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OPINION

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Increasing the organic carbon stocks in mineral soils sequesters large amounts of phosphorus

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Abstract

Despite the fact that phosphorus (P) is critical for plant biomass production in many ecosystems, the implications of soil organic carbon (OC) sequestration for the P cycle have hardly been discussed yet. Thus, the aims of this study are, first, to synthesize results about the relationship between C and P in soil organic matter (SOM) and organic matter inputs to soils, second, to review processes that affect the C:P ratio of SOM, and third, to discuss implications of OC storage in terrestrial ecosystems for P sequestration. The study shows that the storage of OC in mineral soils leads to the sequestration of large amounts of organic phosphorus (OP) since SOM in mineral soils is very rich in P. The reasons for the strong enrichment of OP with respect to OC in soils are the mineralization of OC and the formation of microbial necromass that is P-rich as well as the strong sorption of OP to mineral surfaces that prevents OP mineralization. In particular, the formation of mineral-associated SOM that is favorable for storing OC in soil over decadal to centennial timescales sequesters large amounts of OP. Storage of 1,000 kg C in the clay size fraction in the topsoils of croplands sequesters 13.1 kg P. In contrast, the OC:OP ratios of wood and of peatlands are much larger than the ones in cropland soils. Thus, storage of C in wood in peatlands sequesters much less P than the storage of OC in mineral soils. In order to increase the C stocks in terrestrial ecosystems and to lock up as little P as possible, it would be more reasonable to protect and restore peatlands and to produce and preserve wood than to store OC in mineral soils.

KEYWORDS
4 per mille initiative, phosphorus cycling, soil OC:OP ratios, soil organic carbon storage, soil organic matter stoichiometry

1 | INTRODUCTION

Both the carbon (C) cycle and the phosphorus (P) cycle have been strongly affected by human activities during the last two centuries, leading to massive changes in the global distribution of C and P across different pools. While large amounts of C have been moved from fossil reservoirs to the atmosphere (IPCC, 2013), large quantities of P have been transported from phosphate rock to aquatic ecosystems and sewage sludge dumps (Chen & Graedel, 2016; Cordell, Drangert, & White, 2009; Elser & Bennett, 2011) as well as to plant-unavailable inorganic P pools in cropland soils (Chen & Graedel, 2016; MacDonald, Bennett, Potter, & Ramankutty, 2011; Sattari, Bouwman, Giller, & van Ittersum, 2012). Currently, we are increasingly understanding that the shift in the global distribution of C and P is causing major problems for human life on Earth. While the growing concentration of C in the form of carbon dioxide (CO_2) in the atmosphere leads to fast changes in Earth's climate, the exploitation of rock phosphate and the movement of P to aquatic ecosystems causes eutrophication (Elser & Bennett, 2011). Furthermore, transport of the essential macronutrient P to aquatic ecosystems, sewage sludge dumps, and plant-unavailable P pools is not sustainable since rock phosphate suitable for fertilizer production is a finite resource that will be largely used up during the next century (Cooper, Lombardi, Boardman, & Carliell-Marquet, 2011; Cordell & White, 2015). Thus, solutions that lead to a more favorable distribution of C and P across global pools and a more sustainable use of P are urgently needed.

The idea to decrease the CO_2 concentration in the atmosphere by storing organic C (OC) in soils was raised in the late 1980s (Bouman, 1990; Post et al., 1990). Following this idea, the French Ministry of Agriculture launched the “4 per mille” initiative in 2015. The aim of this initiative is to promote land management practices leading to a removal of CO_2 from the atmosphere and an increase in the global stock of soil organic C (SOC) at a rate of 4 per mille of the initial stock per year (0.04/year) for 20 years (Chabbi et al., 2017). If this rate of C sequestration was achieved for all soils globally to a depth of 40 cm, the annual removal of C from the atmosphere would equal current annual CO_2-C emissions from fossil fuels (Minasny et al., 2017). The initiative has received applause as well as criticism. Some authors pointed out that such a strong increase in the SOC stock is not feasible due to socioeconomic reasons (Amundson & Biardeau, 2018), others questioned whether such a strong increase in the SOC stock is realistic based on observations made during long-term field experiments (Poulton, Johnston, Macdonald, White, & Powlson, 2018). In addition, the concern has been raised that soil organic matter (SOM) does not only contain C but also nutrients, and that a C sequestration rate of 1,200 Tg C/year would require 100 Tg N/year which equals about 75% of the current global annual N-fertilizer production (Van Groenigen et al., 2017a). The implications of an increase in SOC sequestration for the P cycle have hardly been discussed yet, despite the fact that the P cycle is also critical for the human population on Earth (Richardson, Kirkby, Banerjee, & Kirkegaard, 2014; Soussana et al., 2017; Van Groenigen et al., 2017b). Therefore, the aims of this article are to (a) synthesize results about the relationship between C and P in organic matter (OM) inputs to soils and SOM, (b) review the processes that affect the C:P ratio of SOM, and (c) discuss the implications of C storage in terrestrial ecosystems for P sequestration.

2 | C:P RATIOS OF SOM AND OM INPUTS TO SOILS

As a basis for the discussion of the implications of SOC sequestration for the P cycle, I review C:P ratios in the organic inputs to soils and OC:OP ratios in soils. Most of these results are derived from peer-reviewed synthesis and meta-analysis studies (McGroddy, Daufresne, & Hedin, 2004; Spohn, 2020; Tipping, Somerville, & Luster, 2016; Xu, Thornton, & Post, 2013; Yuan & Chen, 2009; Yuan, Chen, & Reich, 2011). In addition, I conducted a synthesis of data for some OM inputs for which, to my knowledge, no synthesis study is available. These OM inputs are non-decomposed woody debris (of angiosperms and gymnosperms) as well as fine woody debris, and further, anthropogenic organic inputs such as biochar (produced from plant residues and wastewater sludge), organic fertilizer, and compost. I searched for peer-reviewed studies that report C and P contents of the organic inputs to soil pools via Google Scholar, using the terms dead wood, woody debris, coarse woody debris, fine woody debris, biochar, compost, manure, and organic fertilizer in combination with the terms element content, element concentration, carbon, carbon content, carbon concentration, phosphorus, phosphorus content, phosphorus concentration, element ratio, and carbon:phosphorus ratio. All studies had to report total C contents determined using an element analyzer, and total P determined by inductively coupled plasma atomic emission spectroscopy after digestion of the OM in order to be included in the synthesis. Non-peer reviewed studies and studies that used other methods were excluded. Molar C:P ratios (in mol per mol, as opposed to g per g) and their arithmetic means and standard deviations were calculated for all OM input pools (see Data S1). In addition, molar OC:OP ratios were calculated for the soils and soil fractions (based on the molecular weight of C and P). For further information on the collection of data derived from synthesis studies, see the individual studies.

Woody (Figure 1a) and non-woody (Figure 1b) plant residues, that form an important input of OM to soils, have higher C:P ratios than mineral soils (Figure 2b) (please notice the different scales of the *x* axes). In particular, coarse woody debris (Figure 1a), and to a lesser extent also fine woody debris (Figure 1a) and roots with diameter > 5 mm (Figure 1b), are very P-poor. The C:P ratio of non-decomposed coarse woody debris of gymnosperms and angiosperms (Figure 1a) is on average 33 and 17 times higher, respectively, than the C:P ratio of the mineral topsoil of temperate forests (Figure 2b). Only anthropogenic inputs such as compost, manure, and charred waste-water sludge have C:P ratios (Figure 1b) in the same range as those of mineral soils (Figure 2b).

The OC:OP ratio is much larger in organic soils (Figure 2a) than in mineral soils (Figure 2b). The OC:OP ratio in the topsoils of peatlands is 5.4 and 8.1 times higher than in the topsoils of croplands in the tropics and in the temperate zone, respectively (Figure 2a). The OC:OP ratio in the topsoils of croplands in the temperate zone is 78.6 and 40.4 times lower than the C:P ratio of the deadwood of gymnosperms and angiosperms, respectively. In mineral topsoils, the OC:OP ratio is affected by land use (Figure 2b). The OC:OP ratio of the organic horizon and the mineral topsoil of forests is 4.6 and 2.4 times higher, respectively, than in the topsoils of croplands in the temperate zone. In the tropics, the OC:OP ratio of the mineral topsoil of forests is 2.1 times higher than in the topsoils of croplands.

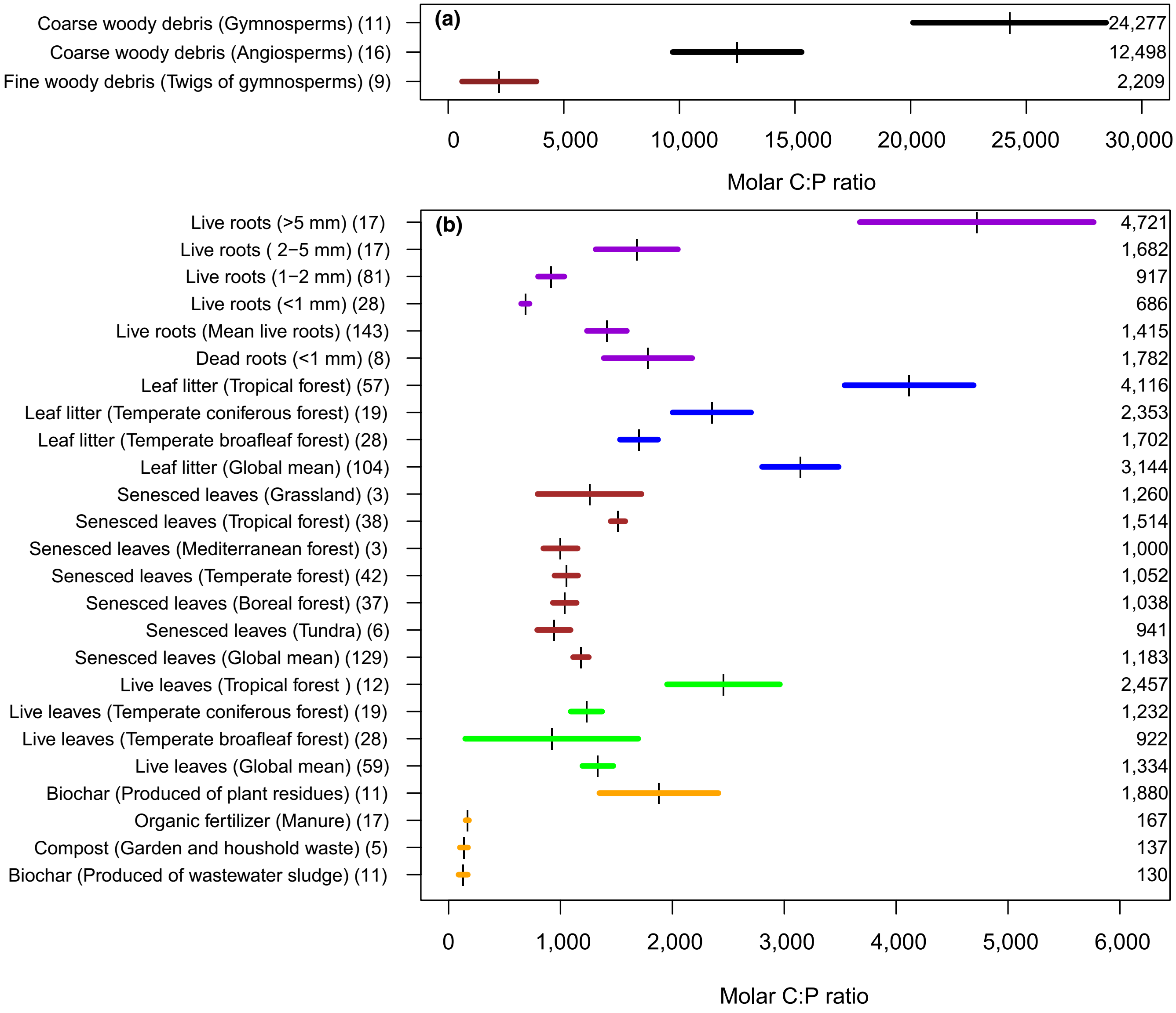

FIGURE 1 Molar carbon-to-phosphorus (C:P) ratio of organic inputs to soil, including non-decomposed woody debris (a) and non-woody organic inputs (b). Please notice the different scales of the *x*-axes. Horizontal bars depict standard errors and vertical lines indicate the means, which are also given as numbers at the right margin of the figure. Numbers in brackets in the labels of the *y*-axes depict the number of observations. Data source: Woody debris: this study (see Data S1); live roots: Yuan et al. (2011); leaf litter: McGroddy et al. (2004); senesced leaves: Yuan and Chen (2009); live leaves: Yuan and Chen (2009); biochar, organic fertilizer and compost: this study (see Data S1)

The OC:OP ratio decreases from the sand size to the silt size to the clay size fraction in mineral soils (Figure 2c). The mean OC:OP ratio of the sand size fraction is 3.8 times higher than the OC:OP ratio of the clay size fraction both in topsoils of croplands and in topsoils under native vegetation (Figure 2c). In the subsoil, the OC:OP ratio of the clay size fraction is to only 115 (Figure 2c) and is in the same range as the OC:OP ratio of biochar produced from wastewater sludge (Figure 1b). The OC:OP ratio of the clay size fraction in the subsoil is 211 and 108 times lower than those of coarse woody debris of gymnosperms and angiosperms, respectively. The lowest OC:OP ratio of all pools reviewed here is found in the soil microbial biomass, with a value of only 42 (Figure 2c).

3 | ENRICHMENT OF OP OVER OC IN SOILS

The review of the OC:OP ratios of soils indicates that OP in soil is enriched over OC in comparison to plant-derived OM inputs to soils. In the following, I will discuss the reasons for this.

3.1 | The OC:OP ratios of plant inputs decrease towards soil microbial biomass C:P ratios

The C:P ratios of wood, roots, and leaves decreases strongly during their decomposition (Berg & McClaugherty, 1989; Moore, Trofymow,

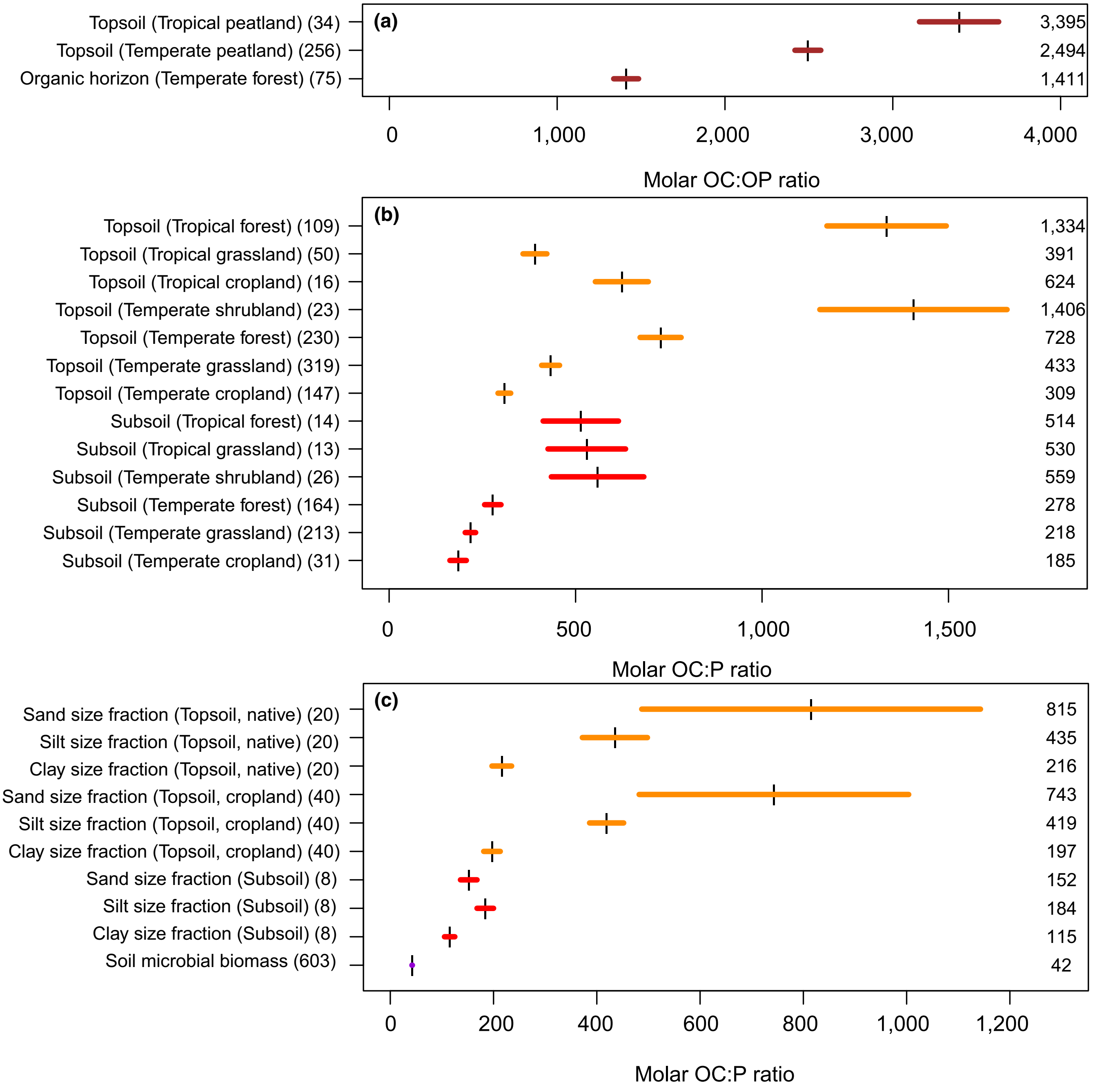

FIGURE 2 Molar organic carbon-to-organic phosphorus (OC:OP) ratio of soils and soil fractions, including organic soils and organic soil horizons (a), mineral soils (b), and fractions of mineral soils (c). Please notice the different scales of the *x*-axes. Horizontal bars depict standard errors and vertical lines indicate the means, which are also given as numbers at the right margin of the figure. Numbers in brackets in the labels of the *y*-axes depict the number of observations. Data source: Organic soils: Tipping et al. (2016); mineral soils: Tipping et al. (2016); soil particle size fractions: Spohn (2020); soil microbial biomass: Xu et al. (2013)

Prescott, & Titus, 2011; Zechmeister-Boltenstern et al., 2015). The decrease in the C:P ratio can be fast and large if the conditions for decomposition are favorable. It has been shown that during 732 days, the C:P ratio of leaf litter decreased quickly in temperate broadleaf forests, namely from 525 to 305 in flowering dogwood litter, from 1,137 to 405 in red maple litter, and from 894 to 508 in chestnut oak litter (Blair, 1988). For temperate forests in Europe, it has been reported that the C:P ratio decreased considerably over 4–5 cm of the organic horizon. It decreased from the top of the Oe to the bottom of the Oa horizon from 1,020 to 711 in beech forests, from 1,163 to 853 in spruce forests, and from 1,178 to 812 in mixed spruce-beech forests (Spohn & Chodak, 2015).

The strong and fast decrease in the C:P ratio of OM during the early stages of decomposition is due to the fact that biota, mostly microorganisms, that catalyze the decomposition, respire a large share of the OC. The respiration rate per unit microbial biomass decreases with decreasing C:P (Spohn & Chodak, 2015) and C:N ratio (Spohn, 2015) of the litter that is being decomposed. The reason for this is that the C:N and C:P ratio of the OM become more favorable for the microbial metabolism as they decrease (Spohn, 2015, 2016; Spohn & Chodak, 2015). While mineralized C leaves the soil in the form of CO_2, mineralized P remains in soils, and thus might be turned into OP again by soil microorganisms.

During its decomposition, the C:P ratio of OM (Figure 1) approaches the C:P ratio of the soil microbial biomass (Figure 2c). This is in part due to the fact that plant-derived OM that has large C:P ratios is converted into soil microbial biomass that has a much lower C:P ratio (42 as a global mean; see Figure 2c). As microbes die, their biomass turns into so-called necromass, which contributes strongly to the formation of persistent SOM that remains in soil for decades to centuries (Liang, Amelung, Lehmann, & Kästner, 2019; Miltner, Kindler, Knicker, Richnow, & Kästner, 2009). It has been estimated that microbial necromass C can make up more than half of the soil OC (Liang et al., 2019). The large contribution of the soil microbial biomass C to soil OC is derived from the observation that SOM contains many compounds that are typical for soil microbial biomass, such as amino sugars, especially in old SOM fractions (Kallenbach, Frey, & Grandy, 2016; Liang et al., 2019; Mambelli, Bird, Gleixner, Dawson, & Torn, 2011; Miltner et al., 2009; Simpson, Simpson, Smith, & Kelleher, 2007; Sollins et al., 2009).

While a large proportion of OM inputs is quickly decomposed, sorption of organic compounds to mineral surfaces can protect them against decomposition, and can affect the SOM stoichiometry, as discussed in the following section.

3.2 | OP binds strongly to mineral surfaces in soil

Phosphodiesters constitute the majority of fresh OP inputs to soils (Anderson, 1980), but they decompose rapidly and represent only a small fraction (approximately 10%–20%) of soil OP (Condron, Turner, & Cade-Menun, 2005). The dominant forms of OP in mineral soils are inositol phosphates and other, more labile phosphomonoesters (Darch, Blackwell, Hawkins, Haygarth, & Chadwick, 2014; Deiss, Moraes, & Maire, 2018). In a synthesis paper it has been shown that across all analyzed soils, labile phosphomonosters made up 43% of all OP, inositol phosphates made up 40%, and phosphodiesters made up 17% of all OP (Darch et al., 2014). Phosphodiesters, such as DNA and RNA, have on average a C:P ratio between 9 and 10, depending on the abundance of the four bases, while inositol phosphates have a molar C:P ratio between 1 and 6, depending on the number of phosphate moieties of the molecule.

Due to the negative charge of the OP moiety, many OP compounds sorb strongly to positively charged mineral surfaces of amorphous Al and Fe oxides and the edges of clay minerals (Berg & Joern, 2006; Celi & Barberis, 2005; McKercher & Anderson, 1989; Ruttenberg & Sulak, 2011). Phosphomonesters, and in particular those with multiple phosphate groups, have a very high capacity to sorb to charged mineral surfaces (Berg & Joern, 2006; Celi & Barberis, 2005; McKercher & Anderson, 1989; Ruttenberg & Sulak, 2011). The multiple phosphate moieties can all bind individually to charged mineral surfaces (Ognalaga, Frossard, & Thomas, 1994). Phosphodiesters have a lower charge density than phosphomonoesters since their phosphate groups are considerably shielded, resulting in a lower capacity to compete for sorption sites in soils (Stewart & Tiessen, 1987).

Inorganic P and many OP compounds are more effective in competing for binding sites than non-phosphorylated organic compounds (Afif, Barron, & Torrent, 1995; Berg & Joern, 2006; Celi & Barberis, 2005; Fransson & Jones, 2007; McKercher & Anderson, 1989; Schneider et al., 2010). For instance, compounds such as glucose or adenosine have a lower capacity to compete for binding sites in soil than their phosphorylated derivatives (glucose-P, adenosine-P; Fransson & Jones, 2007). Sorption protects organic compounds against decomposition because it physically hinders enzymatic catalysis (Kleber, Sollins, & Sutton, 2007; Kögel-Knabner et al., 2008; Schmidt et al., 2011). Thus, the strong sorption of OP likely makes many OP compounds more persistent in soil than non-phosphorylated organic compounds which leads to relatively low OC:OP ratios in soil compared to OM inputs (Spohn, 2020). The stronger sorption capacity of phosphomonoesters over phosphopodiesters is very likely also the reason why phosphomonoesters are more abundant in soil than phosphpodiesters.

The strong capacity of many OP compounds to compete successfully for binding sites against non-phosphorylated compounds explains why the OC:OP ratio is smaller in the clay size fraction, which contains many charged surfaces, than in the sand size fraction (Figure 2c). Similarly, it has been found that the light SOM fraction of topsoils of croplands and grasslands contained significantly less OP than the heavy, mineral-associated fraction (Kirkby et al., 2011). Furthermore, it has been shown that the heavy fraction in the topsoil of temperate forests had much lower OC:OP ratios than the light fraction (Stahr et al., 2018). The strong enrichment of OP in the mineral-associated fraction indicates that OP is mostly stabilized in soil through interaction with mineral surfaces.

Due to their strong affinity to sorb to charged surfaces, OP compounds may contribute to the sorptive stabilization of SOM, in the sense that they establish the connection with minerals, forming organo-mineral complexes (Kleber et al., 2007). Yet, the importance of OP for the formation of organo-mineral complexes is only poorly understood so far (Newcomb, Qafoku, Grate, Bailey, & De Yoreo, 2017) despite the fact that organo-mineral complexes are increasingly believed to play an important role in the stabilization of OM against microbial decomposition in soil (Kleber et al., 2007; Kögel-Knabner et al., 2008; Schmidt et al., 2011).

Taken together, this review showed that SOM in mineral soils is very rich in P compared to the OM inputs to soil. The reasons for the enrichment of OP over OC in soil are (a) the mineralization of OC, and (b) the formation of microbial necromass that is rich in P as well as (c) the strong sorption of OP to mineral surfaces in soil that stabilizes OP compounds against mineralization. In the following, I will discuss the implications of OC sequestration in soils for P storage and cycling.

4 | THE P COST OF SOIL OC STORAGE

In order to close the P cycle, it is necessary that the amount of P that is removed with the biomass during harvest is returned to soils in the form of plant detritus or detritus-derived products and is made available for plants through mineralization. The return of P from industries and waste water stations to soils could help prevent eutrophication of aquatic ecosystems, and is therefore desirable. However, if the soil OP stock increases (inputs > outputs) it forms a sink for P in soil which might compete with plants for P.

An increase in the SOC stock that has a significant effect on the global C cycle, as suggested by the 4 per mille initiative (Minasny et al., 2017), would require sequestration of a large amount of P. In order to limit global warming to less than 2°C relative to preindustrial levels, 8.9 Gt C/year need to be removed from the atmosphere (Meinshausen et al., 2009). Storage of 1,000 kg C in the topsoil of temperate and tropical croplands, sequesters 8.4 and 4.1 kg P, respectively (see Figure 2b). Hence, it can be estimated that to store 8.9 Gt C/year in the topsoil of croplands, between 37 and 75 Mt P are needed every year.

Particularly large amounts of P are necessary for the formation of OM associated with minerals in the clay size fraction of soils (Figure 2c) or in the heavy fraction (Kirkby et al., 2011; Spohn, 2020; Stahr et al., 2018). OC in the clay size fraction is only mineralized at a low rate (Anderson & Paul, 1984; Kögel-Knabner et al., 2008; Ludwig, John, Ellerbrock, Kaiser, & Flessa, 2003; Lützow et al., 2006; Tiessen, Cuevas, & Chacon, 1994). Thus, storage of OC in the mineral-associated fraction likely allows storage of OC in soils over decadal to centennial timescales which is beneficial for the removal of CO_2 from the atmosphere. However, the OC:OP ratios of the clay size fraction (Figure 2c) indicate that storage of 1,000 kg C in the clay size fraction of the subsoil sequesters 22.4 kg P, while for storage of 1,000 kg C in the clay size fraction in the topsoils of croplands 13.1 kg P are needed.

The comparison of OC:OP ratios in different mineral soils (Figure 2b) shows that there is some variability among soils, and that, for instance, the OC:OP ratios is 1.4 times higher in the topsoil of temperate grasslands than in the topsoil of temperate croplands. Yet, the comparison of different land-use types also indicates that the extent to which the OC:OP ratio of soils can be increased is limited. The best option for increasing the OC:OP ratio of soils seems to be afforestation since the OC:OP ratio in the organic horizon of forest soils (Figure 2a) is 4.6 times higher than the OC:OP ratio in the topsoil of croplands (Figure 2b). In addition, it might be possible, to some extent, to increase the proportion of OM in mineral soils that is present in particulate form and not in nutrient-rich, mineral-associated form (Cotrufo, Ranalli, Haddix, Six, & Lugato, 2019). The most efficient way to do so is to establish forests since forest soils, especially when dominated by ectomycorrhizal fungi, contain a larger percentage of C in the form of nutrient-poor particulate OM than croplands and grasslands (Cotrufo et al., 2019).

If our aim is to increase the stocks of OC in mineral soils, we must answer the question where the large amounts of P that this requires can come from. First, it is possible to use inorganic P fertilizer to build up SOM as shown in field and incubation experiments (Kirkby, Richardson, Wade, Conyers, & Kirkegaard, 2016; Kirkby et al., 2014). However, given that rock P suitable for the production of inorganic P fertilizer is a finite and dwindling resource (Cooper et al., 2011; Cordell & White, 2015), it seems more reasonable to use the remaining rock-derived fertilizer resources for plant nutrition. Second, it has been pointed out that many cropland soils contain a surplus of P (MacDonald et al., 2011). However, it is questionable whether this P can be mobilized within a few decades, which would be necessary in order to convert it into SOM and sequester C at a timescale relevant to combat climate change (Van Groenigen et al., 2017b). Furthermore, if it is possible to mobilize these soil P pools (Menezes-Blackburn et al., 2018; Sattari et al., 2012), it seems more reasonable to use them as a long-term P source for plant nutrition. Third, we might use manure, biochar, and compost as an OP source for SOM. These resources are not only very rich in P (see Figure 1b) but their application to cropland soils also has the advantage that it could contribute to closing the P cycle. However, the closure of the P cycle would require mineralization of the OP of these inputs, to render the P available to plants, and it seems more reasonable to use these resources for plant nutrition than for C sequestration, especially if there are less P-costly alternatives for C storage.

The review showed that peatlands have very large OC:OP ratios and that deadwood of gymnosperms has even 10 times higher OC:OP ratios than peatlands. Storage of 1,000 kg C in peatlands only requires 0.3 kg P in the tropics and 1.3 kg P in the temperate zone. Furthermore, storing 1,000 kg C in the deadwood of gymnosperms and angiosperms only requires 0.1 and 0.2 kg P, respectively. Thus, an increase in the amount of C stored in peatlands and in wood would have much smaller P costs than the storage of C in mineral soils. In addition, peatlands have a very high potential for sequestering large amounts of C per area, which makes them very suitable for removing CO_2 from the atmosphere (Freeman, Fenner, & Shirsat, 2012; Leifeld & Menichetti, 2018). Likewise, wood can be used in large quantities for construction, which also has a high potential to sequester C for decades to centuries if forests are managed sustainably and conversion efficiencies from wood to products are high (Schulze et al., 2020). The formation of peatlands and the use of wood for construction, which both significantly decrease the rate of decomposition of P-poor OM, have a large potential to store C with a relatively small P cost. Thus, the use of wood for construction and the protection and restoration of peatlands would allow C sequestration with a much smaller footprint on the P cycle than OC sequestration in mineral soils. Future research should explore the transit time of C and P in mineral soils in comparison to peatlands and wood in order to evaluate the timescale of C and P storage in these pools. A conceptual framework for comparing the transit times and the ages of elements in multipool systems that can be used for this purpose, has recently been presented (Metzler & Sierra, 2018; Spohn & Sierra, 2018).

5 | CONCLUSION

Since P is a macronutrient that limits primary production in many ecosystems, it is desirable that the removal of C from the atmosphere does not lock up large amounts of P. This study shows that storage of OC in mineral soils requires large amounts of OP since OM in mineral soils is very rich in P, especially in comparison to OM inputs to soils. The reasons for the strong enrichment of OP in soils are the mineralization of OC and the formation of microbial necromass that is rich in P as well as the strong sorption of OP to mineral surfaces that prevents OP mineralization. In particular, the formation of mineral-associated SOM that is favorable for storing C in soil over decadal to centennial timescales, sequesters large amounts of OP. In contrast, the OC:OP ratios of wood are much larger than those in the topsoils of croplands, by a factor of 40–79. Thus, the sequestration of C in wood retains much less P than the storage of OC in mineral soils. In order to store the amounts of C that are emitted today as CO_2 due to human activities, as is the aim of the 4 per mille initiative, and to lock up as little P as possible, it would be much more reasonable to protect and restore peatlands and to produce wood than to store OC in mineral soils.

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SUPPORTING INFORMATION

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