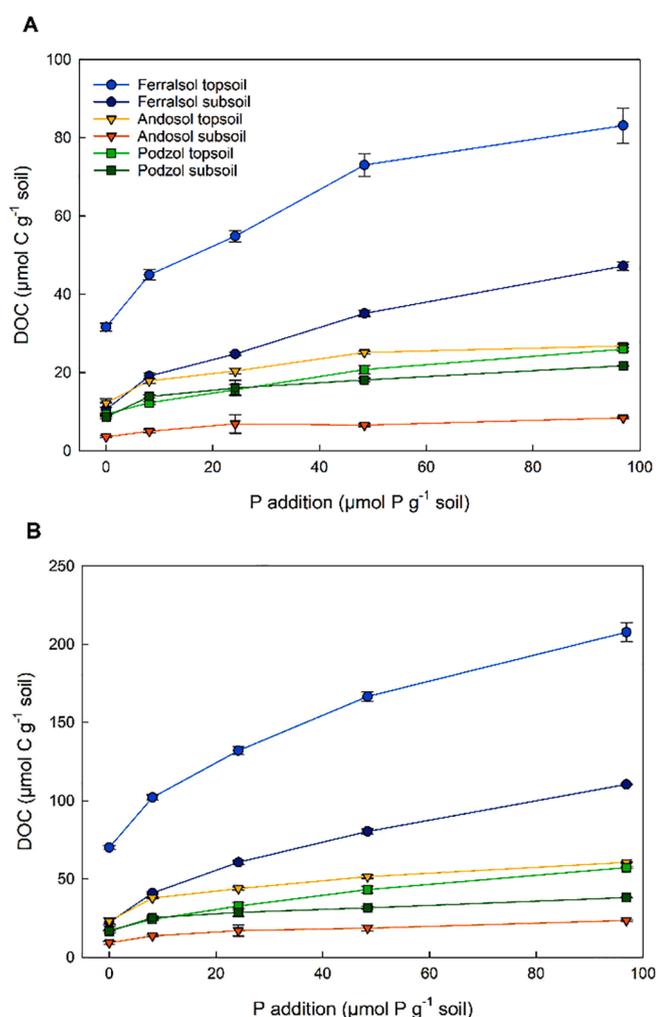


Fig. 1. The DOC concentration in the soil solution as a function of the amount of added P at the end of the first cycle of the short desorption experiment (A) and cumulated across all three cycles of the experiment (B) in the top- and subsoil of a Ferralsol, an Andosol, and a Podzol. Shown are means, and the error bars indicate the standard deviations calculated based on three independent replicates. Please notice the different scales of the two y-axes.

the phosphate solution at 5 °C. The DOC concentration increased strongly with the amount of added phosphate in the top- and subsoil of the Ferralsol and much less in the Andosol and the Podzol (Fig. 1A). The DOC concentration was elevated most strongly after the first addition of the highest P dose (3.00 mg P g⁻¹ soil) in the top of the Ferralsol, namely by a factor of 4.5 compared to the control. The DOC:DN ratio only increased in the Ferralsol due to the P addition by a factor of 2.0, comparing the control treatment to the highest phosphate addition treatment in both soil depths.

The DOC concentration increased further after the second and third phosphate addition in all soils (Fig. 1B and Table S2). This increase in DOC was strong in the Ferralsol (both depths) and smaller in the Andosol and the Podzol. The DOC concentration in the extracts decreased from the first to the second, to the third phosphate addition in all soils (Table S2). Still, even in the third phosphate addition cycle, the DOC concentration in the highest phosphate addition treatment made up between 23% (Podzol subsoil) to 83% (Andosol subsoil) of the DOC after the first phosphate addition (Table S2). After three cycles of phosphate addition, DOC concentration (Fig. 1B) and the total amount of DOC that desorbed due to phosphate addition (i.e., the difference in DOC between the P treatment and the control, see Section 2.7) decreased in the order Ferralsol topsoil >>> Ferralsol subsoil >> Podzol topsoil = Andosol topsoil > Podzol topsoil > Andosol subsoil (Table 4). If the amount of desorbed DOC was normalized by TOC concentration, the order was as follows; Podzol subsoil > Podzol topsoil > Ferralsol subsoil > Ferralsol topsoil > Andosol subsoil > Andosol topsoil (Table 4).

The amount of DOC that desorbed due to phosphate addition (i.e., the difference in DOC between the P treatment and the control, see Section 2.7) was correlated with the amount of P that adsorbed across the five different levels of repeated phosphate addition in the Ferralsol and the Andosol, but not in the Podzol (Table 5 and Fig. S1). The slope of regression indicates that 2.63 and 1.22 mol DOC desorbed per mol P that adsorbed to the soil solid phase in the top- and subsoil of the Ferralsol, respectively, while in the Andosol, 0.40 and 0.08 mol DOC desorbed per mol P that adsorbed in the top- and subsoil, respectively (Table 5). The control experiment showed that the elevated pH had no or even a negative effect on the DOC concentration in the subsoil horizons. However, in the topsoil horizons, the DOC concentration was elevated due to the increased pH compared to the control, namely by 5% in the Ferralsol, 12% in the Andosol, and 10% in the Podzol.

3.3. Long desorption experiment

At the end of the 10-day experiment, the DOC concentrations in the P addition treatment were between 5.5 and 18.0 times higher than in the control treatment (Fig. 2). Part of the DOC had been converted into CO₂ at the end of the experiment, especially in the Andosol topsoil (Fig. 2).

Table 4

Desorbed DOC in the short desorption experiment in the highest P addition treatment (3.00 mg P g⁻¹ soil) cumulated over the three cycles as well as in the P addition treatment (also 3.00 mg P g⁻¹ soil) at the end of the long desorption experiment. The amount of DOC desorbed includes the C that was converted into CO₂ during the incubation. The amount of desorbed DOC is given per soil and TOC. Shown are means ± standard deviation of 3 independent replicates.

Soil	Depth	Short experiment		Long experiment	
		DOC desorbed (µg C g ⁻¹ soil)	DOC desorbed (µg C mg ⁻¹ TOC)	DOC desorbed (µg C g ⁻¹ soil)	DOC desorbed (µg C mg ⁻¹ TOC)
Ferralsol	topsoil	1654 ± 74	36 ± 2	4408 ± 46	96 ± 1
Ferralsol	subsoil	1061 ± 7	54 ± 0	2302 ± 45	118 ± 2
Andosol	topsoil	451 ± 7	7 ± 0	1285 ± 63	19 ± 1
Andosol	subsoil	171 ± 6	9 ± 0	492 ± 7	27 ± 0
Podzol	topsoil	482 ± 7	69 ± 1	1124 ± 39	161 ± 6
Podzol	subsoil	261 ± 2	122 ± 1	425 ± 67	200 ± 32

Table 5

Desorbed DOC as a function of the adsorbed P across five different levels of repeated phosphate addition (0.0, 0.25, 0.75, 1.50, 3.00 mg P g⁻¹) in the short desorption experiment. Given is the function that determines the relationship, where x is the amount of P that adsorbed (in $\mu\text{mol P g}^{-1}$ soil), and y is the amount of DOC that desorbed (in $\mu\text{mol C g}^{-1}$ soil) as well as the R² and the p-value (see also Fig. S1).

Soil	Depth	Function	R ²	p Value
Ferralsol	topsoil	$y = 2.63x + 9.9$	0.82	<0.05
Ferralsol	subsoil	$y = 1.22x + 7.6$	0.64	<0.05
Andosol	topsoil	$y = 0.40x + 4.3$	0.66	<0.05
Andosol	subsoil	$y = 0.08x + 2.2$	0.20	<0.05
Podzol	topsoil			>0.05
Podzol	subsoil			>0.05

The total amount of DOC that desorbed due to P addition in the long term-experiment (i.e., the difference in C desorption between the P treatment and the control, see Section 2.7) was between 1.6 and 2.9 times larger in the long experiment than in the short term experiment (Table 4). The total amount of desorbed DOC in the six soil horizons decreased in the same order as in the short experiment from the top of the Ferralsol to the Podzol subsoil (Table 4). The pH of the solution in the P addition treatment was increased compared to the control (Table 6). In contrast to the phosphate addition, in the chloride addition, DOC concentration was not significantly larger than in the control (Fig. 2). Thus, the amount of DOC desorbed due to Cl addition amounted to zero in all soils.

The phosphate addition affected the DOC distribution across the four different size classes differently in the six soil horizons (Fig. 3). In both investigated soil horizons of the Ferralsol and the topsoil of the Andosol, the relative contribution of the two medium molecular size fractions to the DOC pool (10–100 and 100–1000 kDa) increased due to P addition, while the contribution of the smallest and the largest molecular size fractions to the DOC pool decreased in response to P addition (Fig. 3). Similarly, in the Andosol subsoil, DOC in the second-largest molecular size fraction (100–1000 kDa) increased due to P addition. In contrast, in the Podzol, the largest particle size fraction (>1000 kDa) increased due to P addition, while the two medium molecular size fractions decreased (Fig. 3).

The Cl treatment had a strong effect on the DOC distribution across the four different size classes, i.e., the DOC percentage in the four size classes (Fig. 3). The Cl addition increased the smallest molecular size class (<10 kDa) in all soils. This fraction made up between 45.0 and 64.6% of the DOC across all soils in the Cl addition treatment. The increase in the relative contribution of the < 10 kDa fraction to the DOC pool in response to Cl addition was largest in the Andosol and the subsoil of the Podzol. In the Andosol, the percentage of DOC in this size fraction increased from 15.3 and 9.5% in the control treatment to 54.0 and 59.3% in the Cl treatment in the top- and subsoil, respectively. Similarly, in the Podzol subsoil, the proportion of DOC in this fraction increased from 9.1% in the control treatment to about 64.6% in the Cl treatment (Fig. 3).

3.4. DOC retention experiment

In the control treatment, the DOC retention decreased in the following order, Andosol subsoil > Andosol topsoil > Ferralsol subsoil > Ferralsol topsoil > Podzol topsoil = Podzol subsoil (Fig. 4). The P addition treatment led to a strong decrease in DOC retention in the Ferralsol and the Andosol. In the Ferralsol, the DOC retention was 2.1 and 2.9 times lower when treated previously with phosphate than in the control in both the top- and subsoil. In the Andosol, the DOC retention was 2.1 times lower in the P treatment than in the control, in both top- and subsoil. However, phosphate addition had no significant effect on DOC retention in the Podzol. In contrast to phosphate addition, chloride addition had no strong or consistent effect on DOC retention in the six

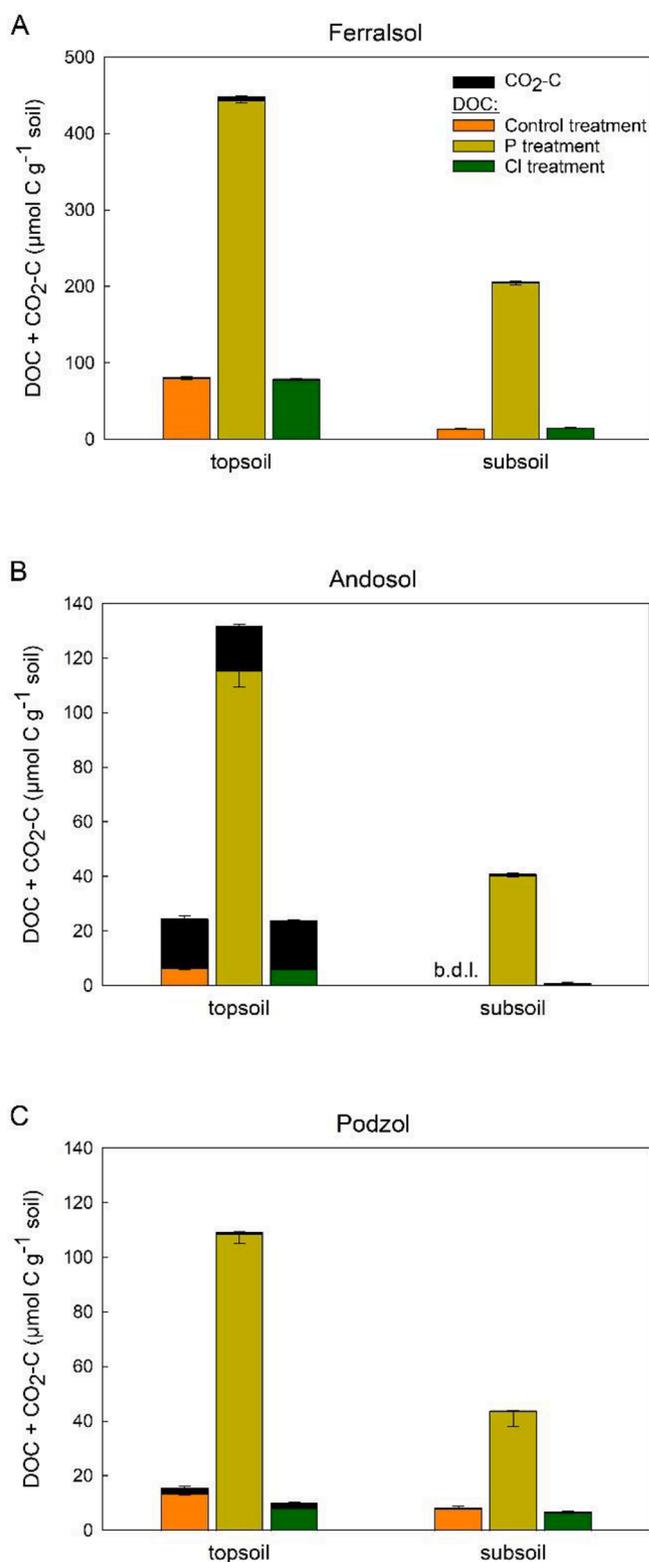


Fig. 2. DOC in the soil solution and CO₂-C in the gas phase in the control and phosphate (P) and chloride (Cl) addition treatments at the end of the long desorption experiment. The results are shown for the top- and subsoil of a Ferralsol (A), an Andosol (B), and a Podzol (B). Bars show means, and error bars indicate the standard deviations calculated based on three independent replicates. Positive error bars relate to CO₂-C, and negative error bars relate to DOC. b.d.l. stands for below detection limit. Please notice the different scales of the y-axes.

Table 6

pH at the end of the long desorption experiment in the control (water only) and in the P addition treatment.

Soil	Depth	pH	
		Control treatment	P addition treatment
Ferralsol	topsoil	4.32 ± 0.0	5.86 ± 0.0
Ferralsol	subsoil	4.39 ± 0.0	6.64 ± 0.0
Andosol	topsoil	6.38 ± 0.0	7.68 ± 0.0
Andosol	subsoil	5.37 ± 0.0	7.76 ± 0.0
Podzol	topsoil	4.42 ± 0.0	7.39 ± 0.0
Podzol	subsoil	4.82 ± 0.0	7.71 ± 0.0

soil horizons. In the top of the Andosol, it slightly decreased the DOC adsorption by a factor of 1.2, while it caused a slight increase in the subsoil of the Andosol by a factor of 1.1 relative to the control treatment (Fig. 4).

4. Discussion

We found that phosphate addition to soils led to desorption of organic matter, and it also decreased subsequent adsorption of organic matter. Phosphate addition increased mostly the desorption of DOC of medium molecular size (10–100 and 100–1000 kDa) in the Ferralsol and the Andosol and of large molecular size (>1000 kDa) in the Podzol. In contrast, chloride addition had no significant effect on the amount of DOC but affected the apparent size of the DOC compounds.

4.1. Effect of phosphate addition on DOC desorption

Phosphate addition to the six soil horizons caused a strong increase in DOC concentration, resulting from the desorption of organic C from the soil solid phase. The reason for this is most likely that phosphate competes more effectively for sorption sites on mineral surfaces than many organic compounds (Violante and Gianfreda, 1993; Afif et al., 1995; Fransson and Jones, 2007; Schneider et al., 2010; Spohn and Schleuss, 2019; Spohn, 2020). Thus, the added phosphate adsorbed to mineral surfaces and thereby caused the sorbed organic matter to desorb. Our finding that phosphate addition to soil leads to desorption of organic C is in accordance with previous studies demonstrating that phosphate addition to soils leads to an increase in the DOC concentration in the soil solution (Kaiser and Zech, 1999; Kahle et al., 2004; Zhang and Zhang, 2010; Scott et al., 2015; Spohn and Schleuss, 2019; Li et al., 2020).

The short desorption experiment showed that the effect of P addition on the DOC concentration of the soil solution was abiotic since the low temperature (5 °C) minimized microbial activity, and the short time that the experiment lasted (5 min) makes it highly unlikely that microbial activity led to the substantial increase in DOC concentration. This finding is relevant since some previous studies stated that phosphate addition increased microbial activity because it alleviated microbial P limitation, and consequently increased microbial activity; and thus respiration and DOC dynamics (Cleveland et al., 2002; Strickland et al., 2010; Griffiths et al., 2012; Liu et al., 2012; Fisk et al., 2015). In contrast, our findings suggest that the reason for increased microbial activity and soil respiration upon addition of phosphate is caused by increased DOC availability resulting from DOC desorption. Thus, our findings support a recent study showing that phosphate addition leads to a rapid increase in soil respiration because it causes desorption of organic compounds, which are thereby rendered available to microorganisms (Spohn and Schleuss, 2019).

In contrast to phosphate, the addition of chloride did not cause additional DOC desorption compared to the control (Fig. 2). This might indicate that organic matter that desorbed in response to phosphate addition was adsorbed to mineral surfaces by ligand exchange surface complexation. Thus, our results show that adsorption of DOC to mineral

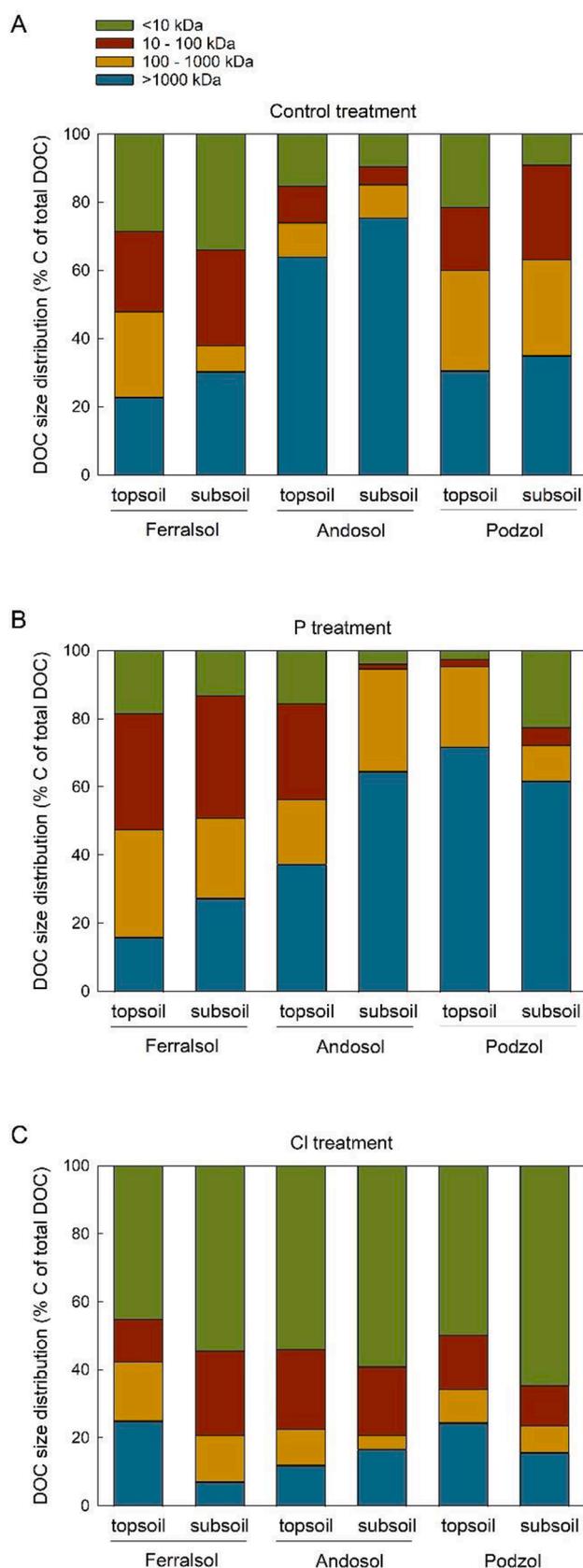


Fig. 3. Percentage of DOC in four molecular size classes in the six soils in the control (A) and in the phosphate (B) and chloride (C) addition treatment in the long desorption experiment. The results are shown for the top- and subsoil of a Ferralsol, an Andosol, and a Podzol.

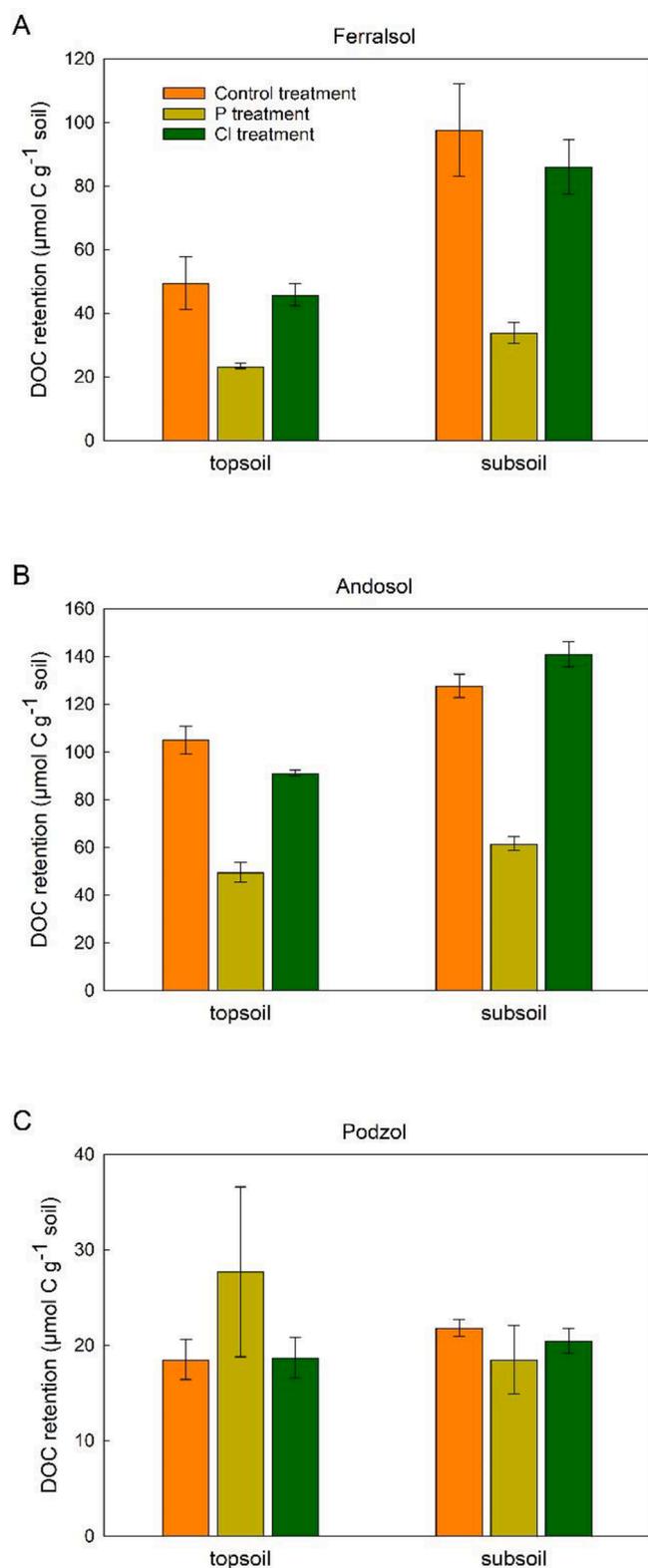


Fig. 4. Retention of DOC in the DOC retention experiment in the soils in the control treatment and the phosphate (P) and chloride (Cl) addition treatments. The results are shown for the top- and subsoil of a Ferralsol (A), an Andosol (B), and a Podzol (C). Bars show means, and error bars indicate the standard deviations calculated based on three independent replicates. Please notice the different scales of the y-axes.

surfaces by ligand exchange surface complexation is very likely an important process that stabilizes SOM against decomposition. Our results agree with Mikutta et al. (2007), who showed that ligand exchange surface complexation was the most important process of DOC adsorption to goethite, using a similar approach as we. However, it also needs to be considered that the addition of P in the form of Na_2HPO_4 does not only affect the phosphate concentration but also increases the pH (see Table 6) and the sodium (Na) concentration. An increase in pH reduces the positive charge of surfaces with pH-dependent charge due to deprotonation, which can lead to OC desorption. The pH-control experiment showed that the pH had no effect on the DOC concentration in the subsoils. However, in the topsoils, the increased pH of the Na_2HPO_4 solution contributed to the DOC desorption although the effect of increased pH was lower than the effect of P addition. Furthermore, the increased Na concentration might have contributed to organic C dispersion.

While several studies have shown that phosphate addition leads to destabilization of organic C, this has so far not been recognized in the analysis of the effect of tillage and land-use change on SOM sequestration, to our knowledge. Changes in organic matter stocks following land conversion to cropland have mostly been attributed to changes in organic matter inputs and destruction of soil aggregates (Post and Kwon, 2000; Don et al., 2011). Our results indicate that P additions to soil should be considered as a potential reason for decreases in soil organic C.

4.2. Effect of phosphate addition: Differences between soil orders

A large proportion of DOC desorbed during the first five minutes after phosphate addition (Fig. 1A), but the reaction had not ended at the end of the short experiment and continued further, albeit at a much lower rate (Figs. 1 and 2; Table S2). This is typical for anion adsorption processes that are initially very fast and then continue at a low rate over days to weeks as the anion penetrates further into the soil (Barrow and Shaw, 1975; Barrow, 1983). The short experiment showed that the reaction of desorption of DOC was rather limited by time than by the amount of added phosphate in the Podzol and the Andosol. This can be seen from the fact that the amount of desorbed DOC increased very little with the amount of added P but kept rising from the first to the third cycle of the experiment (Fig. 1, Table S2). In contrast, in the Ferralsol, the reaction was limited by the amount of added phosphate in all three cycles of the experiment (Fig. 1, Table S2). This finding underlines the Ferralsol's capacity to desorb considerable amounts of OC when treated with phosphate. This finding has important implications because it shows that the addition of phosphate to soils with high contents of Fe and Al oxyhydroxides, and particularly to Ferralsols, leads to desorption of soil OC, thus likely to losses of SOM.

The largest effect of phosphate addition on DOC desorption was observed in the Ferralsol (Table 4), which was against our second hypothesis, stating that the largest effect would be observed in the Andosol. This result indicates that the large effect of P addition was not caused by the high amount of Al oxyhydroxides (and the organic matter adsorbed to them), as hypothesized, since the Al oxyhydroxide content was much higher in the Andosol than in the Ferralsol (Table 1). Instead our findings suggest that the large effect of P addition on OC desorption in the Ferralsol was due to the high content of oxalate-extractable Fe and the type of Fe oxyhydroxides dominating in the Ferralsol, which are hematite and goethite. This interpretation is supported by a study showing that the phosphate addition had a strong negative effect on sorption of DOC onto hematite (Hur and Schlautmann, 2004). It also needs to be considered that the largest amount of DOC per unit soil TOC was desorbed in the Podzol in response to phosphate addition (Table 4). This shows that OM desorption in Podzols is also susceptible to phosphate addition, in agreement with previous studies (Camps-Arbestain et al., 2002; Bonifacio et al., 2013). Furthermore, it needs to be considered that the increase in pH that was induced by the Na_2HPO_4

addition contributed to the desorption of OC, which might explain why we found no correlation between the adsorbed P and the desorbed OC for the Podzol, but only for the Ferralsol and the Andosol (Table 5 and Fig. S1).

4.3. Molecular size of desorbed DOC

Phosphate addition caused desorption of organic matter of medium molecular size (10–100 and 100–1000 kDa) in the Ferralsol and in the Andosol, and of large molecular size (>1000 kDa) in the Podzol. Our findings question statements of recent synthesis studies saying that organic compounds that sorb to mineral surfaces are mostly small (<600 kDa) (Sokol et al., 2019; Basile-Doelsch et al., 2020). Instead, our findings indicate that SOM adsorbed to mineral surfaces includes compounds with sizes of 600–1000 kDa and even > 1000 kDa. However, it needs to be considered that dissolved organic compounds are usually aggregated in soil solution due to their charge and hydrophobicity which makes them act as a supramolecular structure (Piccolo, 2001, 2002; Sutton and Sposito, 2005).

The addition of KCl led to a shift in the size distribution of the DOC in the soil solution towards small compounds (<10 kDa). This is likely because KCl addition affected the aggregation of the DOC compounds. This is supported by previous studies showing that the addition of HCl to DOC strongly affected the apparent size of the DOC compounds because it changed their aggregation (Piccolo, 2002; Simpson et al., 2002) and that organic substances can be connected through K cations (Verdugo et al., 2004). Yet, the different apparent molecular size of the DOC in the KCl treatment compared to control treatment (water only) did hardly have an effect the mineralization of the organic C (Fig. 2).

Taken together, the results indicate that DOC compounds interact in complex ways, which strongly affects their apparent size and likely other DOC properties. Thus, future studies should explore how changes in the soil solution, for instance due to the addition of fertilizers, affect the interactions between DOC compounds and the properties and behavior of this supramolecular structure, rather than trying to isolate single DOC compounds. Furthermore, our results shows that sorption also stabilizes medium and large molecular size organic matter in soils.

4.4. Phosphate addition and organic C retention in soils

We found that phosphate addition decreased OC retention in the Ferralsol and the Andosol. These results indicate that phosphate addition cannot only render adsorbed organic matter available to microbes by desorbing it, but it can also prevent the adsorption of newly added dissolved organic matter (DOM) by occupying potential sorption sites. This might lead not only to a loss of OC directly after phosphate application but might also decrease OC retention in the soil in the long-term because the adsorbed phosphate hampers the capacity of the soil to protect the organic matter against decomposition through sorption. Our results are in accordance with previous sorption experiments reporting that phosphate addition reduced DOC adsorption (Gu et al., 1994; Kaiser and Zech, 1997; Hur and Schlautman, 2004; Kahle et al., 2004; Hunt et al., 2007; Schneider et al., 2010). Our finding that the DOC retention was the largest in the Andosol (both in the control and in the phosphate addition treatment) can likely be attributed to the fact that the soil contained a high amount of amorphous aluminosilicates whose sorption sites were not as saturated with OC as in the Ferralsol, as indicated by the lower TOC content of the Andosol in comparison to the Ferralsol (Table 1).

Our finding that phosphate addition to soils can lead to destabilization of OC and that phosphate blocks sorption sites has crucial implications for the sustainable use of soils. Our study provides a mechanistic explanation of why phosphate addition to soil can impair soil OC sequestration as found in field experiments. For instance, it has been shown that the soil OC stocks declined by 4.2 Mg ha⁻¹ due to combined P and potassium application in comparison to a non-fertilized

control in a 40-year old cropland experiment in Sweden (Poeplau et al., 2016). Further, Mack et al. (2004) showed that 20 years of combined N and P addition in Alaskan tundra decreased the OC concentration by 50% in the mineral topsoil. Moreover, in an alpine meadow on the Tibetan Plateau, four years of phosphate addition decreased the SOC concentration in the upper 20 cm by 13% (Li et al., 2018). Our study suggests that the reduced soil OC contents in these field experiments are due to decreased DOC adsorption caused by P fertilizer application. It is striking that these experiments were all conducted at high latitudinal or altitudinal sites. Our results suggest that the effects of phosphate addition might be largest in Ferralsols, which occur in the tropics and subtropics, mostly at low altitudes. Therefore, future research should explore how long-term phosphate addition affects soil OC sequestration in field experiments in soils with high contents of Fe oxyhydroxides that are typical of the tropics and subtropics. Finally, it also should be considered that other studies found no significant effect of P addition on soil organic C stocks in long-term field experiment (Schipper et al., 2011, 2013; Condon et al., 2012). This might indicate that the effect of P addition on soil C stocks depends on edaphic conditions and does only lead to organic C losses in some but not all soils. However, it could also be that even in these studies that reported no significant changes, P addition caused desorption of organic C which was not detected because it was compensated by increased C inputs due to elevated primary production caused by P fertilization. Furthermore, in many soils, OC that desorbs in the topsoil will be quickly transported to the subsoil and adsorb there. This process may alleviate or even prevent soil OC losses by phosphate amendment and may explain why some authors found no effect of P addition of SOC stocks. However, yet other studies (e.g. Coonan et al., 2020) even found a positive effect of P addition on soil organic C stock, showing that the effects of P addition on soil organic C storage likely depend on multiple factors and can be diverse.

5. Conclusion

This study shows that phosphate addition causes desorption of sorbed soil organic matter and also decreases further adsorption of organic matter. Our first hypothesis was confirmed, which stated that a large proportion of organic matter is desorbed by phosphate but not by chloride addition, which is likely due to the different way phosphate and chloride interact with soil minerals. Against our second hypothesis, we found that the amount of DOC that desorbed by phosphate addition was higher in a Ferralsol than in an Andosol, which is due to the higher content of hematite in the Ferralsol. We found no support for our third hypothesis since P addition also led to desorption of organic compounds substantially larger than 600 kDa, which indicates that sorption also stabilizes medium and large molecular size organic matter in soils. Our fourth hypothesis was confirmed, which said that high phosphate saturation of soils decreases the sorption of DOM and that this effect of phosphate on DOM sorption is especially high in the Andosol. Taken together, our study provides a mechanistic explanation of why phosphate addition to the soil can have a negative effect on soil OC sorption and why this effect might be more relevant in soil with high contents of Al and Fe oxyhydroxides. This mechanism should be considered in the analysis of land use and tillage on SOM sequestration in the future. The results of this study have far-reaching implications since the soil orders studied here represent a substantial part of the Earth's terrestrial surface and are intensively used for mineral fertilizer-based agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2021.115377>.

References

- Afif, E., Barrón, V., Torrent, J., 1995. Organic matter delays but does not prevent phosphate sorption by Cerrado soils from Brazil. *Soil Sci.* 159 (3), 207–211.
- Arai, Y., Sparks, D.L., 2007. Phosphate reaction dynamics in soils and soil components: a multiscale approach. *Adv. Agron.* 94, 135–179.
- Arbestain, M.C., Barreal, M.E., Macías, F., 2002. Phosphate and sulfate sorption in Spodosols with albic horizon from Northern Spain. *Soil Sci. Soc. Am. J.* 66 (2), 464–473.
- Barrow, N.J., 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. *J. Soil Sci.* 34 (4), 733–750.
- Barrow, N.J., Shaw, T.C., 1975. The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease in phosphate concentration in the soil solution. *Soil Sci.* 119 (2), 167–177.
- Basile-Doelsch, I., Balesdent, J., Pellerin, S., 2020. Reviews and syntheses: the mechanisms underlying carbon storage in soil. *Biogeosciences* 17 (21), 5223–5242.
- Beck, M.A., Robarge, W.P., Buol, S.W., 1999. Phosphorus retention and release of anions and organic carbon by two Andisols. *Eur. J. Soil Sci.* 50 (1), 157–164.
- Bertrand, S., Fagel, N., 2008. Nature, origin, transport and deposition of Andosol parent material in south-central Chile (36–42 S). *Catena* 73 (1), 10–22.
- Besoain, M., 1985. *Mineralogía de los Suelos Volcánicos del Centro-Sur de Chile*. In: Tosso, J. (Ed.) *Suelos Volcánicos de Chile*. pp. 109–152.
- Bonifacio, E., Catoni, M., Falsone, G., Said-Pullucino, D., Celi, L., 2013. Evolution of surface properties and organic matter stabilisation in Podzolic B horizons as assessed by nitrogen and phosphate sorption. *Biol. Fertil. Soils* 49 (5), 505–516.
- Cleveland, C.C., Reed, S.C., Townsend, A.R., 2006. Nutrient regulation of organic matter decomposition in a tropical rain forest. *Ecology* 87 (2), 492–503.
- Cleveland, C.C., Townsend, A.R., Schmidt, S.K., 2002. Phosphorus limitation of microbial processes in moist tropical forests: evidence from short-term laboratory incubations and field studies. *Ecosystems* 5 (7), 0680–0691.
- Condrón, L.M., Black, A., Wakelin, S.A., 2012. Effects of long-term fertiliser inputs on the quantities of organic carbon in a soil profile under irrigated grazed pasture. *N. Z. J. Agric. Res.* 55 (2), 161–164.
- Coonan, E.C., Richardson, A.E., Kirkby, C.A., Macdonald, L.M., Amidy, M.R., Strong, C. L., Kirkegaard, J.A., 2020. Carbon stability in a texture contrast soil in response to depth and long-term phosphorus fertilisation of grazed pasture. *Soil Res.* 58 (1), 21–34.
- Doetterl, S., Asifiwe, R., Baert, G., Bamba, F., Bauters, M., Boeckx, P., et al., 2021. Organic matter cycling along geochemical, geomorphic and disturbance gradients in forests and cropland of the African Tropics-Project TropSOC Database Version 1.0. *Earth System Science Data Discussions*, 1–46.
- Don, A., Schumacher, J., Freibauer, A., 2011. Impact of tropical land-use change on soil organic carbon stocks—a meta-analysis. *Glob. Change Biol.* 17 (4), 1658–1670.
- Eusterhues, K., Rumpel, C., Kögel-Knabner, I., 2005. Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores. *Eur. J. Soil Sci.* 56 (6), 753–763.
- Fisk, M., Santangelo, S., Minick, K., 2015. Carbon mineralization is promoted by phosphorus and reduced by nitrogen addition in the organic horizon of northern hardwood forests. *Soil Biol. Biochem.* 81, 212–218.
- FAO (Food and Agriculture Organization of the United Nations), 2006. *Guidelines for Soil Description*, fourth ed. Food and Agriculture Organization of the United Nations, Rome. (97 pp).
- Fransson, A.M., Jones, D.L., 2007. Phosphatase activity does not limit the microbial use of low molecular weight organic-P substrates in soil. *Soil Biol. Biochem.* 39 (5), 1213–1217.
- Goldberg, S., Sposito, G., 1985. On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: a review. *Commun. Soil Sci. Plant Anal.* 16 (8), 801–821.
- Griffiths, B.S., Spilles, A., Bonkowski, M., 2012. C: N: P stoichiometry and nutrient limitation of the soil microbial biomass in a grazed grassland site under experimental P limitation or excess. *Ecol. Processes* 1 (1), 6.
- Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* 28 (1), 38–46.
- Guan, X.-H., Shang, C., Chen, G.-H., 2006. Competitive adsorption of organic matter with phosphate on aluminum hydroxide. *J. Colloid Interface Sci.* 296 (1), 51–58.
- Heuck, C., Weig, A., Spohn, M., 2015. Soil microbial biomass C: N: P stoichiometry and microbial use of organic phosphorus. *Soil Biol. Biochem.* 85, 119–129.
- Hingston, F.J., Atkinson, R.J., Posner, A.M., Quirk, J.P., 1967. Specific adsorption of anions. *Nature* 215 (5109), 1459–1461.
- Hunt, J.F., Ohno, T., He, Z., Honeycutt, C.W., Dail, D.B., 2007. Inhibition of phosphorus sorption to goethite, gibbsite, and kaolin by fresh and decomposed organic matter. *Biol. Fertil. Soils* 44 (2), 277–288.
- Hur, J., Schlautman, M.A., 2004. Effects of pH and phosphate on the adsorptive fractionation of purified Aldrich humic acid on kaolinite and hematite. *J. Colloid Interface Sci.* 277 (2), 264–270.
- Jackson, R.B., Lajtha, K., Crow, S.E., Hugelius, G., Kramer, M.G., Piñeiro, G., 2017. The ecology of soil carbon: pools, vulnerabilities, and biotic and abiotic controls. *Annu. Rev. Ecol. Evol. Syst.* 48 (1), 419–445.
- Kahle, M., Kleber, M., Jahn, R., 2004. Retention of dissolved organic matter by phyllosilicate and soil clay fractions in relation to mineral properties. *Org. Geochem.* 35 (3), 269–276.
- Kaiser, K., Guggenberger, G., 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Org. Geochem.* 31 (7–8), 711–725.
- Kaiser, K., Zech, W., 1997. Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. *Soil Sci. Soc. Am. J.* 61 (1), 64–69.
- Kaiser, K., Zech, W., 1999. Release of natural organic matter sorbed to oxides and a subsoil. *Soil Sci. Soc. Am. J.* 63 (5), 1157–1166.
- Kirsten, M., Mikutta, R., Vogel, C., Thompson, A., Mueller, C.W., Kimaro, D.N., Bergsma, H.L.T., Feger, K.-H., Kalbitz, K., 2021. Iron oxides and aluminous clays selectively control soil carbon storage and stability in the humid tropics. *Sci. Rep.* 11 (1) <https://doi.org/10.1038/s41598-021-84777-7>.
- Kleber, M., Bourg, I.C., Coward, E.K., Hansel, C.M., Myneni, S.C., Nunan, N., 2021. Dynamic interactions at the mineral–organic matter interface. *Nat. Rev. Earth Environ.* 1–20.
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Mineral–organic associations: formation, properties, and relevance in soil environments. In *Advances in Agronomy* (vol. 130, pp. 1–140). Academic Press.
- Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., Leinweber, P., 2008. Organo-mineral associations in temperate soils: integrating biology, mineralogy, and organic matter chemistry. *J. Plant Nutr. Soil Sci.* 171 (1), 61–82.
- Li, J.H., Hou, Y.L., Zhang, S.X., Li, W.J., Xu, D.H., Knops, J.M.H., Shi, X.M., 2018. Fertilization with nitrogen and/or phosphorus lowers soil organic carbon sequestration in alpine meadows. *Land Degrad. Development* 29 (6), 1634–1641.
- Li, Y., Wang, T., Camps-Arbestain, M., Suárez-Abelenda, M., Whitty, C.P., 2020. Lime and/or phosphate application affects the stability of soil organic carbon: evidence from changes in quantity and chemistry of the soil water-extractable organic matter. *Environ. Sci. Technol.*
- Liu, F., He, J., Colombo, C., Violante, A., 1999. Competitive adsorption of sulfate and oxalate on goethite in the absence or presence of phosphate. *Soil Sci.* 164 (3), 180–189.
- Liu, L., Gundersen, P., Zhang, T., Mo, J., 2012. Effects of phosphorus addition on soil microbial biomass and community composition in three forest types in tropical China. *Soil Biol. Biochem.* 44 (1), 31–38.
- Lützow, M.V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *Eur. J. Soil Sci.* 57 (4), 426–445.
- Mack, M.C., Schuur, E.A., Bret-Harte, M.S., Shaver, G.R., Chapin, F.S., 2004. Ecosystem carbon storage in arctic tundra reduced by long-term nutrient fertilization. *Nature* 431 (7007), 440–443.
- Mayer, L.M., 1994. Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* 58 (4), 1271–1284.
- Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., Jahn, R., 2007. Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochim. Cosmochim. Acta* 71 (10), 2569–2590.
- Miyazawa, M., Takahashi, T., Sato, T., Kanno, H., Nanzyo, M., 2013. Factors controlling accumulation and decomposition of organic carbon in humus horizons of Andosols. *Biol. Fertil. Soils* 49 (7), 929–938.
- Munevar, F., Wollum, A.G., 1977. Effects of the addition of phosphorus and inorganic nitrogen on carbon and nitrogen mineralization in andepts from Colombia 1. *Soil Sci. Soc. Am. J.* 41 (3), 540–545.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.
- Neff, J.C., Hobbie, S.E., Vitousek, P.M., 2000. Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils. *Biogeochemistry* 51, 283–302.
- Nottingham, A.T., Turner, B.L., Stott, A.W., Tanner, E.V.J., 2015. Nitrogen and phosphorus constrain labile and stable carbon turnover in lowland tropical forest soils. *Soil Biol. Biochem.* 80, 26–33.
- Piccolo, A., 2001. The supramolecular structure of humic substances. *Soil Sci.* 166 (11), 810–832.
- Piccolo, A., 2002. The supramolecular structure of humic substances: a novel understanding of humus chemistry and implications in soil science. *Adv. Agron.* 75, 57–134.

- Poepflau, C., Bolinder, M.A., Kirchmann, H., Kätterer, T., 2016. Phosphorus fertilisation under nitrogen limitation can deplete soil carbon stocks: evidence from Swedish meta-replicated long-term field experiments. *Biogeosciences* 13 (4), 1119–1127.
- Post, W.M., Kwon, K.C., 2000. Soil carbon sequestration and land-use change: processes and potential. *Glob. Change Biol.* 6 (3), 317–327.
- Schipper, L.A., Dodd, M.B., Fisk, L.M., Power, I.L., Parendee, J., Arnold, G., 2011. Trends in soil carbon and nutrients of hill-country pastures receiving different phosphorus fertilizer loadings for 20 years. *Biogeochemistry* 104 (1), 35–48.
- Schipper, L.A., Dodd, M.B., Pronger, J., Mudge, P.L., Upsdell, M., Moss, R.A., 2013. Decadal changes in soil carbon and nitrogen under a range of irrigation and phosphorus fertilizer treatments. *Soil Sci. Soc. Am. J.* 77 (1), 246–256.
- Schlüter, T., Trauth, M.H., 2006. Geological atlas of Africa: with notes on stratigraphy, tectonics, economic geology, geohazards and geosites of each country. Springer, Berlin, New York.
- Schneider, M.P.W., Scheel, T., Mikutta, R., van Hees, P., Kaiser, K., Kalbitz, K., 2010. Sorptive stabilization of organic matter by amorphous Al hydroxide. *Geochim. Cosmochim. Acta* 74 (5), 1606–1619.
- Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. *Zeitschrift für Pflanzenernährung, Düngung, Bodenkunde* 105 (3), 194–202.
- Simpson, A.J., Kingery, W.L., Hayes, M.H., Spraul, M., Humpfer, E., Dvorsak, P., Kerssebaum, R., Godejohann, M., Hofmann, M., 2002. Molecular structures and associations of humic substances in the terrestrial environment. *Naturwissenschaften* 89 (2), 84–88.
- Scott, J.T., Lambie, S.M., Stevenson, B.A., Schipper, L.A., Parfitt, R.L., McGill, A.C., 2015. Carbon and nitrogen leaching under high and low phosphate fertility pasture with increasing nitrogen inputs. *Agric. Ecosyst. Environ.* 202, 139–147.
- Sokol, N.W., Sanderman, J., Bradford, M.A., 2019. Pathways of mineral-associated soil organic matter formation: Integrating the role of plant carbon source, chemistry, and point of entry. *Glob. Change Biol.* 25 (1), 12–24.
- Sollins, P., Homann, P., Caldwell, B.A., 1996. Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma* 74 (1-2), 65–105.
- Spohn, M., 2020. Phosphorus and carbon in soil particle size fractions: a synthesis. *Biogeochemistry* 147 (3), 225–242.
- Spohn, M., Schless, P.-M., 2019. Addition of inorganic phosphorus to soil leads to desorption of organic compounds and thus to increased soil respiration. *Soil Biol. Biochem.* 130, 220–226.
- Strickland, M.S., Callahan, M.A., Davies, C.A., Lauber, C.L., Ramirez, K., Richter, D.D., Fierer, N., Bradford, M.A., 2010. Rates of in situ carbon mineralization in relation to land-use, microbial community and edaphic characteristics. *Soil Biol. Biochem.* 42 (2), 260–269.
- Stumm, W., Kummert, R., Sigg, L., 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croat. Chem. Acta* 53 (2), 291–312.
- Sutton, R., Sposito, G., 2005. Molecular structure in soil humic substances: the new view. *Environ. Sci. Technol.* 39 (23), 9009–9015.
- Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., Hendricks, D.M., 1997. Mineral control of soil organic carbon storage and turnover. *Nature* 389 (6647), 170–173.
- Verdugo, P., Alldredge, A.L., Azam, F., Kirchman, D.L., Passow, U., Santschi, P.H., 2004. The oceanic gel phase: a bridge in the DOM–POM continuum. *Mar. Chem.* 92 (1-4), 67–85.
- Violante, A., Gianfreda, L., 1993. Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex. *Soil Sci. Soc. Am. J.* 57 (5), 1235–1241.
- Zhang, M., Zhang, H., 2010. Co-transport of dissolved organic matter and heavy metals in soils induced by excessive phosphorus applications. *J. Environ. Sci.* 22 (4), 598–606.