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Title: The role of silicon in the supply of terrestrial ecosystem services for food security and environmental concerns

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Abstract

In everyday life, silicon (Si) is omnipresent in manufactured objects such as electronic chips or cosmetic products. However, a growing number of studies on Si in plants and soils highlight its interest in today's environmental concerns such as food security, carbon regulation or cultural heritage. Here we review the state of knowledge of the Earth's terrestrial silicon cycle and show its importance in the framework of the ecosystem services concept. We show that silicon can participate in the inherent and manageable properties involved in all ecosystem services. As records of the past, phytoliths can be useful parameters in cultural services. Si is involved in provisioning services because it may influence the production of food and fibers. Si is also involved in regulating services because of its involvement in C sequestration. Regulating and provisioning services may be improved through Si management not only by the application of Si fertilizer to soil but also by foliar application in the field. The soil and plant silicon status should be considered in assessment of ecosystem services as much as essential nutrients are considered, and the cost-benefit balance of Si remains poorly quantified.

Keywords Silicon. Terrestrial ecosystems. Phytoliths. Provisioning ecosystem services. Regulating ecosystem services. Cultural ecosystem services

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1. Introduction

In everyday life, silicon (Si) is a major component of everyday manufactured products as evidenced by glass, electronic chips, silicones or more recently nanoparticles (Pradha et al. 2021). As a natural element, silicon is also known as a major constituent of beach sand and dust that cause silicosis. The benefits of Si in major environmental issues remains however largely underestimated. Silicon is the second-most common element on the Earth's surface, after oxygen. It is an essential nutrient for aquatic microorganisms such as diatoms that are of utmost importance in the aquatic food chain and play a major role in global biogeochemical cycles (Tréguer and Della Rocha, 2013). The Si biogeochemical cycle in aquatic ecosystems is strongly dependent on the terrestrial biogeochemical cycle (Struyf et al. 2009), as the supply of Si for diatom development depends on the processes that occur on land, particularly in soils where Si-bearing solid phases are weathered and transfer Si to rivers, lakes and seas. While marine diatoms sequester 240 Tmol Si yr⁻¹ (Tréguer et al. 1995), the amount of Si fixed by terrestrial biomes is estimated to be 84 Tmol Si yr⁻¹ with 35% in cultivated lands (Carey and Fullweiler 2012) because the most important crops such as cereals are Si accumulators (Guntzer et al. 2012a).

In plants, the first measurements of Si concentrations were performed by de Saussure (1804), who suggested that Si was an essential nutrient because of its high concentration in grasses. Si, however, was not considered as an essential element in the first inventories of the elements that are essential for the growth and survival of plants (Sachs 1865). Since the 20th century, the benefits of Si have been particularly well documented for crops such as rice, wheat, sugarcane, soybean, tomato, and cucumber (Liang et al. 2015) and for fibers such as hemp (Luycks et al. 2017), bamboo (Collin et al. 2014) and cotton (Rodriguez and Datnoff 2015; Fichhof et al. 2018).

Although the role of Si in plants deserves more research (Klotzbücher et al. 2017), a large body of empirical literature has shown its benefits and attracted the interest of agrobusiness (International Plant Nutrition Institute: Nutri-Facts Sheet: Silicon ref. #14#15056).

Ecosystem services are defined as “the benefits that people obtain from ecosystems”. Although diatoms are well recognized as providers of ecosystem services in aquatic ecosystems because they impact many human beneficiaries (Rhodes et al. 2017), Si is not mentioned in the framework of terrestrial ecosystem services and related utmost important issues such as food security or carbon sequestration. Indeed, Si is not mentioned in the “key soil properties” that are related to soil-based ecosystem services (Adhikari et al. 2016) or in the list of soil quality indicators (Drobnik et al. 2018; Bünemann et al. 2018). The concept of ecosystem services has been largely popularized in recent decades since the seminal papers of Costanza et al. (1997) and Daily et al. (1997). The services provided by ecosystems are complex and have been classified into three main categories (CICES, 2011): 1) provisioning e.g. food, water, timber, fiber, and fuel production, 2) regulating and maintenance e.g. carbon sequestration, water and waste recycling, and 3) cultural e.g. recreational, aesthetic and spiritual; a fourth category of ecosystem services, namely, supporting services, is often added to the list (Millennium Ecosystem Assessment, 2005). Here we review the importance of Si in the framework of terrestrial ecosystem services (Dominati et al. 2010; CICES, 2011; MEA, 2005). We describe how the Si biogeochemical cycle is part of the supporting processes as defined by Dominati et al. (2010) and discuss the Si contribution to different ecosystem services, namely, cultural, regulation and provisioning services. Finally, we show how Si should be added to soil and plants to manage or improve ecosystem services.

2. The Si biogeochemical cycle: A supporting process

According to the Millennium Ecosystem Assessment (2005), supporting services are necessary to produce all other ecosystem services. Unravelling the terrestrial biogeochemical cycle of Si makes it possible to characterize the factors that control Si fluxes and the transfer between ecosystem compartments and hence its bioavailability (Figure 1) and impact on ecosystem services.

2.1 Terrestrial Si cycling at a glance

Si is found in the various biotic and abiotic compartments of terrestrial ecosystems (Figure 1). The input of Si by rainfall and dust is generally small and neglected in the Si budget (Sommer et al. 2006). In the solid soil phase, Si is included in primary minerals such as quartz, feldspar, in secondary minerals e.g. phyllosilicates and short range-ordered aluminosilicates and amorphous biogenic silica from plants namely phytoliths and microorganisms e.g. testate amoebae, diatoms, sponges. It is also adsorbed on soil particles such as Fe oxides (Cornelis et al. 2011) or clays (Nguyen et al. 2017). Weathering of the solid phase results in the release of Si in solutions, referred below as DSi, most generally in the form of silicic acid $\text{Si}(\text{OH})_4$. The dissolution of silicate depends on the solid phase properties e.g. solubility, kinetics, grain size, on edaphic factors e.g. pH, ionic strength, biota and on climate. The pH level has contrasting effects on the dissolution of silicates: quartz and biogenic silica dissolution is higher under alkaline conditions, while aluminosilicates are more soluble at low pH levels (Frayse et al. 2009).

Si solubilization can also be mediated by biological activities (Figure 1). Terrestrial plants and microorganisms can extract their essential nutrients from the dissolution of minerals through the release of organic compounds (Banfield et al. 1999; Neaman et al. 2006). Some bacteria, for example, have been found to specifically solubilize silicates (Sheng et al. 2008), resulting in an increased dissolution rate of minerals as resistant as quartz when colonized by cyanobacteria (Brehm et al. 2005). The role of fungi in increasing the release of Si from silicates is also well documented. The fungi attack silicates to varying degrees (Henderson and Duff 1963). For example, *Verticillium leptobactrum* extracted more Si from chrysotile than did *Fusarium oxysporum* (Daghino et al. 2009); *Penicillium simplissimum* solubilized 31% of Si from

powdered rocks after 7 days of incubation (Silverman 1970); and the presence of a mycorrhizal fungus in the soil significantly increased the release of Si into drainage water (Van Hees et al. 2004). The presence of lichens resulted in a fourfold increase in the Si flux compared to bare mica-schist, as shown in laboratory experiments (Aghamiri and Schwartzman, 2002).

Soil fauna and megafauna also modify the Si cycle by ingesting minerals, which results in an increase in Si solubilization. Bityutskii et al. (2016) showed that the concentration of water-extractable Si in earthworm casts was higher than that in bulk soil. Bioavailable Si, extracted by CaCl_2 , was higher in termite mounds than in bulk soil (Jouquet et al. 2020). Vandevenne et al. (2013) showed that the feces of various herbivores produced a higher release of Si than that of fresh hay and concluded that grazers likely play a significant role in enhancing the availability of Si in the soil.

Once in the soil solution, DSi is either lost through drainage, sorbed onto mineral surfaces or taken up by plant roots or microorganisms. In plants, as DSi reaches the leaves, water evaporates through the stomata, creating an ascendant sap flux, while silicon accumulates in leaf and stem cells, polymerizing and forming solid clusters called phytoliths. Phytoliths play a major role in the Si cycle (Alexandre et al. 1997; Sommer et al. 2013; Yang and Zhang 2018). Indeed, the dissolution of 0.1% to 1% of the soil phytolith pool is enough to explain the Si concentrations in surface waters (Frayse et al. 2010). Si uptake by testate amoebae can significantly lower the amount of Si released into solutions, as shown by Aoki et al. (2007). Sommer et al. (2013) measured a 17 kg Si ha^{-1} uptake by testate amoebae, accounting for approximately half of the annual Si uptake by plants (35 kg Si ha^{-1}).

The Si budget in cultivated areas is still poorly documented. It may be impacted when irrigation and Si fertilizers are applied (Desplanques et al. 2006; Riotte et al. 2018) and when plant residues are exported. Indeed, if the removal of Si by plant exportation is not compensated, the soil may be depleted of phytoliths (Desplanques et al. 2006; Vandevenne et al. 2011; Clymans et al. 2011; Guntzer et al. 2012b). Assuming that the phytoliths are the only source of Si for crops, a simple calculation shows that the phytolith pool would be depleted within a few decades, considering an export of $50\text{-}100 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ and an initial pool of Si from phytoliths of $1000 \text{ kg Si ha}^{-1}$ (Keller et al. 2012). The situation is more complex when considering soluble Si: while Ma and Takahashi (2002) found soluble Si depletion in 250-yr-old paddy fields in Japan, Caubet et al. (2020) observed an increase in CaCl_2 -extracted Si in temperate,

aerobic, cultivated soils that developed on sedimentary rocks due to pH variations. Cultivation may increase the pedogenic silica pool that is related to the clay fraction (Vandevenne et al. 2015; Caubet et al. 2020; Keller et al. 2021).

2.2 Si status, an inherent and manageable soil property fully involved in soil pedogenesis

To evaluate soils, Dominati et al. (2010) defined the concept of natural capital. This natural capital is formed and maintained by supporting processes and is characterized by two main groups of properties: the inherent properties that are stable over decadal to century time scales and the manageable properties that may change on an infradecadal time scale (Figure 2). The Si status belonging to both categories depends on its form (Figure 2). The main procedures that are currently available to quantify the various pools of Si forms are summarized in Table 1. For the quantification of Si in minerals and plants, the procedure may take place in 2 steps: the first step consists of destroying the material and releasing Si in a solution, which is generally alkaline, and the second step consists of measuring the concentration of dissolved Si, generally by spectrophotometry. Other nondestructive methods are also available, such as MIRS or portable X-ray fluorescence (Table 2). For the analysis of phytoliths, the extraction procedures require the destruction of the matrix (plants or soils) and separation using heavy liquid flotation. While Si is involved in minerals that evolve over the long term (Rounsvell et al. 1999), the Si soluble pool may depend on agricultural management e.g., liming, crop type and therefore may evolve on a much shorter time scale with yet to be defined kinetics.

3. Cultural services

“Cultural services include all non-material ecosystem outputs that have symbolic, cultural or intellectual significance” (CICES, 2011). Phytolith records such as pollen records provide “scientific” service type benefits from the “Intellectual and experiential” class (Figure 2). Indeed, phytolith assemblages that are preserved from dissolution in paleosols containing hominin fossils or human artifacts such as stone tools, pottery, grinding stones, and hearths are now widely studied, as they help document the early history of the human lineage, cultural behaviors and practices, plant domestication and early agricultural and pastoral practices. Thanks to their

recognizable shapes, some phytoliths allow the identification of certain plant taxa. They are particularly diagnostic of the Poaceae, Cyperaceae, Arecaceae, Commelinaceae, conifers, ferns, Musaceae, and Cucurbitaceae (Piperno, 2006; Eichhorn et al. 2010; Ball et al. 2016).

At paleoanthropological sites, phytoliths have helped to characterize the paleovegetation associated with some of the earliest hominins known to date (Figure 3) (Novello et al. 2017; WoldeGabriel et al. 2009) and have shown that the first bipedal human ancestors lived in savannah-covered landscapes, but their habitat was restricted to forested environments located along rivers, lakeshores or springs (Barboni et al. 2019). At Olduvai Gorge, a World Cultural Heritage archaeological site in Tanzania, phytoliths have helped document the paleoenvironmental context associated with the emergence of early cultural practices: hunting and stone tool use at Olduvai 1.8 million years ago may have occurred because freshwater springs attracted prey and carnivores that were easily hunted by *Homo* species hiding in easy-to-climb palm trees. Phytoliths have also proven useful for documenting the beginning of crop domestication such as rice in China (Luo et al. 2016; Ma et al. 2016) and maize and squash in Central and South America (Lombardo et al. 2020; Piperno et al. 2009; Ranere et al. 2009), and the grinding of wild grasses in West Africa (Radomski and Neumann 2011) during the Holocene. Phytolith studies are also applied to identify and characterize agro-pastoral activities and economies (Ball et al. 2016; Roberts and Rosen 2009; Rosen and Weiner 1994). Although less reliable, phytolith assemblages trapped in dental calculus were tentatively used for documenting the paleodiet of australopithecines (Henry et al. 2012).

4. Regulation services

Regulation services include “all the ways in which ecosystems control or modify biotic or abiotic parameters that define the environment of people, i.e., all aspects of the 'ambient' environment”. Here, we document that Si is involved in the “C sequestration” service (CICES 2011) (Figure 2). Indeed, Si weathering may help remove atmospheric CO₂. Soils are the main place where weathering takes place. At the geological scale, weathering links the Si and C cycles because the chemical alteration of silicates consumes CO₂ from the atmosphere and produces dissolved acid carbonate that is eventually deposited in the ocean as Ca or Mg carbonates by streams

providing services at the terrestrial scale if we consider crops as “material outputs”. Hereafter, we show how Si benefits crops and how this benefit depends on the soil Si status and environmental stressors.

5.1 Si and nutrient uptake

Ma and Takahashi (2002) showed that Si had a positive effect on rice growth under phosphate deficiency stress. They attributed the effect of Si to the enhanced availability of internal P due to the reduced uptake of excess Fe and Mn. In addition, when P was supplied at a high concentration, a chlorosis effect on rice leaves was not observed in the presence of Si. However, the mechanisms involved were not clear. The role of Si in mobilizing P was shown in Arctic soils, where a positive correlation between P and Si availabilities was found (Shaller et al. 2019). A decrease in the Fe(II)-phosphate phase was found after Si addition, indicating a mobilization of P from the mineral phase. Adsorption of both silicic acid and phosphate ions on the soil depended on the pH (Hingston et al. 1972; Obihara et al. 1972), but while the maximum Si adsorption peaked at a pH of approximately 8-9, the adsorption of P decreased when the pH increased. If the level of adsorbed phosphate was very low in neutral and alkaline soils, Si adsorbed and displaced P in solution, leading to its uptake by plants (Obihara et al. 1972). Iron III oxides and hydroxides were important sinks and regulators of dissolved Si and phosphate (Sigg and Stumm 1980). These results on soils have been confirmed in plants with evidence of the effect of Si on the P uptake and plant growth in aquatic plants (Schaller et al. 2012) and grasses (Neu et al. 2017). Other experiments, which applied different combinations of Si and P rates, showed that increases in rice yield were not straightforward (Li et al. 2020). Crusciol et al. (2015) showed that the application of silicate and phosphogypsum on Brazilian upland rice affected the number of panicles per m² but not the weight of 1000 grains. More research is required to decipher the complex interaction between Si and P in soils and plants (Matichenkov et al. 2017; Haynes and Zhou 2018). The effect of Si on N nutrition remains poorly understood; for example, Detmann et al. (2012) showed an increase in yield and in harvest index (grain/total biomass ratio) but not in grain N. The availability of other nutrients, such as K and Fe, was found to be positively affected by Si (Tubana and Heckman 2015; Liang et al. 2016).

5.2 Si and abiotic stress

The benefits of silicon on plants that are subjected to drought have been observed for many crops, including rice, sorghum, wheat, and maize (Haynes 2017). Chen et al. (2018) suggested several possible mechanisms at the root level: Si could block reactive oxygen species that inhibit the activity of aquaporins, which are proteins that promote the passage of water molecules; Si could improve the accumulation of soluble substances e.g. sugars and amino acids in xylem sap by osmoregulation; and finally, Si could adjust the growth of the roots and increase the root/stem ratio, which, combined with the improvement in the aquaporins' efficiency and the osmotic motive force, could contribute to the improvement in the hydraulic conductance of the roots. Meunier et al. (2017) showed that silicon attenuated the effects of drought by reinforcing the structure of leaves through preferential phytolith accumulation above the veins. Amorphous silica in the soil may also reduce plant stress by increasing the soil water holding capacity and plant water availability (Schaller et al. 2020; Kuhla et al. 2021). In addition to water stress, the beneficial effect of Si has also been documented for other abiotic stressors such as an excess of salt or UV radiation (Liang et al. 2015).

5.3 Si and soil contamination

Si addition can also be beneficial when organic or inorganic soil contamination induces deleterious effects on crops including rice, corn, and wheat (Tunaba and Heckman 2015; Haynes 2017; Rizwan et al. 2016). The mitigation processes, though still poorly understood, may occur in the soil and at the root or shoot levels. For instance, Rizwan et al. (2016) suggested that in durum wheat, Si reduced the root-shoot translocation of Cd by armoring the root surface with Si. Greger et al. (2016) showed that Si downregulated heavy metal ATPases, which regulated Cd transport from the roots to the shoots in wheat. Silicic acid also decreased the As concentration in rice shoots because the arsenide transported in the roots was shown to share the same high affinity transporter as Si and thus competed with it, indicating that sufficiently available Si in soil would be efficient at reducing As accumulation in rice shoots (Ma et al. 2008). Si can also reduce the transport of Cu from roots to shoots in grasses (Keller et al. 2015; Viera Filho and Monteiro 2020; Collin et al. 2014). Si mitigation may also play a role in the shoots. For instance, Al can be sequestered in phytoliths by codeposition with Si (Hodson and Evans 2020). Delplace et al. (2020) also showed that sequestration of metals in phytoliths may occur for As, Cu, Mn and

Pb in reeds. A more comprehensive review on the silicon-mediated alleviation of heavy metal toxicity in plants can be found in Adrees et al. (2015).

5.4 Si and biotic stress

Si has been shown to be beneficial for many crops such as rice, wheat, sugarcane, soybean corn, and tomato that are affected by herbivores, insects, and fungi (Liang et al. 2015; Rodrigues and Datnoff 2015). In Japan, the effects of Si on rice were discovered at the beginning of the 20th century, with studies showing that Si-rich rice leaves were less infected by blast, a fungal disease, than were Si-poor leaves. However, there is no consensus for explaining the role of Si in plants under biotic stress. Two scenarios are plausible. One scenario involves a physical barrier where a silica layer formed in the cell wall enhances a plant's resistance to biotic stress. According to Coskun et al. (2019), amorphous Si deposited in the apoplast interferes with effectors in case of a parasitic attack, or in the case of abiotic stress, it fortifies barriers around the vasculature, thus preventing the transport of toxicants into the shoots. The second scenario involves a biochemical barrier where Si could stimulate the expression of genes involved in the production of defense enzymes e.g. polyphenol oxidase, glucanase, peroxidase, phenylalanine ammonia-lyase, antimicrobial compounds e.g. phenolic, flavonoids, phytoalexins, pathogenesis-related proteins in plants, or substances that play a role in the signal transduction pathways involved in immune defenses e.g., salicylic acid, jasmonic acid, ethylene; cytokinin (Wang et al. 2017; Markovich et al. 2017).

6. Management of ecosystem services

Si management may improve the regulating and provisioning services not only through better crop management and the application of Si fertilizer to soil but also by foliar application in the field.

6.1 Crop and soil management

Si spreading on soil is directly involved in regulation (and maintenance) services. Indeed, the results from a long-term experiment in Germany showed that approximately 43-60% of Si exports could be prevented by crop straw recycling (Puppe

et al. 2021). Si addition may simply consist of keeping organic residues that are rich in Si in the field, as was done in traditional agriculture for centuries but has been largely abandoned in recent decades in “conventional” practices where removal of residues is common. Song et al. (2021) studied a 39-year-old paddy field amended by a long-term straw return. They showed that the bioavailable Si and rice yield significantly increased when compared to NPK fertilization alone by 29.9 % to 61.6 % and 14.5 % to 23.6 %, respectively. Other plant materials, such as silica-rich biochars, have also been shown to be potential Si fertilizers (Nguyen et al. 2021).

Si fertilization may also consist of applying silicates that have kinetic properties that are compatible with the growth duration of crops, such as silicate materials originating from geological sites, or from industrial byproducts (Liang et al. 2015). For instance, the application of Si as diatomite containing amorphous silica, in a pot experiment using soil from south Indian paddy (rice) fields, led to an increase in rice grain yield in acidic soils using the recommended doses of N, P, and K (Sandhya et al. 2018). Hence, Si may be a limiting element for crops, and Si fertilizer may be recommended for rice in certain soil types. Acidic soils that are depleted in nutrients and silica are common in tropical regions where heavy rainfalls and high temperatures lead to intense weathering (Cornelis and Delvaux 2016).

Except for some slags that may contain high levels of metal contaminants, silicate fertilizers are considered to be environmentally friendly and, depending on their cost, may constitute a positive investment. The cost-benefit calculations on integrating calcium silicates as fertilizers in agricultural practices have been estimated to provide savings of approximately \$74 ha yr⁻¹ assuming a yield increase of 12% for rice production in Florida, USA (Alvarez and Datnoff 2001). Because Si application may eliminate the need for fungicides and pesticides in managing rice diseases and may reduce the application of other fertilizers and lime, extra savings of \$50–272 ha yr⁻¹ were estimated (Alvarez and Datnoff 2001). Cost-benefit calculations should require more studies that consider the large variety of crops and soils around the world and the cost and availability of Si fertilizers that are produced from byproducts or specifically formulated.

The fraction of soil Si that is available to plants can be empirically measured in an extracting solution mixed with soil (Table 1). If a positive correlation is obtained between soluble Si extracted by the procedure and the Si concentration in plants growing in the same soil, then the procedure can be used as a proxy for the

measurement of plant bioavailable Si (referred below as PAS). Owing to the importance of quantifying bioavailable Si, many extractants have been proposed (Table 1), as well as the associated thresholds to identify critical levels of bioavailable Si. If the PAS is below the critical level, Si fertilization may be required. Based on 200 soil samples from rice fields in southern India and Si extraction using a 0.01 M CaCl₂ solution and 0.5 M acetate-acetic acid, Meunier et al. (2018) estimated that between 38 % and 88 % of the soils were below critical levels and could be considered depleted in PAS. In China, a chronological study from 1990 to 2010 on rice field soils showed a significant decline of 14.1 % in PAS values using 1 M acetic acid- sodium acetate buffer at pH 4 (Yang et al. 2021). In French soils, Caubet et al. (2020) showed that 4 % of the soils cultivated for wheat are below the critical level of 20 mg kg⁻¹ using a 0.01 M CaCl₂ and could be considered deficient in PAS and would benefit from Si addition.

6.2 Foliar application

Compared to Si application on soil, relatively few studies document the beneficial effects of foliar Si on plants, and the underlying mechanisms are rarely discussed. Among these, Guevel et al. (2007), who studied powdery mildew on wheat, showed that both root and foliar Si application were beneficial, but foliar application was less effective. They concluded that foliar application did not lead to a significant absorption of Si by the plant and that the prophylactic effect was not directly attributable to Si but to a deleterious effect that the product deposited on the leaf had on the fungus. In their review on foliar Si application, Puppe and Sommer (2018) showed numerous examples of the positive effects of foliar Si application on mitigating the effect of diseases on crops, but in the absence of biotic or abiotic stress, the effects were not systematically observed. Foliar application of Si nanoparticles has also been tested and shown to be beneficial, especially for mitigating the effect of Cd (Wang et al. 2015). Foliar application deserves more research, especially since it may be used instead of synthetic chemical compounds such as pesticides, whose deleterious effects on the environment and health are recognized.

7. Conclusion

We have shown that Si, despite its status as a nonessential element, is an important component of both terrestrial and aquatic ecosystems. In terms of soil

capital, Si is both an inherent property e.g., phytoliths, total Si, Si minerals and a manageable property e.g. PAS. Under its available form, Si is beneficial to plants such as commercial crops and fibers and therefore contributes to provisioning services. In the form of phytoliths, Si becomes a record of the past and therefore contributes to cultural services. Si also contributes to climate regulation through silicate weathering. This makes Si an important natural element to consider when defining soil indicators for ecosystem services, and its status needs to be assessed in addition to those of other soil properties. Since long-term cultivation could deplete the soil to a point where a PAS deficiency can be recorded, it has become a challenge to maintain high levels of bioavailable Si in cultivated fields. The costs and benefits of Si application in agricultural management are, however, still poorly documented.

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Figure and table captions

Figure 1. The main pools and fluxes in the terrestrial Si cycle. Adapted from Monger and Kelly, 2001; Sommer et al. 2006; Cornelis and Delvaux 2016; Tubana and Heckman, 2015, Schaller et al, 2021. (1) Mineral e.g. slag, diatomite and organic e.g. compost, biochar; (2) BSi: biogenic silicon; (3) SRO: short ranged-order aluminosilicates; (4) SSB: silicate solubilizing bacteria).

Figure 2. The Si terrestrial ecosystem service framework

Figure 3. Scanning electron microscopy micrographs of phytoliths and diatoms from paleosols with high cultural values. Phytolith ELONGATE SINUOUS, common to many plant taxa, (a) and diatom frustule (b) from the silica-rich sediments of the Toros Menalla paleoanthropological locality TM 266 in Chad, which yielded the cranial remains and teeth of *Sahelanthropus tchadensis*, the oldest hominin known so far, dated ca. 7 million years. Phytolith SPHEROID DECORATED, common to many woody plants, from the paleoanthropological locality of Koro Toro in Chad, which yielded the lower jaw and teeth of *Australopithecus bahrelghazali* dated ca 3.6 million years.

Table 1. Procedures for measuring the forms of Si in terrestrial ecosystems. (1) ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectroscopy; (2) XRF: X-Ray Fluorescence; (3) ICP-MS: Inductively Coupled Plasma-Mass Spectrometry; (4) MIRS: Microwave Integrated Retrieval System.

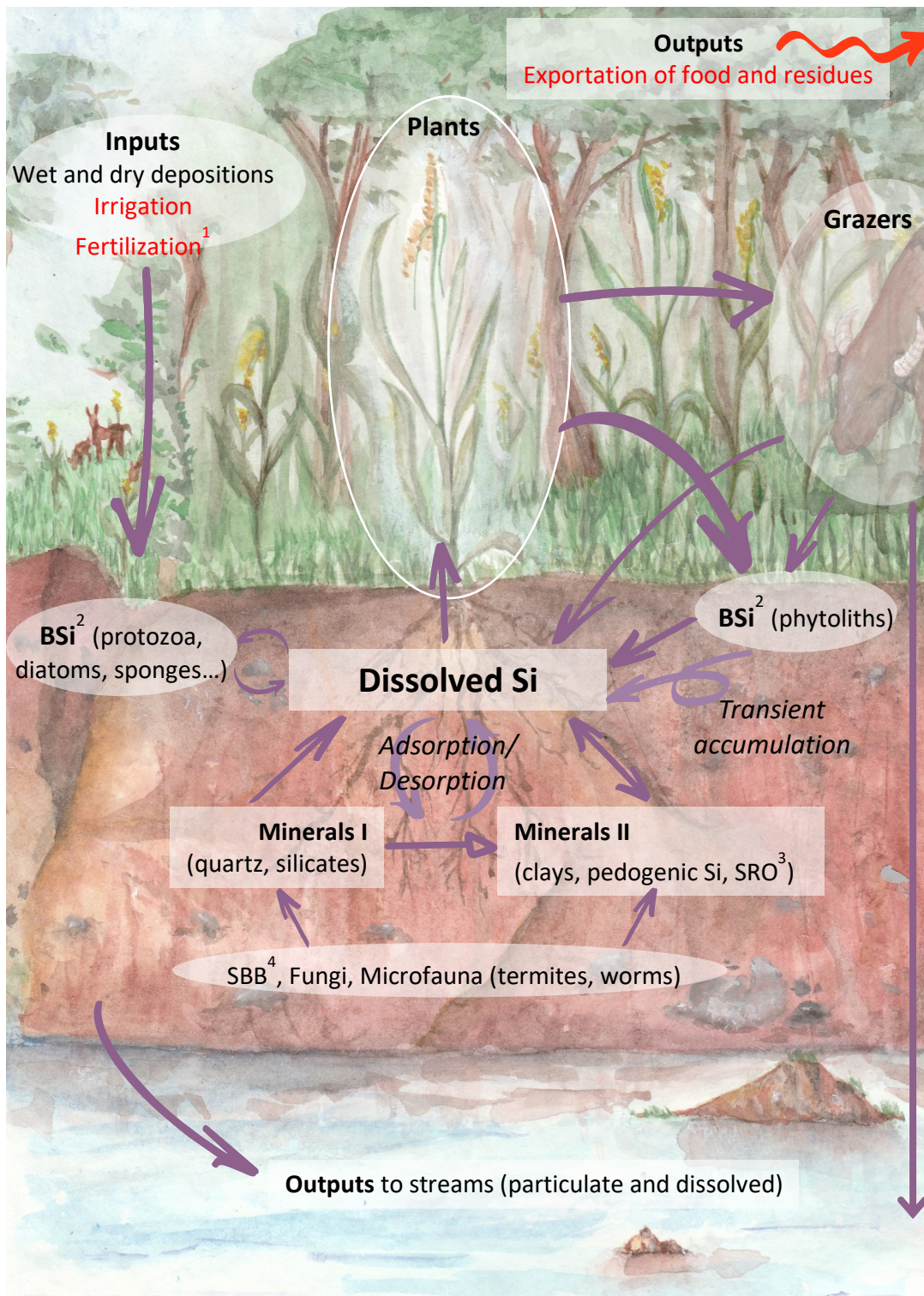


Figure 1

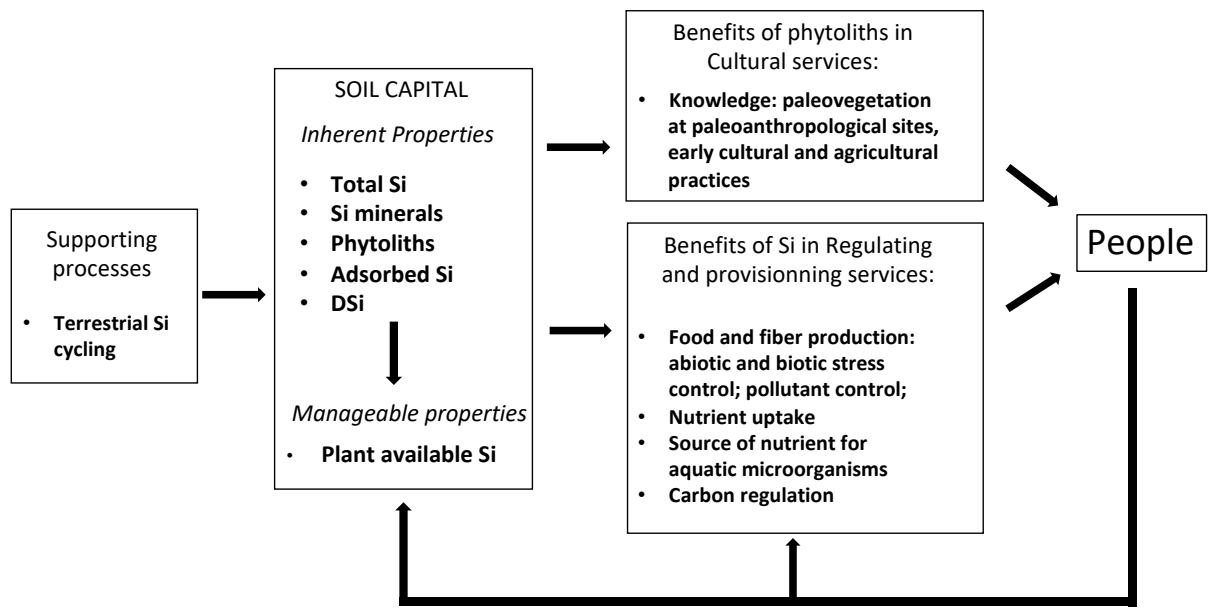


Figure 2

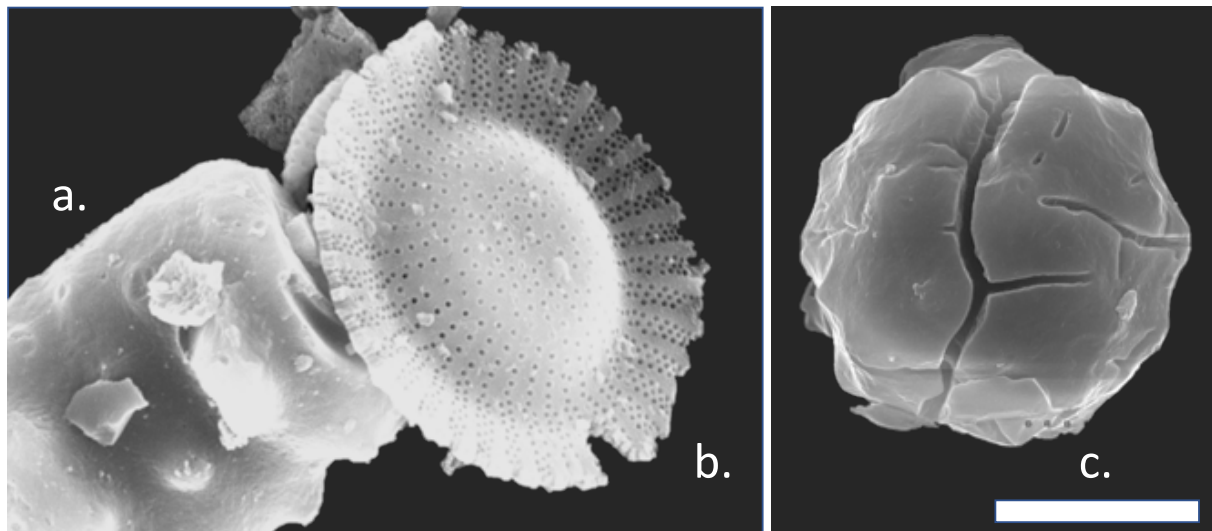


Figure 3

Table 1

| Forms of Si | Procedures | References |
|--|--|--|
| Total (solid) | ICP-AES ¹ after alkaline fusion | Germanique (1994) |
| | XRF ² after alkaline fusion | Germanique (1994) Aureli et al. (2020) |
| | ICP-MS ³ after HF digestion | Landré et al. (2018) |
| | MIRS ⁴ | Liang et al. (2015) |
| Amorphous (solid) | Gravimetry | |
| | Spectrophotometry after NaOH extraction | Barao et al. (2015) |
| | Spectrophotometry after Na ₂ CO ₃ extraction | Saccone et al. (2007); Meunier et al. (2014) |
| Plant available, adsorbed (dry soil) | Tiron extraction | Kendrick and Graham (2004) |
| | CaCl ₂ extraction | Haysom and Chapman (1975) |
| | Acetate-acetic acid | Korndorfer et al. (2001) |
| | Others | Liang et al. (2015); Tubana and Heckman (2015) |
| Dissolved Si | Spectrophotometry (monosilicic acid) | Zini et al. (1985); Wang et al. (2004) |
| | ICP-AES ¹ (total DSi) | Wang et al. (2004) |
| Plant | Alkaline extraction | Elliott and Snider (1991); Meunier et al. (2014) |
| | Tiron extraction | Guntzer et al. (2010) |
| | HF extraction | Saito et al. (2005) |
| | Electrothermal vaporization | Masson et al. (2007) |
| | combined with ICP-AES ¹ | |
| | Laser-induced breakdown spectroscopy | De Souza et al. (2013) |
| | Portable X-ray fluorescence spectrometry | Reidinger et al. (2012) |
| Extraction of phytoliths and other biogenic silica particles | Plant: wet or dry ashing | Parr et al. (2001); Corbineau et al. (2013); Kamenik et al. (2013) |
| | Soil and sediments: heavy liquid flotation | Lentfer & Boyd (1998) |
| | Microwave digestion | Parr (2002) |