Review

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Interaction of Silicon-Phosphorus: The Unexplored Connection in the Soil Ecosystem

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Abstract: Phosphorus (P) is an essential element in food production, but it is often largely unavailable for plants as it persists in soils in immobilized forms. Farmers have been using P fertilizers extensively to overcome this unavailability, leading to the exhaustion of non-renewable deposits of phosphorite, rising fertilizers prices and causing several environmental impacts such as eutrophication. Its large-scale utilization is also inefficient since most of the added P becomes quickly unavailable for the plants. Therefore, farming solutions that improve P uptake, P use efficiency of plants and P mobilization in soils are highly important. In this narrative review, we summarized and explored the link between the Silicon (Si) and P cycles in soils. Silicon is quasi-essential for plants, and it has been established that its presence in soil and uptake by plants has several benefits, especially in toxic and nutrient-deficient conditions. Here, we established that Si in soils can affect crop production in P-deficient conditions through: 1) the pH effect – Si improves organic matter decomposition and decreases Al^{3+} availability; the Si uptake effect – the deposited Si in the plant improves its photosynthetic performance, improves the root ability to uptake P, improves organic matter decomposition and increases P/Mn ration in plant, improving P use; and 3) the Si soil effect – Si stimulates phosphorite rocks weathering and competes with P for the binding places at the surface of Ak and Fe hydroxides, releasing P into soil solution. This positive effect of Si on P mobilization in soils and consequent use by crops should be further disseminated to farmers and other relevant stakeholders.

Keywords: Si fertilization; P use efficiency; P mobilization; soil cycles; Si plant uptake

1. Introduction

Phosphorus (P) is an essential element for life and crucially required for crop production, especially pertinent in the current context of overpopulation [1]. The assimilated P in plants is intimately involved with cellular bioenergetics and metabolic regulation and is also an important structural component of essential biomolecules such as DNA, RNA, phospholipids, ATP, and sugar-phosphates. Phosphorus plays a central role in virtually all major metabolic processes in plants, particularly photosynthesis and respiration [2]. Although present in soils in both organic and mineral forms, the actual available P for crop use is rather limited [3]. One reason for this is the fact that mineral phosphorus stocks in soils are lower when compared to carbonate or silicate minerals [4]. Also, organic P present in soils is lower compared to carbon or nitrogen, decreasing the quantity of available P from organic decomposition. Moreover, the soluble forms of P resulting from dissolution/decomposition processes are often immobilized through precipitation and adsorption processes, and quickly become unavailable for the plants[5,6]. To overcome this problem, farmers have been resorting to adding inorganic P fertilizers to soils to replenish the available P stocks in soil water [7]. These activities have however, originated environmental and economic problems, severely hampered during the last 50 years with the intensification of agriculture and the dramatic increase of P fertilization [8]. On the one hand, P fertilizers originated from the mining of large phosphorite deposits, which are not renewable resources and are now reaching their limit, compromising the P

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fertilizer production in the future [9]. Consequently, P fertilizers prices have been rising, creating economic and social constraints for farmers. One the other hand, the massive use of P fertilization has contributed for the eutrophication of coastal waters and lakes, due to soil erosion and transport of P to ecosystems where this nutrient was the limiting one [10]. Suggestions on reducing P fertilization by farmers and/or reduce their environmental impacts, are not fully satisfactory as they either compromise crop productivity or are mainly focused on the P recovery potential downstream [11]. Better solutions should reduce the upstream source of P by decreasing P waste [12] and maximizing the efficiency of P conversion from soil and into food [13]. By using great quantities of P fertilizers over the past 50 years, farmers have contributed to the build-up of the immobile P pool in soils, while depleting the phosphorite deposits [14]. This stock, although still unavailable for plants, has gained some importance recently as the new big potential source of P in our food chain [15].

In the last two decades research has started to focus on the benefits of Si for crops, especially Si-accumulators. Although Si is not considered as an essential element for crop growth, it has been shown that it improves crop performance in stressful situations [16] and ameliorates several diseases and toxicity [17–19]. Although sometimes recognized, the effect that Si has on the P availability and uptake by the plants is rather limited and its myriads of possible interferences and scattered [20]. The objective of this narrative review is therefore to bring together all the information related to the Si and P link and the benefits that Si fertilization may have directly on the plant, by promoting available P in the soils and improving its uptake by the plant.

2. Phosphorus and Silicon Cycles in Soils

Both P and Si cycles in soil share the particularity of not having an atmosphere part. P and Si remain solely in the solid form in soil particles and/or dissolved forms in soil water [6,21], while cycles as nitrogen also have compounds in the gaseous form. The organic forms of P exist in a gradient of organic matter dissolving rates, ranging from labile (more available) to refractory (more stable)[22,23]. The portion of P in these pools in soils is rather low compared to other crucial nutrients such as carbon and nitrogen. The input of P through litter is therefore limited and very important.

In the process of organic matter decomposition, bacteria feed on the organic compounds. As a side effect, CO_2 is released into the atmosphere and part of the organic nutrients are transform into inorganic material [24], which in turn will feed the plants through root uptake in the rhizosphere. Often, this process is only possible if enough organic N and P are present in the organic soil matrix. On contrary, if the material is low in these organic nutrients, bacteria cannot use them, and must work the process inversely, by transforming mineral N and P first [25,26]. Part of the organic P in the litter is lost through runoff processes, depending on the slope of the land and the occurrence and intensity of rain [2,10]. P lost through this process is one of the highest contributions to eutrophication of water bodies located downstream.

The organic Si material, often called biogenic Si, refers to the Si present in structures named phytoliths. After Si uptake by roots, Si precipitates in the cell walls of shoots and leaves primarily, forming rigid skeletons in cell plants [27,28]. When litter is mixed with the topsoil, the process of phytolith dissolution begins, and slowly Si is detached from the organic structure and becomes available as ortosilicic acid [29]. This process is highlighted in the Si cycle due to the amorphous structure of Si in the phytoliths, which provides them with quicker dissolution rates, compared to the slower rates we found in Si bonded in the crystalline structures of minerals [30]. As so, the organic material in P and Si compounds are different, while the organic P is dissolved through bacterial decomposition, Si biogenic material dissolution is mainly a chemical process.

The mineral part of the P and Si cycle in soil is the most important and complex due to the myriads of forms and processes occurring. Inorganic P produced during the organic matter decomposition, often in PO_4^{3-} form, can quickly be targeted by Al and Fe hydroxides that adsorb it at their surface [6]. This process of precipitation is responsible for most of the inorganic P unavailability in soils [11,31]. Since soluble P can easily be bonded with these hydroxides, its concentration in soil water is normally under detection limits and other chemical processes do not have the opportunity to occur. Inorganic Si is not so reactive as P, and while it might also be adsorbed on the surface of the

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same hydroxides it can also undergo other processes [32,33]. Ortosilisic acid may precipitate into amorphous Si compounds, when concentration is high enough and chemical conditions allow the process to occur. In this case, opal A and CT are produced in soils, with similar amorphous structure as phytoliths and equal higher dissolution rates. But the same Si can also reprecipitate in secondary minerals, if pH, temperature and other mineral concentrations are present and optimal. In this case, there is a chemical equilibrium between re-precipitation and dissolution that depends on these factors and vary within different soil types and soil layers along the profile [34–36].

Both Si and P can ultimately originate from primary mineral weathering. In this process, the inorganic Si and P present in the minerals which comprise the Earth crust, slowly dissolved through water effect [37]. While Si is widely present in most of the minerals that one can find in the terrestrial systems, such as quartz, feldspar, olivine etc., P is present only in phosphorite [38]. So, Si is one of the most abundant elements, but P is often limited.

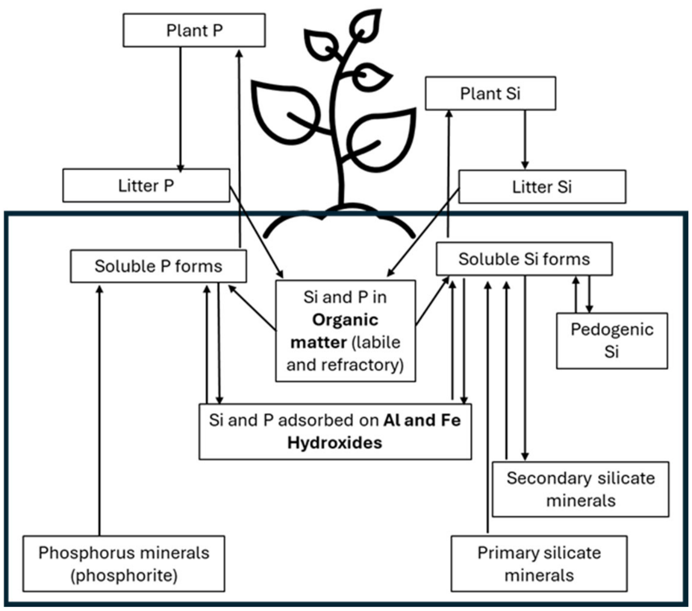

Figure 1. Silicon and Phosphorus cycles in soil (solid and soluble forms).

3. The Link between Si and P

The interference of Si in P plant uptake has been suggested firstly by [39] and [40], without however detailing how Si affects the processes occurring in the soil-plant system that potentiate the crop efficiency increase under P limitations. They register that dry weight was positively impacted by the addition of silicate when phosphorus solution was limited, but almost negligible if the plant had enough P available. Later, [41,42] also conducted experiments where silicon and phosphorus were both provided to rice in a gradient of concentrations. In the first experiment Si and P were provided through a nutrient solution and rice shoots dry weight was observed to always increase with the surplus of Si despite the level of P in the solution. When P input was low, shoot dry weight also increased when Si was added, but it was not followed by an increase of organic P in the shoot. In the second experiment, silicates were added on a pot experiment with P-deficient soil. Results showed higher dry weight, but no increase in P concentration in shoots. However, P/Mn ratio increased. The better performing results for crops growing with silicates without the increase of P content had also been reported by [43] and [44] were a study was conducted in a greenhouse with pot experiments and no P uptake increase was observed with the addition of several different Si supplies, while the yield was positively impacted by it.

Other studies have shown different outcomes. Rice growing under Si fertilization in the Everglade soils (low in Si concentration) had higher concentrations of P compared to no silicon-

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supply fertilization [45]. Another study [46] also focused on the Si supply effect on wheat growing in acid soils with low P and showed that P concentration increased in the shoots and dry weight was also higher. In pot experiments [47,48], silicon supply clearly affects positively P use efficiency of wheat and sorghum, in the case when P exists in the soluble form but also when P is added in the insoluble form. In China, one field trial showed that fertilization with Si (and straw return to soil, which is also enriched in Si) provided a higher P uptake and use efficiency, while also increasing grain yield [49]. The effect of Si fertilization in the growth of pigeonpea in acidic and P deficient soils resulted in higher dry weights, increase in nitrogen and phosphorus plant content and optimum P:Mn ratios, while the plant-available water in the soil was also higher, which enhanced leaf erectness [50]. In wheat, the increase in Si uptake was followed by an increase in aboveground biomass and gran yield, while P plant concentration also increased [51].

One can state that while the effect of Si has not always been translated in the higher uptake of P and/or increase of its use efficiency, its administration has resulted in higher yields and/or dry weights. This was especially important in studies where the soil was deficient in P or the studied crop was growing under limited access of available P. Based on this evidence, the summary of observed/suggested mechanisms for the pathway of Si influencing P concentration/uptake are described below and presented in Figure 2.

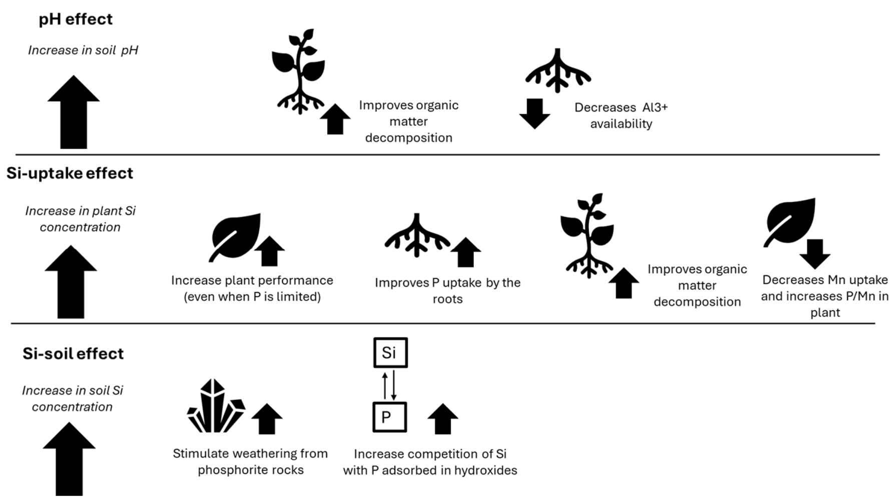

Figure 2. Summary of the Silicon effects on the soil ecosystem that benefit P mobilization and uptake.

The pH Effect

The addition of silicate fertilization increases soil pH, which is specifically important in acidic conditions (when soluble P concentration is lower). Under neutral or alkaline pH, the soil organic matter decomposition rate is higher, which increases the availability of inorganic nutrients for plant uptake such as inorganic N [41,42]. Depending on the soil type, organic matter pools availability and quantity, this effect may be higher or lower. Also, indirect benefits occur since soil pH increase lowers the concentration of rhizotoxic Al species (primarily Al^{3+}) that can further decrease P acquisition due to root damage [46]. Exudation of malate and citrate anions by wheat roots has been considered as predominant Al tolerance mechanisms. Therefore, reducing Al availability in the rhizosphere, improves root exudation [46]. The exudation of organic anions such as citrate and malate potentiate the mobilization of both inorganic and organic P [2].

The Si-Uptake Effect

The fact that Si is available, and its uptake by the plant increases, induces alterations that benefit the plant such as the leaf erectness, photosynthetic activity, stomatal water loss resistance [20,50,52]. This means that even when P is limited in the soil and restricts the plant growth, the presence of Si ameliorates the situation, by providing the plant with extra tools to optimize its performance [41,42]. While not directly linked to phosphorus uptake or availability, the addition of silicate fertilization can enhance crop performances even when P is limited in the soil [49]. Also, the silicate fertilization is known to induce some alterations on root morphology [53,54]. Consequently, higher root mass distribution, root length, root surface area, and number and length of root hairs and lateral roots [55,56] benefit the plant by increasing the uptake of several nutrients, including P. One study [45] observed that the presence of silicate enhanced organic matter decomposition, which will in turn provide the soil with extra mineral nutrients, including P that becomes more available to plants. Contrary to studies cited above, this reported effect of silicate input was attributed not to pH alteration, but to the increase of root exudation of organic acids that mobilized P in the rhizosphere, while also regulating the P transporters in the wheat roots [46–48]. Additionally, Si uptake is also linked to the decrease of Mn uptake by the plant. Even when no direct increase in P uptake is observed, the silicate fertilization decreases the Mn concentration in the plant, which can cause symptoms of toxicity and limit its growth. More important, lower Mn/P ratios improve P usability and efficiency of the plant [41,42,50]. Certain facts suggest that P availability may be controlled by the levels of Mn and Fe in plants when P is low. P is translocated and redistributed in plants as inorganic P, and since a strong affinity exists between P and Fe or Mn, the relationship of these elements may affect P nutrition [57,58]. Recently, increased leaf P accumulation in wheat plants supplied with Si has been attributed to improved P availability and involvement of Si in C and P metabolism with subsequent effects on leaf nutrient stoichiometry [51]. Additionally, uptake of Si promotes the oxidation power of roots and thus decreases the solubility and uptake of Fe and M, which in turn increase P availability in the shoots [41].

The Si-Soil Effect

The presence and availability of a higher concentration of Si in soils impacts P availability (which in the end will translate in higher uptake rates by the plant). Studies [47,48] suggested that the silicate weathering also releases insoluble and less available P (from phosphorite rocks), although the exact mechanism has not been fully established. Since phosphorite rocks are not abundant in soils compared to other minerals, such Si-effect is not so important compared to the desorption potential of P from Al/Fe hydroxides. This Si-P interaction [59] includes the ability of Si to adsorb to hydroxides surfaces and therefore compete with P [49,60]. This mechanism has been studied and documented in marine sediments, where P was shown to be released from hydroxides surfaces when Si was present in excess on the pore water [61].

Silicate minerals have very low solubility and Si availability in the pore water is dependent on many factors, including climate and soil weathering degree [62], ranging from 3x10-3 to 4.5x10-1 gSi kg^{-1} soil. Also, the affinity of Si to the hydroxides is expected to be lower when compared to P, as it is the case of other ligands such as sulphate and bicarbonate, suggesting that a higher quantity of bioavailable Si is necessary to release P from the hydroxides surface [63]

4. Moving towards the Future

Si fertilization is one option to potentiate the benefits that Si has on the availability of P in soils, P uptake and P use efficiency in plants. The presence of Si contributes positively to the plant growth, and it may also replace partially or totally the P fertilization necessary (depending on the P stocks in the soil, soil conditions and climate). The use of Si fertilizers is already relatively common, especially in countries across the African, Asian and American continents [64,65]. They are mainly used in Si-accumulator crop cultures such as rice, wheat, sugarcane and sugar beet. Lately this approach has spread to other regions and to other crops, in parallel with new discoveries related to Si benefits in agriculture and forestry, also for non-accumulator plants [66,67]. Also, the latest scenarios concerning climate change suggest that agriculture will face more and more extreme events of rain and temperature [68], and therefore crops will be subjected to more stressful situations. In this future context, Si accumulation in plants will become increasingly crucial for their efficient growth, providing mechanisms to deal with limiting and stressful conditions. The addition of Si-fertilizers to soils has therefore high potential for application in a wide range of soils and climates, but so far research has overlooked and underexplored its ability to stimulate P mobilization from the immobile P stock present in soils heavily subjected to fertilization in the past and improve its uptake and usability by plants [63].

The first step to leverage the potential of Si-fertilizers is to assess the potential sources. This selection must take into consideration that the source of Si introduced in the soils must be readily available, otherwise the dissolution period will exceed the acceptable time for the Si-P biogeochemical processes to take place in a crop growth environment. The potential Si-sources can be biogenic, such as crop residues that are kept by farmers after harvest and are re-introduced in the soil [69]. This process prevents the interruption of the Si cycle that takes place when all plant residues are removed from the farm soil [32,70]. This is especially important in soils growing Si-accumulator crops, since these plants accumulate Si in the form of amorphous silica – phytoliths – in the cell walls of leafs and shoots [27]. The amorphous configuration confers them high solubility when compared with the silicate minerals [60]. Other potential sources of Si-fertilizers include inorganic forms such as sodium silicate, calcium silicate and potassium silicate. All three fertilizes have been used in the recent past in studies to test the effect of Si in plant development, because they provide readily available Si in the soil solution [64].

However, large scale use of any of these inorganic fertilizers as a replacement of P fertilization (full or partial) raises questions about their own environmental performance, since their synthesis also involves several physical/chemical processes, with consumption of raw materials, water and energy. Moreover, if the amount of Si fertilizer required to release P from soils is more material and energy intensive than the production of P fertilizers, it is possible that the solution is environmentally unviable. A recent preliminary study [71] conducted a simplified life cycle assessment (LCA) comparing the environmental impacts during production of superphosphate fertilizer with the most common inorganic Si fertilizers in use (calcium and sodium silicate fertilizers). The study concluded that generally the production of Si fertilizers has lower environmental impacts for Si:P replacement ratios up to 4:1 for emission of greenhouse gases or as high as 26:1 for freshwater eutrophication potential, in the case of sodium silicate. For calcium silicate produced from lime, sand and water, the viable replacement ratios were generally even higher. Calcium silicate has particularly low impacts in categories such as human toxicity, freshwater ecotoxicity and water, mineral and fossil renewable resources. These results suggest that the supply of Si fertilizers has better indirect environmental performance than P fertilizers even if the amount of Si-fertilizer necessary to mobilize P is higher than the amount of P-fertilizer itself. However, more detailed LCA studies involving the complete production cycle of different Si-fertilizers, their use and disposal must be carried out to assess their actual environmental performance.

5. Conclusions

The beneficial effects of silicon for plants are widely disseminated nowadays, especially due to the ability of silicon to capacitate the plants with higher resistance to herbivory and parasites attacks, resistance through water scarcity and metal toxicity environments. Other less developed beneficial roles of having high levels of soluble Si in soils and readily used for plants, include the improved ability of plants to uptake nutrients, such as phosphorus. However, the evidence for this benefit for growing crops in low deficient P soils and/or its ability to improve crop P use efficiency is scattered through the literature and hardly ever recognized by important reviews about P use sustainability. This is surprising since P is often limited in soils for crop use and farmers apply high loads of P fertilization with high economic and environmental impacts. In this narrative review, we have summarized the documented links between the silicon and phosphorus cycles in soils, to understand the potential benefits that high Si concentrations in soil solution can bring to P mobilization and uptake. We have concluded that Si in soils may contribute to a higher P crop uptake through 3 mechanisms: 1) the pH effect, since silicates turn the soil pH more neutral/alkaline and that improves organic matter (and organic P) decomposition while decreasing the Al^{3+} presence and toxicity; 2) the Si uptake effect, since the Si transported through the plants improves its photosynthetic activity (even when P is low), its presence in the roots improves the uptake of P while also decreasing the Mn uptake (which is toxic) and increasing P/Mn ratio which is linked to the plant P use efficiency; 3) the Soil-Si effect, since Si present in the soil potentiates phosphorite weathering and increases competition with P adsorbed to the surface of hydroxides, which may be mobilized and ready for uptake. Future research should focus on each benefit individually, considering the soil characteristics and the P concentration of each pool for a more efficient use of the Si supplementation. Those documented effects should also be integrated in biogeochemical models to provide more accurate depictions of the soil processes involved. Those models can then better inform and advise policymakers and farmers. There is also a need for more research on the environmental sustainability of Si fertilizers, to ensure that they do not carry higher burdens than the continued use of P while deposits are not depleted.

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