Soil Biology and Biochemistry 194 (2024) 109428

Contents lists available at ScienceDirect

Soil Biology and Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

Preferential adsorption of nitrogen- and phosphorus-containing organic compounds to minerals in soils: A review

Marie Spohn

Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), Lennart Hjelms Väg 9, P.O. Box 7014, 75007, Uppsala, Sweden

ARTICLE INFO

Keywords:
Organo-mineral interaction
Soil organic matter
Stoichiometry
Organic phosphorus
Organic nitrogen
Adsorption

ABSTRACT

There is growing evidence that many nitrogen- and phosphorus-containing organic compounds in soils have on average a higher affinity for adsorption to mineral surfaces than nutrient-free organic compounds. This leads to preferential enrichment of organic nitrogen and phosphorus on mineral surfaces and has important implications for the architecture of organo-mineral associations in soils. Furthermore, the preferential adsorption of organic nitrogen and organic phosphorus compounds likely also influences carbon, nitrogen, and phosphorus cycling in terrestrial ecosystems since sorption of organic compounds to minerals slows down their decomposition. This contribution reviews studies on the sorption of soil organic nitrogen and phosphorus to minerals, guided by the questions; what compounds are soil organic nitrogen and phosphorus composed of and why do these compounds have a comparably high affinity to adsorb to minerals? How do soil properties influence adsorption of organic nitrogen and phosphorus to minerals and why does preferential adsorption of organic nitrogen and phosphorus matter for element cycling? Furthermore, this article identifies hypotheses for future research about the structure of organo-mineral associations, biochemical element cycling, and the role of stoichiometry for soil organic matter dynamics.

1. Introduction

Soil organic matter is rich in organic nitrogen (ON) and organic phosphorus (OP) compared to plant detritus (Zechmeister-Boltenstern et al., 2015; Spohn, 2020a). This is because microorganisms respire a large share of the carbon (C) during the decomposition of plant detritus, leading to relative enrichment of ON and OP in the organic matter, and they build up microbial biomass, which is nitrogen- and phosphorus-rich compared to plant litter (Xu et al., 2013; Zechmeister-Boltenstern et al., 2015; Spohn, 2020a). In addition, soil organic matter is nitrogen (N) and phosphorus (P) rich compared to plant detritus because ON and OP preferentially adsorb to mineral surfaces, which likely decreases their decomposition in soils relative to N- and P-free organic compounds.

Organic phosphorus compounds contain one or more phosphate group(s), while many ON compounds contain at least one amino and one carboxyl group. These functional groups give ON and OP compounds a high affinity to adsorb to mineral surfaces, which leads to their preferential enrichment in mineral-associated organic matter. The results of preferential enrichment of ON and OP on mineral surfaces can be observed at the spatial scale of soil fractions and soil horizons. Spohn (2020a, b) reviewed data on OP and organic carbon (OC) in soil particle size fractions and found that OP is more strongly enriched in the clay size fraction than OC, leading to relatively low OC:OP ratios in the clay size fraction. In addition, Amorim et al. (2022) reviewed data on OC and ON in soil particle size fractions and showed that the OC:ON ratio was lower in the clay size fraction than in the sand size fraction. These results are in accordance with studies about element ratios of mineral-associated organic matter. For instance, Cotrufo et al. (2019) reported that the C:N ratio of mineral-associated organic matter was lower and less variable than that of particulate organic matter. Furthermore, it was found that ON, and particularly OP, were more strongly concentrated than OC in fine-textured soils compared to coarse-textured soils (Spohn and Stendahl, 2022, 2024). The reason for these spatial patterns of OC, ON, and OP is very likely the high affinity of ON and OP compounds to adsorb to mineral surfaces, leading to preferential adsorption of nutrient-rich organic matter on mineral surfaces.

Sorption of ON and OP compounds to mineral surfaces can reduce their decomposition, and thus the rate at which they are converted into inorganic N and P (von Lützow et al., 2006; Kögel-Knabner et al., 2008; Schmidt et al., 2011; Kleber et al., 2015; Hemingway et al., 2019; Wiesmeier et al., 2019). This is relevant for primary production since ON and OP decomposition limit the supply of N and P for primary

---

E-mail address: marie.spohn@slu.se.

https://doi.org/10.1016/j.soilbio.2024.109428
Received 3 October 2023; Received in revised form 7 April 2024; Accepted 11 April 2024
Available online 13 April 2024

production in many ecosystems (Vitousek et al., 2010; Cleveland et al., 2013; Terrer et al., 2019) since plants cannot take up organic P (Vance et al., 2003) and only take up limited amounts of organic N (Jones et al., 2005; Näsholm et al., 2009). The preferential adsorption of ON and OP may contribute to the sorptive stabilization of organic matter (Kleber et al., 2007). Yet, the importance of ON and OP for the formation of organo-mineral complexes is poorly understood (Newcomb et al., 2017), despite the fact that it is increasingly believed that organo-mineral complexes play an important role in the stabilization of soil organic matter (von Lützow et al., 2006; Kleber et al., 2007; Kögel-Knabner et al., 2008; Schmidt et al., 2011).

The objective of this paper is to review studies about sorption of OC, ON, and OP with the aim to synthesize widely dispersed studies about this topic and to identify hypotheses for future research about soil organic matter and nutrient cycling. I will not tackle the question of how minerals affect plant and microbial N and P uptake since this is discussed in previous reviews (Hinsinger, 2001; Jilling et al., 2018). Instead, I concentrate on synthesizing emerging answers to the questions of why there is preferential adsorption of ON and OP in soils, which factors affect the sorption processes, and why this is important for the architecture of soil organic matter and element cycling. The first part of this review briefly summarizes chemical properties of soil organic matter and different interactions in which it can engage with minerals. The following parts of the review compile results about sorption of N- and P-containing organic compounds, in particular under conditions in which they compete for binding sites with other compounds. Subsequently, the review summarizes studies about the question, how sorption of ON and OP is affected by specific minerals, soil pH, and ionic strength. In the following part of the review, the importance of sorption and desorption for decomposition of ON and OP compounds is reviewed, and finally, hypotheses for future research are derived and conclusions are drawn.

2. Soil organic matter and its interaction with minerals

Soil organic matter contains multiple functional groups with pH-variable charge, which allow soil organic matter to adsorb to minerals. Carboxyl, hydroxyl, phosphate, thiol, and phenolic groups are negatively charged upon deprotonation, while amino groups are positively charged when protonated (Blume et al., 2015; Newcomb et al., 2017). The protonation, and therefore the charge of these functional groups depends on the soil pH. The carboxyl group is the most abundant functional group of soil organic matter, and the acid dissociation constant (the pK_a value) of carboxyl groups ranges between 2 and 6, depending on the functional groups in their vicinity (Blume et al., 2015). Hence, the net charge of organic matter is negative.

Sorption of soil organic matter to minerals depends not only on the charge of the organic matter but also on the surface charge of minerals. Oxides and hydroxides of iron, aluminum, silicon, and manganese as well as allophanes and imogolites have pH-variable surface charge and are positively charged under acidic conditions. In contrast, most silicates in soils have mainly permanent negative surface charge and some pH-variable charge at their edges (Blume et al., 2015; Kleber et al., 2015). An organic compound can adsorb to a positively charged mineral via a negatively charged functional group (for instance a phosphate group). Furthermore, organic matter can adsorb to a negatively charged mineral through a positively charged group (for instance an amino group) or through a negatively charged group and a multivalent metal cation that acts as a metal bridge (von Lützow et al., 2006; Kögel-Knabner et al., 2008; Kunhi Mouvenchery et al., 2012; Kleber et al., 2015).

Soil organic matter adsorbs to mineral surfaces in different ways. Organic matter sorbs onto minerals through electrostatic interaction, commonly referred to as outer-sphere complexation or non-specific sorption. In addition, some organic compounds, for instance OP compounds, can bind to minerals through ligand exchange-surface complexation, also called inner-sphere complexation or specific sorption (Gu et al., 1994, 1996; Stumm et al., 1980). Ligand exchange-surface complexation refers to structural metal cations, mostly iron and aluminum, replacing their coordinative OH or OH_2 ligand with another ligand, which can be an organic or inorganic anion (Stumm et al., 1980). The energies associated with ligand exchange-surface complexation are much higher than those of electrostatic interactions (Gu et al., 1994, 1996; Stumm et al., 1980; Kleber et al., 2015). In addition to specific and unspecific sorption, hydrophobic interactions and hydrogen bonding also contribute to organo-mineral interactions in soils (Kaiser and Guggenberger, 2000; Kleber et al., 2015).

OP compounds and amino acids can adsorb to mineral surfaces via ligand exchange-surface complexation (i.e., inner-sphere complexation), which creates a high-energy bond, in contrast to many N- and P-free organic compounds. OP compounds can adsorb to minerals through ligand-exchange surface complexation via their phosphate moiety (Gu et al., 1994, 1996; Stumm et al., 1980; Omoike et al., 2004; Kleber et al., 2015). Specifically, OP compounds with multiple phosphate moieties, such as inositol-hexa-phosphate (also called phytate; Fig. 1), can bind via several of these functional groups to minerals through ligand-exchange surface complexation (Ognalaga et al., 1994). Furthermore, amino acids can adsorb to minerals through ligand-exchange surface complexation via their carboxyl groups (Gu et al., 1994, 1996; Duckworth and Martin, 2001; Parikh et al., 2011).

While soil organic matter is N- and P-rich compared to plant litter, N- and P-containing organic compounds still constitute only a small proportion of the soil organic matter (Kögel-Knabner, 2006; Kirkby et al., 2011; Zechmeister-Boltenstern et al., 2015; Tipping et al., 2016; Spohn, 2020a). Soil organic matter is dominated by N- and P-free organic compounds that tend to have a comparatively low charge density. Specifically, soil organic matter consists to a large extent of polysaccharides and aromatic compounds which have only a low affinity to bind to minerals (Guggenberger et al., 1995 ; Kölbl and Kögel-Knabner, 2004; Vancampenhout et al., 2009), in contrast to N- and P-containing compounds. In their phosphorylated form (i.e., as a phosphomonoester), organic compounds have a much higher affinity to adsorb to minerals than in their non-phosphorylated form (Fransson and Jones, 2007).

Taken together, many N- and P-containing organic compounds can hold charge through their functional groups and can adsorb to minerals through ligand-exchange surface complexation, creating a more stable bond than compounds only interacting with minerals through non-specific sorption or hydrophobic interactions. In the following two chapters, I will tackle the questions, what compounds are soil organic nitrogen and phosphorus composed of and why do these compounds have a comparably high affinity to adsorb to minerals?

3. Sorption of ON to minerals

Soil ON consists mainly of proteinaceous material, peptides, and amino acids, while a smaller proportion of the total soil ON consists of amino sugars as well as DNA and RNA (Knicker, 2004, 2011). Organic N compounds, and especially amino acids, have a high charge density. All amino acids hold at least one carboxyl group and one amino group. In addition, some amino acids (aspartic acid and glutamic acid) have a second carboxyl group, while others (lysine, arginine, and histidine) have a second amino group (Fig. 1A), giving them a net negative or net positive charge. The amino groups of amino acids have a pK_a of approximately 9.0–10.5, and the carboxyl groups have a pK_a of approximately 2.0–2.4 (Nelson and Cox, 2004). Thus, in most soils, the amino group is protonated and the carboxyl group is deprotonated. Carboxylates, such as amino acids, adsorb via strong ligand-exchange surface complexation through their carboxyl groups at low pH, while electrostatic interaction predominates at neutral and alkaline pH (Boily et al., 2000; Hwang and Lenhart, 2008; Strahm and Harrison, 2008; Parikh et al., 2011).

Amino acids have a high affinity for adsorption to mineral surfaces (Knicker, 2004) and they bind on average more strongly to minerals than the total dissolved organic matter pool (Aufdenkampe et al., 2001).

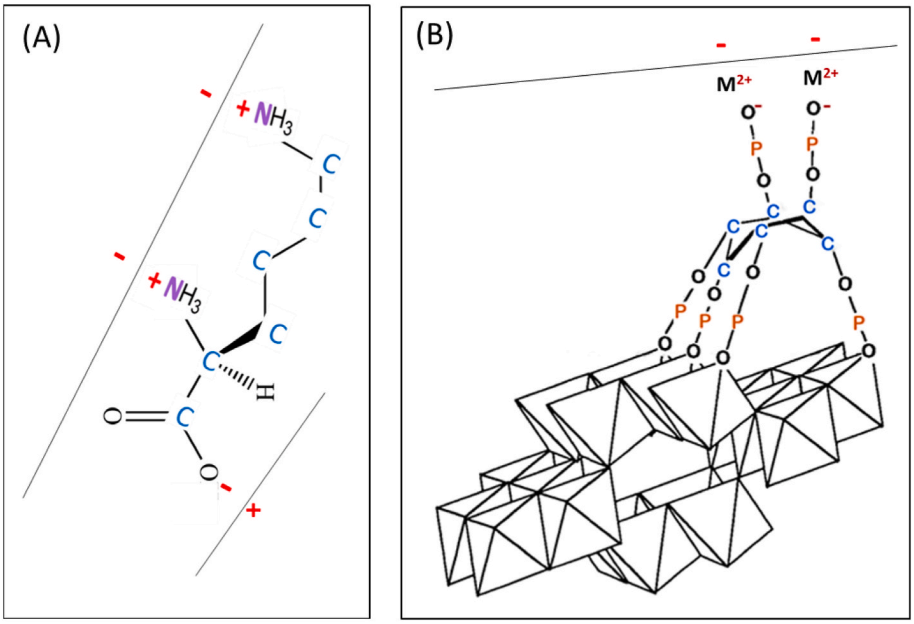

Fig. 1. Many organic nitrogen and organic phosphorus compounds have a high charge density and a high affinity to adsorb to charged mineral surfaces. For example, (A) the amino acid lysine contains several charged functional groups through which it can adsorb to negatively and positively charged mineral surfaces and interact with metal cations (M^{2+}). In addition, (B) phytate (also called inositol-hexaphosphate) contains several phosphate groups, which allow it to adsorb through ligand exchange-surface complexation to iron oxides (for example goethite) and to negatively charged clay minerals via bivalent metal cations (M^{2+}). Panel B is adapted from Ognalaga et al. (1994).

Specifically, positively charged amino acids have a higher adsorption coefficient than neutral or negatively charged amino acids (Wang and Lee, 1993; Jones and Hodge, 1999; Aufdenkampe et al., 2001; Ding and Henrichs, 2002; Rothstein, 2009; Moon et al., 2016, 2019). For instance, it was shown that positively charged amino acids were 431% enriched in mineral-associated organic matter compared to the whole soil (Moon et al., 2016). The only study, known to me, that specifically examined the sorption of sulfur-containing amino acids found that they have an even higher affinity for binding to minerals than positively charged amino acids (Moon et al., 2019).

While amino acids and peptides can adsorb to minerals via strong ligand-exchange surface complexation at low pH, small proteins interact with minerals through electrostatic interactions and they can intercalate in the interlayers of clay minerals (Yu et al., 2013). Yet, large proteins typically interact with minerals through weak van der Waals forces and hydrophobic interactions (Haynes and Norde, 1994; Yu et al., 2013). Furthermore, the nucleic acids DNA and RNA adsorb through the charge at their nucleobases (adenine, guanine, and cytosine) to minerals via electrostatic interactions as well as through the phosphate group at their ends via ligand exchange-surface complexation (Cai et al., 2007; Yu et al., 2013).

4. Sorption of OP to minerals

Phosphorus is present in soil organic matter in the form of phosphomonoesters, such as inositol-hexa-phosphate (Fig. 1B), adenosine-phosphates, nucleotides, and sugar-phosphates as well as phosphodiesters, such as DNA, RNA and some phospholipids. To a lesser extent P also occurs in soils in the form of phosphonates (Condron et al., 2005). The dominant OP compound in mineral soils is the phosphomonoester inositol-hexaphosphate, also called phytate (Darch et al., 2014; Deiss et al., 2018). Phytate accounts for approximately 40% of the total soil OP, while other phosphomonoesters account for 43%, and phosphodiesters account for 17% of the total soil OP pool (Darch et al., 2014). The phosphate group can release up to three protons, and the corresponding pK_a values are 2.1, 7.2, and 12.7 (Nelson and Cox, 2004). Thus, the phosphate group in most soils has a single negative charge ($H_2PO_4^-$).

Organic P compounds adsorb to metal oxides mostly through ligand exchange-surface complexation as well as through electrostatic interaction (Goldberg and Sposito, 1985; Ognalaga et al., 1994; Cagnasso et al., 2010; Fang et al., 2012; Parikh et al., 2014; Chen and Arai, 2019). For instance, extracellular polymeric substances from bacteria bind to iron on goethite mainly via inner-sphere complexation of phosphate-containing molecules (Omoike et al., 2004; Cagnasso et al., 2010; Fang et al., 2012; Parikh et al., 2014; Chen and Arai, 2019). The importance of inner-sphere bonds between OP and iron was also confirmed specifically for soil organic matter (Eusterhues et al., 2023).

Organic phosphorylated compounds differ in their affinity to sorb to charged surfaces in soil. Phosphomonoesters with multiple phosphate groups (for instance inositol-phosphates) have a very high affinity to sorb to minerals and they can bind to metal oxides through several of their phosphate groups (McKercher and Anderson, 1989; Ognalaga et al., 1994; Martin et al., 2004; Celi and Barberis, 2005; Berg and Joern, 2006; Ruttenberg and Sulak, 2011; Yan et al., 2014). In contrast, most phosphodiesters have a lower charge density than orthophosphate and phosphomonoesters and their charge is considerably shielded, which results in a lower affinity of phosphodiesters to adsorb to minerals in soils (Stewart and Tiessen, 1987; Darch et al., 2014).

The persistence of different OP compounds in soils varies. Although phosphodiesters constitute the majority of OP inputs from plant litter to soils, they decompose rapidly and therefore represent only a small fraction (approximately 10–20%) of OP in soils (Stewart and Tiessen, 1987; Condron et al., 2005). In the mineral soil, phosphomonoesters dominate over phosphodiesters, and the reason for this is likely that phosphodiesters have a lower charge density, which results in a lower affinity for adsorption to soil minerals (Stewart and Tiessen, 1987), and hence in a lower protection against decomposition (see chapter 8). Yet, sorption of OP and ON compounds also depends on other solutes, as discussed in the next chapter.

5. Competitive sorption of OC, ON, and OP

Several studies quantified the competitive adsorption of dissolved OC, ON, and OP to minerals in batch experiments. Many of these studies used extracellular polymeric substances (EPS), which are compounds released by microorganisms. Cao et al. (2011) investigated adsorption of EPS-C, EPS-N, and EPS-P to montmorillonite, kaolinite, and goethite, and determined the affinity constant K for the three elements based on Langmuir sorption isotherms (Fig. 2). The affinity constant K characterizes the adsorption affinity of a compound. Cao et al. (2011) reported that the affinity constant K was 3.5 times larger for EPS-N than for EPS-C in experiments with montmorillonite, and 6.1 times larger in experiments with kaolinite. Furthermore, Cao et al. (2011) reported that the affinity constant K was larger for EPS-P than for EPS-C by a factor of 648, 16, and 7 in experiments with montmorillonite, kaolinite, and goethite, respectively. Omoike and Chorover (2006) also determined the affinity constant K based on Langmuir isotherms for EPS-C, EPS-N and EPS-P in experiments with goethite. In accordance with Cao et al. (2011), they reported that the affinity constants were much larger for EPS-P than for EPS-C. Specifically, K was larger for EPS-P than for EPS-C by a factor of 714–2397, at an ionic strength of 1 and 100 mM, respectively. Furthermore, Omoike and Chorover (2006) observed that the affinity constant K for adsorption to goethite was larger for EPS-N than for EPS-C. In particular, K for EPS-N was between 3 and 17 times larger than for EPS-C at anion strengths of 1 and 100 mM, respectively. Taken together, these results indicate, first, that OP compounds have a higher affinity for adsorption to different minerals than ON and OC, and second, that ON has a higher affinity than OC for adsorption to clay minerals.

Other studies also quantified the adsorption of dissolved OC, ON, and OP in batch experiments, but they did not determine the affinity constant using Langmuir isotherms, making it more difficult to compare the affinity of OC, ON, and OP to adsorb to a mineral. Nevertheless, these studies allow semi-quantitative comparisons. Mikutta et al. (2011) studied the adsorption of EPS to short-range order aluminum oxides and reported that the proportion of adsorbed EPS increased in batch experiments in the order EPS-C < EPS-N < EPS-P. Similarly, Zhang et al. (2021) studied adsorption of EPS to ferrihydrite (i.e., a short-range order iron oxide) and also reported that the proportion of adsorbed EPS increased in the order EPS-C < EPS-N < EPS-P. Furthermore, Lin et al. (2016) investigated adsorption of EPS-C, EPS-N, and EPS-P to montmorillonite, kaolinite, and goethite, and their findings confirmed the results of Cao et al. (2011).

One outstanding study explored the competitive sorption of a very diverse pool of microbial metabolites to ferrihydrite, using a lysate prepared from a bacterium (Swenson et al., 2015). After incubation with the mineral, phosphate-containing metabolites showed the highest degree of sorption followed, first, by dicarboxylates, i.e., compounds containing two carboxyl groups, and second, by metabolites containing both N and an aromatic moiety (Fig. 3). Thus, the study demonstrates that ON compounds, and particularly OP compounds, have a high affinity to adsorb to mineral surfaces. Still, it also indicates that compounds containing two carboxyl groups have a high affinity to adsorb to ferrihydrite, even if they do not contain N, as in the case of fumarate (Fig. 3). Strong sorption of N-rich compounds of soil organic matter to mineral surfaces (Kopittke et al., 2018) and particularly to iron oxides (Keiluweit et al., 2012) was also demonstrated in incubation studies using nano-scale secondary ion mass spectrometry (NanoSIMS). Taken together, these results indicate, first, that OP compounds have a higher affinity for adsorption to clay minerals and iron oxides than ON and OC, and second, that ON has a higher affinity than OC for adsorption to clay minerals, likely with the exception of OC compounds that contain several carboxyl groups. How sorption of ON and OP is affected by the specific properties of different minerals will be discussed in the next chapter.

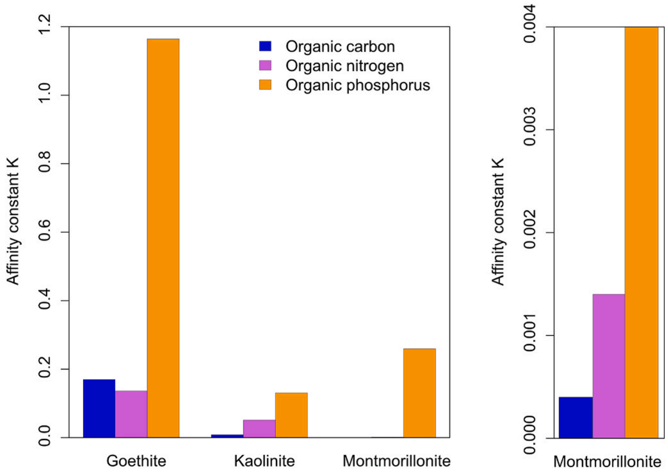

Fig. 2. The affinity constant K of organic carbon (OC), organic nitrogen (ON), and organic phosphorus (OP) for sorption to the iron oxide goethite and the clay minerals kaolinite and montmorillonite. The affinity constant K was derived from Langmuir adsorption isotherms. Due to the very low values, the affinity constants for montmorillonite are also shown in a second graph with an adjusted y-axis. The figure was prepared based on results presented in Cao et al. (2011).

6. Sorption of ON and OP to different minerals

Minerals differ in their affinity to adsorb ON and OP compounds. Several studies showed that iron oxides have a higher affinity to adsorb ON or OP compounds than clay minerals. For instance, Cao et al. (2011) reported that OC, ON, and OP had a higher affinity to adsorb to the iron oxide goethite than to the clay minerals montmorillonite and kaolinite (Fig. 2). In addition, Celi et al. (1999) found that the maximum amount of adsorbed phytate was 0.27 μmol m^{-2} on kaolinite, 0.38 μmol m^{-2} on illite, and 0.64 μmol m^{-2} on goethite. Furthermore, Ding and Henrichs (2002) showed that the affinity constant for the adsorption of the protein Rubisco to minerals increased in the order illite < montmorillonite < goethite.

ON and OP sorb more strongly to short-range order iron and aluminum (oxyhydr)oxides than to other iron and aluminum (oxyhydr) oxides. Yan et al. (2014) investigated the adsorption of various OP compound to three aluminum (oxyhydr)oxides (short-range order $Al(OH)_3$, boehmite, and α-Al_2O_3), and observed that the maximum amounts of OP sorbed to aluminum (oxyhydr)oxides increased with decreasing crystallinity of the minerals. This finding is in accordance with studies reporting large amounts of OP and ON adsorbed to short-range order iron oxides (Zhang et al., 2021) and short-range order aluminum oxides (Mikutta et al., 2011). Swenson et al. (2015) showed that the short-range order iron oxide ferrihydrite adsorbed several OP compounds in large quantities as well as the negatively-charged amino acids aspartate and glutamate, but not the positively-charged amino acids arginine and lysine (Fig. 3).

Taken together, these studies suggest that iron and aluminum (oxyhydr)oxides, particularly those of short-range order, have a high affinity to adsorb OP compounds and negatively charged amino acids. The reason why short-range order oxides have a higher affinity for adsorbing ON and OP compounds than more crystalline (oxyhydr)oxides is most likely their higher charge density which is related to their high specific surface area (Wang et al., 2013). Given the large contents of short-range order iron and aluminum (oxyhydr)oxides in soils in the tropics (Coward et al., 2017), preferential sorption of ON and OP might be particularly strong in tropical soils. Sorption of ON and OP does not only depend on the specific minerals present in a soil, but also on soil pH and ionic strength, as discussed in the following chapter.

7. Sorption of ON and OP depends on pH and ionic strength

Sorption of organic compounds is pH-dependent since the pH affects the protonation of the pH-variable charge of minerals and organic matter and their binding form. For instance, DNA adsorbs very strongly to negatively charged minerals at pH < 5.0 due to the protonation of adenine, guanine, and cytosine in the DNA (Cai et al., 2007). In addition, the pH influences the binding form. At low pH, ligand-exchange surface

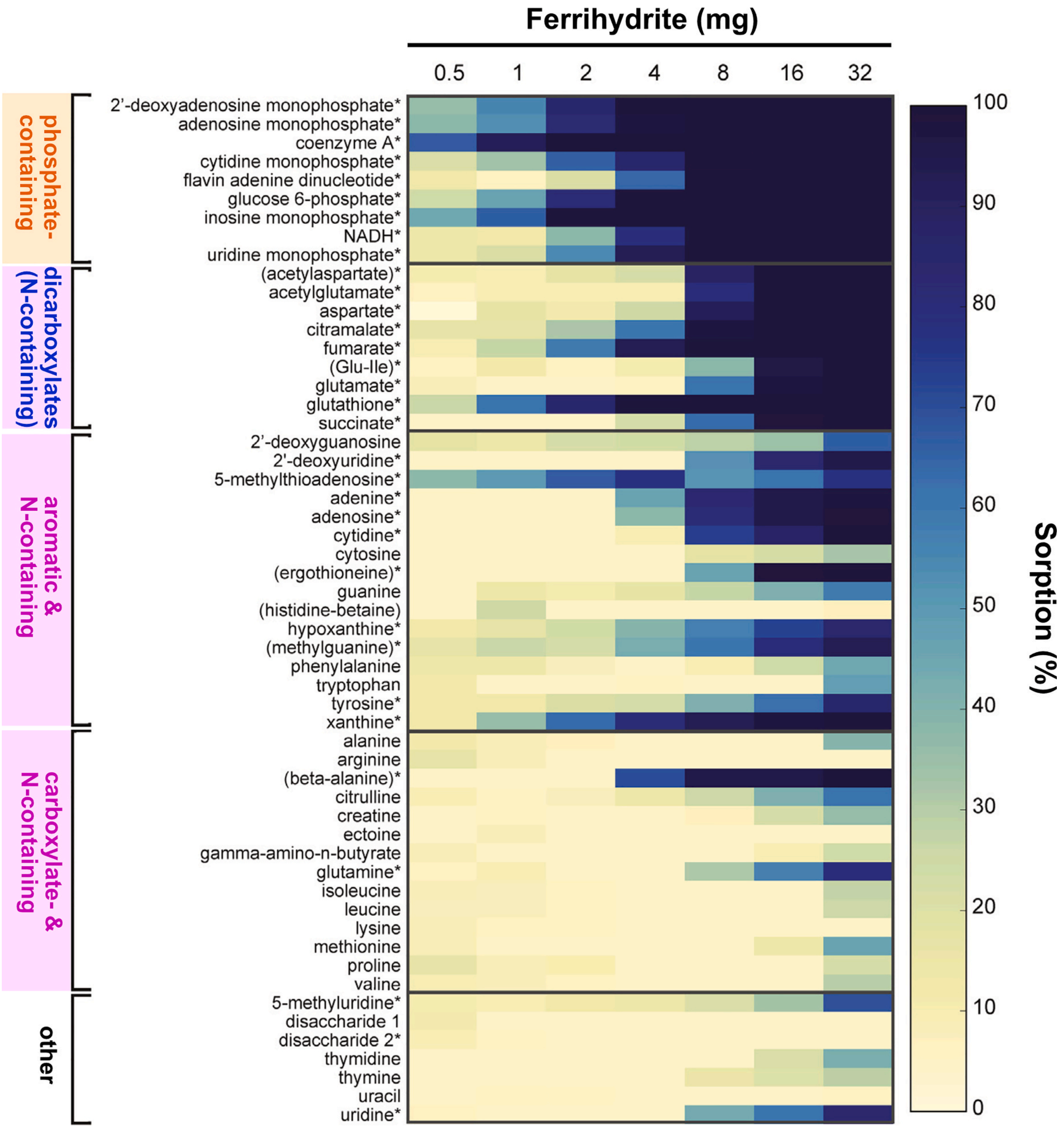

Fig. 3. Sorption of organic compounds to the short-range order iron oxide ferrihydrite. The compounds are grouped into phosphorus- and nitrogen-containing compounds as well as dicarboxylates (of which many also contain nitrogen). The dissolved compounds were incubated with different amounts of ferrihydrite, and their concentrations were determined using liquid chromatography/mass-spectrometry. Asterisks indicate significant differences ($P < 0.05$) in the concentrations of the compounds after incubation with the mineral compared to the solution before it was in contact with the mineral ($N = 5$). Figure adapted from Swenson et al. (2015).

complexation of carboxylates occurs, while at neutral and alkaline pH, usually non-specific sorption of carboxylates dominates (Boily et al., 2000; Hwang and Lenhart, 2008; Parikh et al., 2011). Thus, sorption of amino acids to clay minerals as well as iron and aluminum (hydr-)oxides is pH-dependent, and at low pH (pH < 4.0), a higher proportion of amino acids and other carboxylates is adsorbed than at elevated pH (Gu et al., 1996; Filius et al., 2000; Strahm and Harrison, 2008). Furthermore, pH affects the type of innersphere complexes that OP compounds and carboxylates form with minerals (Gao et al., 2009; Fang et al., 2012). For example, extracellular polymeric substances form monodentate innersphere complexes at pH 3.0, while they form bidentate inner-sphere complexes at pH 9.0 (Fang et al., 2012).

The pH also affects sorption of proteins. The highest number of molecules of a specific protein is adsorbed when the pH is close to the point of zero charge of the protein (Haynes and Norde, 1994; Meissner et al., 2015). This is because proteins contain multiple potentially charged domains, and at the point of zero charge, the electrostatic repulsion among proteins and between proteins and minerals is minimal (Meissner et al., 2015). Proteins differ widely in their point of zero charge (Haynes and Norde, 1994), which makes general predictions about protein adsorption in soils difficult.

In addition to pH, adsorption of OC, ON, and OP to minerals also depends on the ionic strength. Omoike and Chorover (2006) reported that the amounts of all three elements that adsorbed to goethite decreased strongly with increasing ionic strength (from 1 to 100 mM). However, the comparison of the K values for EPS-C and EPS-P at different ionic strengths (see section 5) also indicates that the preferential adsorption of OP relative to OC increases with increasing ionic strength. Sorption of organic compounds is strongly affected by ions that can form innersphere complexes. For instance, Spohn et al. (2022)

showed that even a small increase in the concentration of ions that are able to form innersphere complexes, such as ortho-phosphate, led to desorption of OC in soil, whereas an increase in the concentration of chloride ions that do not from innersphere complexes had no significant effect on OC desorption. Furthermore, it was shown in an experiment with a ^{14}C-labeled OP compound that the addition of ortho-phosphate even caused the desorption of the OP compound adenosine-monophosphate (Spohn and Schleuss, 2019). In addition to pH and ionic strength, redox conditions likely also affect sorption processes in soil, yet this aspect is comparatively little understood.

Soil microorganisms and plants can strongly contribute to desorption of adsorbed organic matter by altering the pH or the solute concentration (Hinsinger, 2001; Keiluweit et al., 2015; Bailey et al., 2019). This has very large effects on sorption and desorption of organic matter, for example in the rhizosphere, and hence also on the decomposition of organic compounds, as discussed in the following.

8. Desorption and decomposition

Sorption is one of the most important mechanisms that slows down decomposition of organic matter in soils. Sorption protects organic compounds against decomposition by steric hindrance since it physically prevents exoenzymes from binding to adsorbed organic compounds and catalyzing their decomposition. Furthermore, adsorbed compounds cannot be taken up by microorganisms (von Lützow et al., 2006; Kögel-Knabner et al., 2008; Schmidt et al., 2011; Kleber et al., 2015; Hemingway et al., 2019; Wiesmeier et al., 2019). Based on experiments with ^{15}N labeled amino acids, it has been shown that sorption to minerals restricts the uptake and mineralization of amino acids by microorganisms (Hunter et al., 2016). In addition, sorption can slow down the biodegradation of amino acids in soil (Vieublé Gonod et al., 2006). Specifically, Miltner et al. (2009) found that amino acids decomposed more slowly than the bulk organic matter in soil. They added ^{13}C labeled bacterial biomass to soil, and observed that after 224 days, the ^{13}C in the amino acid pool only decreased to 95% of its initial amount, while the total ^{13}C in the soil decreased to 44% of its initial amount. The results indicate that amino acids and peptides decompose more slowly than N-free organic compounds, which is likely due to their interaction with soil minerals. This has important implications for both N and C cycling because it implies that N remains in soil organic matter on average longer than C. In addition, it implies that C bound to N remains in soil for a longer period of time than the C of N-free organic compounds.

In contrast to ON, much less is known about the decomposition of OP compounds in soils. It seems likely that sorption has a very strong impact on the persistence of OP compounds in soils. This is indicated by the fact that phosphodiesters constitute the majority of OP in plant litter, but phosphomonoesters, which have a higher affinity to adsorb to minerals, dominate in soil (see chapter 4). However, little is known about decomposition of OP in soils. One main reason for this is that there is currently no compound-specific isotope method for determining the C isotope signature of OP compounds. Such a method would allow us to measure the decomposition of OP compounds both in experiments with ^{13}C labeled organic matter and at field sites with a historic, well-documented change in the isotopic signature of the organic matter inputs.

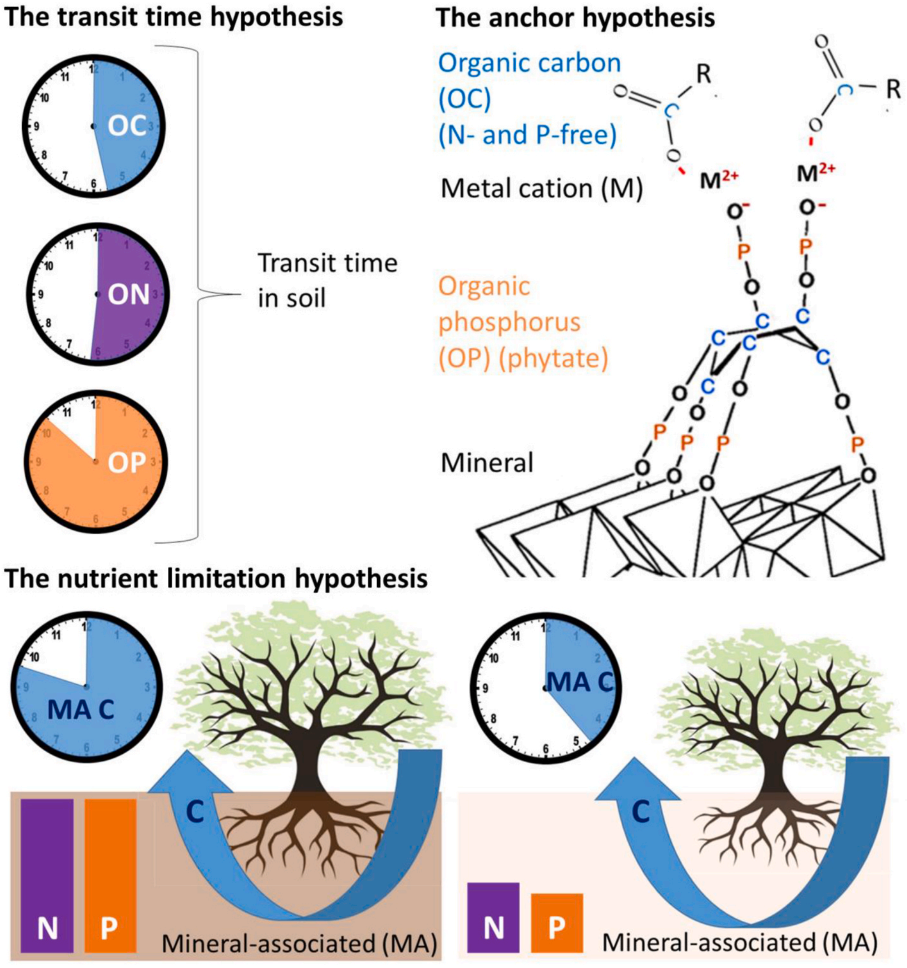

Fig. 4. Three hypotheses for future research about biochemical element cycling, the structure of organo-mineral associations, and the role of stoichiometry for soil organic matter dynamics.

9. Three hypotheses for future research

Based on this review, several hypotheses about the structure of organo-mineral associations in soil as well as about C, N, and P cycling in terrestrial ecosystems can be formulated. Here, I propose three (independent) hypotheses (Fig. 4) that should be tested in the future as they have the potential to significantly improve our understanding of the structure of organo-mineral associations, biogeochemical element cycling, and the role of stoichiometry for soil processes.

The transit time hypothesis: N and P have a longer transit time in soil organic matter than C because ON and OP are, to a larger extent than OC, directly adsorbed to minerals which protects them against decomposition. Further, C covalently bound to N and P has a longer transit time in soil organic matter than C of nutrient-free organic matter compounds.

The transit time of C, N, and P in the soil organic matter pool is the time that starts when the elements enter the pool (by entering the soil as organic matter or by being incorporated into the soil organic matter) and that ends when the elements leave the pool (through mineralization, leaching or erosion). This hypothesis has far-reaching implications for organic matter decomposition, nutrient cycling, and the interactions of the C, N, and P cycles since it indicates that the transit times of the three elements in soil organic matter differ. The hypothesis can best be tested in the field, rather than in laboratory incubation experiments since soil organic matter has a mean transit time ranging from decades to centuries. Given the short half-life of P isotopes, testing this hypothesis requires the development of new compound-specific isotope techniques that allow determining the isotopic signature of C in OP compounds in order to quantify the decomposition of OP in soils.

The anchor hypothesis: ON and OP compounds bind N- and P-free organic matter to mineral surfaces.

Many N- and P-containing compounds, such as amino acids and phytate (Fig. 1), have multiple charged moieties. Hence, these compounds can bind to both minerals and other organic compounds that are less strong in competing for binding sites on mineral surfaces. In other words, N- and P-containing compounds could potentially 'anchor' N- and P-free organic matter to minerals. A similar idea has been expressed in the 'onion-layer model' (Sollins et al., 2006). Yet, more recent studies showed that there are no discrete organic layers around a mineral nucleus as proposed in the 'onion-layer model' (Possinger et al., 2020). Instead, organic matter and (short-range order) minerals form a very complex 3-dimensional structure (Piccolo, 2001, 2002; Tamrat et al., 2019; Wagai et al., 2020). The anchor hypothesis can best be tested in sorption experiments conducted under well-defined conditions. In addition, geochemical modeling and imaging techniques might be helpful to test this hypothesis. However, these imaging techniques would not only have to have a very high resolution but also the ability to distinguish between inorganic and organic N and P.

The nutrient limitation hypothesis: In soils with low N and P availability, formation of mineral-associated organic matter is reduced and mineral-associated organic matter turns over faster than in comparable soils with higher N and P availability.

The idea behind this hypothesis is that low N and P availability can limit the formation of organo-mineral associations because it restricts the amount of compounds that have a very high affinity to adsorb to minerals. In addition, plants and microorganisms in soils with low N and P availability are likely to invest more energy into mobilization of ON and OP, for instance by changing the pH, which could lead to desorption of adsorbed organic matter (Spohn et al., 2013; Keiluweit et al., 2015). The nutrient limitation hypothesis can best be tested under field conditions, similarly as the transit time hypothesis. Specifically, long-term nutrient addition experiments might be utilized for this purpose.

In addition to these three hypotheses, several other hypotheses can be formulated based on the results discussed in this review. For instance, about the extent of preferential adsorption of ON and OP depending on soil mineralogy (larger in soils with high content of short-range order iron and aluminum (oxyhydr)oxides)) or on soil pH (larger in acidic soils (Spohn and Stendahl, 2024)).

10. Conclusions

This synthesis shows that many ON and OP compounds have on average a higher affinity for adsorption to mineral surfaces than nutrient-free organic compounds. This is due to their high charge density and their functional groups, which allow them to form inner-sphere complexes with minerals. Specifically, the review showed that ON and OP have a particularly high affinity to adsorb to short-range order iron and aluminum (oxyhydr)oxides and that adsorption of ON and OP is pH-dependent because the pH influences the protonation of the pH-variable charge and the binding form. Preferential adsorption of N- and P-rich organic matter on minerals has important implications for element cycling as it slows down the decomposition of OC, ON, and OP compounds in soils. Given that microbial biomass is richer in ON and OP than plant litter, the results synthesized here indicate that sorption (and sorptive stabilization) might play a larger role for microbial-derived organic matter than for plant-derived organic matter. Based on this review, I propose hypotheses about the architecture of soil organo-mineral associations as well as C, N, and P cycling. Their exploration has the potential to advance further our understanding of the structure of organic-mineral associations, biogeochemical element cycling, and the role of stoichiometry for soil organic matter dynamics.

CRediT authorship contribution statement

Marie Spohn: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The author declares that she has no conflict of interest.

Data availability

No newly generated data was used for the reseach described in the review article.

Acknowledgment

Funded by the European Union (ERC consolidator grant PHOSCYCLE; grant number 101043387).

References

Amorim, H.C., Hurtarte, L.C., Souza, I.F., Zinn, Y.L., 2022. C: N ratios of bulk soils and particle-size fractions: global trends and major drivers. Geoderma 425, 116026.
Aufdenkampe, A.K., Hedges, J.I., Richey, J.E., Krusche, A.V., Llerena, C.A., 2001. Sorptive fractionation of dissolved organic nitrogen and amino acids onto fine sediments within the Amazon Basin. Limnology & Oceanography 46 (8), 1921–1935.
Bailey, V.L., Pries, C.H., Lajtha, K., 2019. What do we know about soil carbon destabilization? Environmental Research Letters 14 (8), 083004.
Berg, A.S., Joern, B.C., 2006. Sorption dynamics of organic and inorganic phosphorus compounds in soil. Journal of Environmental Quality 35 (5), 1855–1862.
Blume, H.P., Brümmer, G., Hartge, H., Schwertmann, U., 2015. Scheffer/Schachtschabel Soil Science. Springer.
Boily, J.F., Nilsson, N., Persson, P., Sjöberg, S., 2000. Benzenecarboxylate surface complexation at the goethite (α-FeOOH)/water interface: I. A mechanistic description of pyromellitate surface complexes from the combined evidence of infrared spectroscopy, potentiometry, adsorption data, and surface complexation modeling. Langmuir 16 (13), 5719–5729.
Cagnasso, M., Boero, V., Franchini, M.A., Chorover, J., 2010. ATR-FTIR studies of phospholipid vesicle interactions with α-FeOOH and α-Fe_2O_3 surfaces. Colloids and Surfaces B: Biointerfaces 76 (2), 456–467.
Cai, P., Huang, Q., Zhu, J., Jiang, D., Zhou, X., Rong, X., Liang, W., 2007. Effects of low-molecular-weight organic ligands and phosphate on DNA adsorption by soil colloids and minerals. Colloids and Surfaces B: Biointerfaces 54 (1), 53–59.
Cao, Y., Wei, X., Cai, P., Huang, Q., Rong, X., Liang, W., 2011. Preferential adsorption of extracellular polymeric substances from bacteria on clay minerals and iron oxide. Colloids and Surfaces B: Biointerfaces 83 (1), 122–127.

Celi, L., Barberis, E., 2005. Abiotic stabilization of organic phosphorus in the environment. In: Turner, B.L., Frossard, E., Baldwin, D.S. (Eds.), 2005 Organic Phosphorus in the Environment. CABI Pub, pp. 269–294.

Celi, L., Lamacchia, S., Marsan, F.A., Barberis, E., 1999. Interaction of inositol hexaphosphate on clays: adsorption and charging phenomena. Soil Science 164, 574–585.

Chen, A., Arai, Y., 2019. Functional group specific phytic acid adsorption at the ferrihydrite–water interface. Environmental Science & Technology 53 (14), 8205–8215.

Cleveland, C.C., Houlton, B.Z., Smith, W.K., Marklein, A.R., Reed, S.C., Parton, W., et al., 2013. Patterns of new versus recycled primary production in the terrestrial biosphere. Proceedings of the National Academy of Sciences 110 (31), 12733–12737.

Condron, L.M., Turner, B.L., Cade-Menun, B.J., 2005. Chemistry and dynamics of soil organic phosphorus. Phosphorus: Agriculture and Environment 46, 87–121.

Coward, E.K., Thompson, A.T., Plante, A.F., 2017. Iron-mediated mineralogical control of organic matter accumulation in tropical soils. Geoderma 306, 206–216.

Cotrufo, M.F., Ranalli, M.G., Haddix, M.L., Six, J., Lugato, E., 2019. Soil carbon storage informed by particulate and mineral-associated organic matter. Nature Geoscience 12 (12), 989–994.

Darch, T., Blackwell, M.S., Hawkins, J.M.B., Haygarth, P.M., Chadwick, D., 2014. A meta-analysis of organic and inorganic phosphorus in organic fertilizers, soils, and water: implications for water quality. Critical Reviews in Environmental Science and Technology 44 (19), 2172–2202.

Deiss, L., de Moraes, A., Maire, V., 2018. Environmental drivers of soil phosphorus composition in natural ecosystems. Biogeosciences 15 (14), 4575–4592.

Ding, X., Henrichs, S.M., 2002. Adsorption and desorption of proteins and polyamino acids by clay minerals and marine sediments. Marine Chemistry 77 (4), 225–237.

Duckworth, O.W., Martin, S.T., 2001. Surface complexation and dissolution of hematite by C1-C6 dicarboxylic acids at pH= 5.0. Geochimica et Cosmochimica Acta 65 (23), 4289–4301.

Eusterhues, K., Thieme, J., Narvekar, S., Araki, T., Kazemian, M., Kaulich, B., et al., 2023. Importance of inner-sphere PO-Fe bonds in natural and synthetic mineral-organic associations. Science of the Total Environment 905, 167232.

Fang, L., Cao, Y., Huang, Q., Walker, S.L., Cai, P., 2012. Reactions between bacterial exopolymers and goethite: a combined macroscopic and spectroscopic investigation. Water Research 46 (17), 5613–5620.

Filius, J.D., Lumsdon, D.G., Meeussen, J.C., Hiemstra, T., Van Riemsdijk, W.H., 2000. Adsorption of fulvic acid on goethite. Geochimica et Cosmochimica Acta 64 (1), 51–60.

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 Biology and Biochemistry 39 (5), 1213–1217.

Goldberg, S., Sposito, G., 1985. On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: a review. Communications in Soil Science and Plant Analysis 16 (8), 801–821.

Gao, X., Metge, D.W., Ray, C., Harvey, R.W., Chorover, J., 2009. Surface complexation of carboxylate adheres Cryptosporidium parvum Oocysts to the hematite−water interface. Environmental Science & Technology 43 (19), 7423–7429.

Gu, B., Mehlhorn, T.L., Liang, L., McCarthy, J.F., 1996. Competitive adsorption, displacement, and transport of organic matter on iron oxide: I. Competitive adsorption. Geochimica et Cosmochimica Acta 60 (11), 1943–1950.

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. Environmental Science & Technology 28 (1), 38–46.

Guggenberger, G., Zech, W., Haumaier, L., Christensen, B.T., 1995. Land-use effects on the composition of organic matter in particle-size separates of soils: II. CPMAS and solution 13C NMR analysis. European Journal of Soil Science 46 (1), 147–158.

Haynes, C.A., Norde, W., 1994. Globular proteins at solid/liquid interfaces. Colloids and Surfaces B: Biointerfaces 2 (6), 517–566.

Hemingway, J.D., Rothman, D.H., Grant, K.E., Rosengard, S.Z., Eglinton, T.I., Derry, L.A., Galy, V.V., 2019. Mineral protection regulates long-term global preservation of natural organic carbon. Nature 570 (7760), 228–231.

Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. Plant and Soil 237 (2), 173–195.

Hunter, W.R., Niederdorfer, R., Gernand, A., Veuger, B., Prommer, J., Mooshammer, M., et al., 2016. Metabolism of mineral-sorbed organic matter and microbial lifestyles in fluvial ecosystems. Geophysical Research Letters 43 (4), 1582–1588.

Hwang, Y.S., Lenhart, J.J., 2008. Adsorption of C4-dicarboxylic acids at the hematite/water interface. Langmuir 24 (24), 13934–13943.

Jilling, A., Keiluweit, M., Contosta, A.R., Frey, S., Schimel, J., Schnecker, J., et al., 2018. Minerals in the rhizosphere: overlooked mediators of soil nitrogen availability to plants and microbes. Biogeochemistry 139, 103–122.

Jones, D.L., Healey, J.R., Willett, V.B., Farrar, J.F., Hodge, A., 2005. Dissolved organic nitrogen uptake by plants—an important N uptake pathway? Soil Biology and Biochemistry 37 (3), 413–423.

Jones, D.L., Hodge, A., 1999. Biodegradation kinetics and sorption reactions of three differently charged amino acids in soil and their effects on plant organic nitrogen availability. Soil Biology and Biochemistry 31 (9), 1331–1342.

Kaiser, K., Guggenberger, G., 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Organic Geochemistry 31 (7–8), 711–725.

Kirkby, C.A., Kirkegaard, J.A., Richardson, A.E., Wade, L.J., Blanchard, C., Batten, G., 2011. Stable soil organic matter: a comparison of C: N: P: S ratios in Australian and other world soils. Geoderma 163 (3–4), 197–208.

Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., 2015. Mineral protection of soil carbon counteracted by root exudates. Nature Climate Change 5 (6), 588–595.

Keiluweit, M., Bougoure, J.J., Zeglin, L.H., Myrold, D.D., Weber, P.K., Pett-Ridge, J., et al., 2012. Nano-scale investigation of the association of microbial nitrogen residues with iron (hydr) oxides in a forest soil O-horizon. Geochimica et Cosmochimica Acta 95, 213–226.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Mineral–organic associations: formation, properties, and relevance in soil environments. Advances in Agronomy 130, 1–140. Academic Press.

Kleber, M., Sollins, P., Sutton, R., 2007. A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85, 9–24.

Knicker, H., 2004. Stabilization of N-compounds in soil and organic-matter-rich sediments—what is the difference? Marine Chemistry 92 (1–4), 167–195.

Knicker, H., 2011. Soil organic N - an under-rated player for C sequestration in soils? Soil Biology and Biochemistry 43 (6), 1118–1129.

Kögel-Knabner, I., 2006. Chemical structure of organic N and organic P in soil. In: Nucleic Acids and Proteins in Soil. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 23–48.

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., et al., 2008. Organo-mineral associations in temperate soils: integrating biology, mineralogy, and organic matter chemistry. Journal of Plant Nutrition and Soil Science 171 (1), 61–82.

Kölbl, A., Kögel-Knabner, I., 2004. Content and composition of free and occluded particulate organic matter in a differently textured arable Cambisol as revealed by solid-state 13C NMR spectroscopy. Journal of Plant Nutrition and Soil Science 167 (1), 45–53.

Kopittke, P.M., Hernandez-Soriano, M.C., Dalal, R.C., Finn, D., Menzies, N.W., Hoeschen, C., Mueller, C.W., 2018. Nitrogen-rich microbial products provide new organo-mineral associations for the stabilization of soil organic matter. Global Change Biology 24 (4), 1762–1770.

Kunhi Mouvenchery, Y., Kučerík, J., Diehl, D., Schaumann, G.E., 2012. Cation-mediated cross-linking in natural organic matter: a review. Reviews in Environmental Science and Biotechnology 11, 41–54.

Lin, D., Ma, W., Jin, Z., Wang, Y., Huang, Q., Cai, P., 2016. Interactions of EPS with soil minerals: a combination study by ITC and CLSM. Colloids and Surfaces B: Biointerfaces 138, 10–16.

Martin, M., Celi, L., Barberis, E., 2004. Desorption and plant availability of myo-inositol hexaphosphate adsorbed on goethite. Soil Science 169 (2), 115–124.

McKercher, R.B., Anderson, G., 1989. Organic phosphate sorption by neutral and basic soils. Communications in Soil Science and Plant Analysis 20 (7–8), 723–732.

Meissner, J., Prause, A., Bharti, B., Findenegg, G.H., 2015. Characterization of protein adsorption onto silica nanoparticles: influence of pH and ionic strength. Colloid and Polymer Science 293, 3381–3391.

Mikutta, R., Zang, U., Chorover, J., Haumaier, L., Kalbitz, K., 2011. Stabilization of extracellular polymeric substances (*Bacillus subtilis*) by adsorption to and coprecipitation with Al forms. Geochimica et Cosmochimica Acta 75 (11), 3135–3154.

Miltner, A., Kindler, R., Knicker, H., Richnow, H.H., Kästner, M., 2009. Fate of microbial biomass-derived amino acids in soil and their contribution to soil organic matter. Organic Geochemistry 40 (9), 978–985.

Moon, J., Ma, L., Xia, K., Williams, M.A., 2016. Plant–Microbial and mineral contributions to amino acid and protein organic matter accumulation during 4000 years of pedogenesis. Soil Biology and Biochemistry 100, 42–50.

Moon, J., Xia, K., Williams, M.A., 2019. Consistent proteinaceous organic matter partitioning into mineral and organic soil fractions during pedogenesis in diverse ecosystems. Biogeochemistry 142, 117–135.

Näsholm, T., Kielland, K., Ganeteg, U., 2009. Uptake of organic nitrogen by plants. New Phytologist 182 (1), 31–48.

Nelson, D.L., Cox, M.M., 2004. Lehninger Principles of Biochemistry. Springer.

Newcomb, C.J., Qafoku, N.P., Grate, J.W., Bailey, V.L., De Yoreo, J.J., 2017. Developing a molecular picture of soil organic matter–mineral interactions by quantifying organo–mineral binding. Nature Communications 8 (1), 396.

Ognalaga, M., Frossard, E., Thomas, F., 1994. Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. Soil Science Society of America Journal 58 (2), 332–337.

Omoike, A., Chorover, J., 2006. Adsorption to goethite of extracellular polymeric substances from Bacillus subtilis. Geochimica et Cosmochimica Acta 70 (4), 827–838.

Omoike, A., Chorover, J., Kwon, K.D., Kubicki, J.D., 2004. Adhesion of bacterial exopolymers to α-FeOOH: inner-sphere complexation of phosphodiester groups. Langmuir 20 (25), 11108–11114.

Parikh, S.J., Kubicki, J.D., Jonsson, C.M., Jonsson, C.L., Hazen, R.M., Sverjensky, D.A., Sparks, D.L., 2011. Evaluating glutamate and aspartate binding mechanisms to rutile (α-TiO2) via ATR-FTIR spectroscopy and quantum chemical calculations. Langmuir 27 (5), 1778–1787.

Parikh, S.J., Mukome, F.N., Zhang, X., 2014. ATR–FTIR spectroscopic evidence for biomolecular phosphorus and carboxyl groups facilitating bacterial adhesion to iron oxides. Colloids and Surfaces B: Biointerfaces 119, 38–46.

Piccolo, A., 2001. The supramolecular structure of humic substances. Soil Science 166 (11), 810–832.

Piccolo, A., 2002. The supramolecular structure of humic substances: a novel understanding of humus chemistry and implications in soil science. Advances in Agronomy 75, 57–134.

Possinger, A.R., Zachman, M.J., Enders, A., Levin, B.D., Muller, D.A., Kourkoutis, L.F., Lehmann, J., 2020. Organo–organic and organo–mineral interfaces in soil at the nanometer scale. Nature Communications 11, 6103.

Rothstein, D.E., 2009. Soil amino-acid availability across a temperate-forest fertility gradient. Biogeochemistry 92, 201–215.

Ruttenberg, K.C., Sulak, D.J., 2011. Sorption and desorption of dissolved organic phosphorus onto iron (oxyhydr) oxides in seawater. Geochimica et Cosmochimica Acta 75 (15), 4095–4112.

Schmidt, M.W., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., et al., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478 (7367), 49–56.

Sollins, P., Swanston, C., Kleber, M., Filley, T., Kramer, M., Crow, S., et al., 2006. Organic C and N stabilization in a forest soil: evidence from sequential density fractionation. Soil Biology and Biochemistry 38 (11), 3313–3324.

Spohn, M., 2020b. Phosphorus and carbon in soil particle size fractions: a synthesis. Biogeochemistry 147 (3), 225–242.

Spohn, M., 2020a. Increasing the organic carbon stocks in mineral soils sequesters large amounts of phosphorus. Global Change Biology 26 (8), 4169–4177.

Spohn, M., Schleuss, P.M., 2019. Addition of inorganic phosphorus to soil leads to desorption of organic compounds and thus to increased soil respiration. Soil Biology and Biochemistry 130, 220–226.

Spohn, M., Stendahl, J., 2022. Carbon, nitrogen, and phosphorus stoichiometry of organic matter in Swedish forest soils and its relationship with climate, tree species, and soil texture. Biogeosciences 19 (8), 2171–2186.

Spohn, M., Stendahl, J., 2024. Soil carbon and nitrogen contents in forest soils are related to soil texture in interaction with pH and metal cations. Geoderma 441, 116746.

Spohn, M., Ermak, A., Kuzyakov, Y., 2013. Microbial gross organic phosphorus mineralization can be stimulated by root exudates–a ^{33}P isotopic dilution study. Soil Biology and Biochemistry 65, 254–263.

Spohn, M., Diáková, K., Aburto, F., Doetterl, S., Borovec, J., 2022. Sorption and desorption of organic matter in soils as affected by phosphate. Geoderma 405, 115377.

Stewart, J.W.B., Tiessen, H., 1987. Dynamics of soil organic phosphorus. Biogeochemistry 4, 41–60.

Strahm, B.D., Harrison, R.B., 2008. Controls on the sorption, desorption and mineralization of low-molecular-weight organic acids in variable-charge soils. Soil Science Society of America Journal 72 (6), 1653–1664.

Stumm, W., Kummert, R., Sigg, L., 1980. A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. Croatica Chemica Acta 53 (2), 291–312.

Swenson, T.L., Bowen, B.P., Nico, P.S., Northen, T.R., 2015. Competitive sorption of microbial metabolites on an iron oxide mineral. Soil Biology and Biochemistry 90, 34–41.

Tamrat, W.Z., Rose, J., Grauby, O., Doelsch, E., Levard, C., Chaurand, P., Basile-Doelsch, I., 2019. Soil organo-mineral associations formed by co-precipitation of Fe, Si and Al in presence of organic ligands. Geochimica et Cosmochimica Acta 260, 15–28.

Terrer, C., Jackson, R.B., Prentice, I.C., Keenan, T.F., Kaiser, C., Vicca, S., et al., 2019. Nitrogen and phosphorus constrain the CO_2 fertilization of global plant biomass. Nature Climate Change 9 (9), 684–689.

Tipping, E., Somerville, C.J., Luster, J., 2016. The C: N: P: S stoichiometry of soil organic matter. Biogeochemistry 130, 117–131.

Vancampenhout, K., Wouters, K., De Vos, B., Buurman, P., Swennen, R., Deckers, J., 2009. Differences in chemical composition of soil organic matter in natural ecosystems from different climatic regions–A pyrolysis–GC/MS study. Soil Biology and Biochemistry 41 (3), 568–579.

Vance, C.P., Uhde-Stone, C., Allan, D.L., 2003. Phosphorus acquisition and use: critical adaptations by plants for securing a nonrenewable resource. New Phytologist 157 (3), 423–447.

Vieublé Gonod, L., Jones, D.L., Chenu, C., 2006. Sorption regulates the fate of the amino acids lysine and leucine in soil aggregates. European Journal of Soil Science 57 (3), 320–329.

Vitousek, P.M., Porder, S., Houlton, B.Z., Chadwick, O.A., 2010. Terrestrial phosphorus limitation: mechanisms, implications, and nitrogen–phosphorus interactions. Ecological Applications 20 (1), 5–15.

von Lützow, M., 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. European Journal of Soil Science 57 (4), 426–445.

Wagai, R., Kajiura, M., Asano, M., 2020. Iron and aluminum association with microbially processed organic matter via meso-density aggregate formation across soils: organo-metallic glue hypothesis. Soils 6 (2), 597–627.

Wang, X.C., Lee, C., 1993. Adsorption and desorption of aliphatic amines, amino acids and acetate by clay minerals and marine sediments. Marine Chemistry 44 (1), 1–23.

Wang, X., Liu, F., Tan, W., Li, W., Feng, X., Sparks, D.L., 2013. Characteristics of phosphate adsorption-desorption onto ferrihydrite: comparison with well-crystalline Fe (hydr) oxides. Soil Science 178 (1), 1–11.

Wiesmeier, M., Urbanski, L., Hobley, E., Lang, B., von Lützow, M., Marin-Spiotta, E., et al., 2019. Soil organic carbon storage as a key function of soils - a review of drivers and indicators at various scales. Geoderma 333, 149–162.

Xu, X., Thornton, P.E., Post, W.M., 2013. A global analysis of soil microbial biomass carbon, nitrogen and phosphorus in terrestrial ecosystems. Global Ecology and Biogeography 22 (6), 737–749.

Yan, Y.P., Liu Jr, F., Li, W., Liu, F., Feng, X.H., Sparks, D.L., 2014. Sorption and desorption characteristics of organic phosphates of different structures on aluminium (oxyhydr) oxides. European Journal of Soil Science 65 (2), 308–317.

Yu, W.H., Li, N., Tong, D.S., Zhou, C.H., Lin, C.X.C., Xu, C.Y., 2013. Adsorption of proteins and nucleic acids on clay minerals and their interactions: a review. Applied Clay Science 80, 443–452.

Zechmeister-Boltenstern, S., Keiblinger, K.M., Mooshammer, M., Peñuelas, J., Richter, A., Sardans, J., Wanek, W., 2015. The application of ecological stoichiometry to plant–microbial–soil organic matter transformations. Ecological Monographs 85 (2), 133–155.

Zhang, M., Peacock, C.L., Cai, P., Xiao, K.Q., Qu, C., Wu, Y., Huang, Q., 2021. Selective retention of extracellular polymeric substances induced by adsorption to and coprecipitation with ferrihydrite. Geochimica et Cosmochimica Acta 299, 15–34.