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Allophanes, a significant soil pool of silicon for plants

Sophie Cornu a,*, Jean-Dominique Meunier a, Céline Ratie b, Frédéric Ouedraogo a, Yves Lucas c, Patricia Merdy a, Doris Barboni a, Camille Delvigne a, Daniel Borschneck a, Olivier Grauby a, Catherine Keller a

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1. Introduction

The variability of Si content in soils is large, from < 1 % wt in Histosols to greater than 45 % wt in some Podzols (Sommer et al., 2006). Si is included in a large number of soil solid phases of various origins: (1) minerals derived from the parent material as quartz, feldspar, phyllosilicates (e.g. muscovite, biotite) etc.; (2) solid phases resulting from the transformation by weathering and pedogenesis of the primary minerals into clay minerals (kaolinite, smectite, illite among others), crystalline and amorphous material, including poorly crystalline Fe oxides and short-range ordered (SRO) aluminosilicates (e.g. allophanes and imogolites); (3) amorphous silica particles (BSi) formed by Si biocycling and synthesized by plants (phytoliths), animals (spunge spicules) or protists (testing amoeba shells, diatom frustules) (Sommer et al., 2006; Puppe et al., 2015). While soils offer a wide range of Si sources, plants absorb Si only from the soil solution as Si(OH)4. Therefore, deciphering the source of soluble Si (DSi) is challenging because of the complex biogeochemical interactions involving Si in soils (Schaller et al., 2021). The conversion of forest to cropland was shown to lead to several Si pool changes: (1) a decrease in the phytolith pool (Conley et al., 2008; Struyf et al., 2010; Gunter et al., 2012; Vandevenne et al., 2015), in the easily soluble Si pool (Glymans et al., 2011) and the weathering of silicate minerals (Struyf et al., 2010) and (2) an increase in the pedogenic Si fraction i.e. clays (Vandevenne et al., 2015). In addition, the growing crops such as rice, sugar cane, or wheat (Hodson et al., 2005; Gunter et al., 2012; Katz, 2015) that are among the most important Si accumulators (1 % or more Si by dry weight) are predicted to change the global Si biogeochemistry in the future by increasing the reservoir of BSi on earth (Carey et al., 2016).

Various methods have been used to estimate DSi and bioavailable Si (Liang et al., 2015). Their results suggest that bioavailable Si concentration is both negatively correlated with total Si content, reflecting the predominance of low solubility minerals such as quartz in the soils (Yanai et al., 2016; Landrè et al., 2020) and positively correlated with soil properties such as weatherable aluminosilicates (Li et al., 2020a), phytolith content (Li et al., 2020b; de Tombeur et al., 2020), pH (Klotzbücher et al., 2018; Meunier et al., 2018; Miles et al., 2014; Caubet et al., 2020), soil organic matter, iron oxides (Yanai et al., 2016) and the clay (<2 μm) fraction contents (Liang et al., 2015; Yanai et al., 2016; Caubet et al., 2020).

In temperate soils, despite the observed decrease of soil phytolith content under agriculture, higher DSi (estimated by the CaCl2 method referred to herein as SiCaCl2) concentration was observed under agriculture compared to forest developed on sedimentary rocks (Vandevenne et al., 2015; Caubet et al., 2020). This was related to a higher pH observed in agricultural soils compared to forest soils (Caubet et al., 2020) pointing out two mechanisms: greater phytoliths dissolution, or greater adsorption onto clay minerals at higher pH. Cornu et al. (2012) also observed that the liming of agricultural soils in Europe induced a change in the nature of the clay minerals, and hence, potentially in the relative proportion of the different Si pools. Consequently, despite their lower solubility compared to phytoliths (Frayssé et al., 2009), clays may play an important role in maintaining high values of SiCaCl2, somehow cancelling out the phytolith pool decrease (Vandevenne et al., 2015; Caubet et al., 2020).

To identify the mechanisms controlling SiCaCl2 in temperate soils and to understand the impact of land use on these mechanisms in different soil types, we designed a paired-site approach in which we sampled adjacent soils differing only in their land use while other pedological factors (topography, parent material, climate, and age) were the same. Seven paired sites were selected with calcic and non-calcic soils, developed on sedimentary parent materials (limestone and loess). Beside the SiCaCl2 pool, we measured the pools of Si associated to crystalline and amorphous material, including poorly crystalline Fe oxides and SRO-aluminosilicates, and biogenic Si particles. Only the topsoil horizons (0–0.3 m) were analysed as they were considered the most impacted by land use change.

2. Material and methods

2.1. Identification of the paired sites and sampling strategy

Paired sites are not easy to locate as they have to differ only by their land use, all other pedological factors (parent material, climate, topography, and time) being kept constant between the two sites (Filippi et al., 2016). We chose soils on sedimentary materials as land use impacts SiCaCl2 on these soils, and calcic and non-calcic soils as their behaviour with respect to SiCaCl2 differs (Caubet et al., 2020). In France, most cultivated soils with these characteristics are developed either on limestone or on decarbonised loess. We also
chose to study soils with different degrees of pedogenetic evolution: calcaric and hypereutric Cambisols for limestone; Luvisols and Albeluvisol for loess (WRB, 2006). To identify the paired sites, we used the French Soil Quality Network (RMQS) of 2111 georeferenced sites in France spread over a regular grid (16°*16 km) for which soil type, parent material and land use are provided (Jolivet et al., 2006). All the RMQS sites with the appropriate parent material and soil type either cultivated or under forest, were extracted from the database. For each selected RMQS site, an adjacent site (i.e. with the same climate), with the same topographical position (therefore expected to be on the same type of soil and parent material) and under the complementary land use (either forest or cultivation) was identified on the basis of: (i) the maps of the French National Institute of Geographic and Forest Information (IGN, 1:25000); (ii) Cassini’s maps, the oldest available maps with records of land use (Cassini, 1750), both available on Geoportail (https://www.geoportail.gouv.fr/); (iii) aerial photographs taken at different times during the 20th century. Only paired sites for which the land use change occurred more than 100 years ago were kept. In most cases, the forested areas have been preserved from cultivation because they belonged to the state or to castle parks. Nineteen pairs of adjacent plots were identified. Another paired site of the land use change occurred more than 100 years ago were kept. In most cases, the forested areas have been preserved from ploughing (usually 0–25 cm). In the nearby forested area two samples were taken (usually 0–5 and 5–25 cm). On the basis of the soil morphology, eighteen out of the 20 paired sites were kept and analysed for rare earth element (REE) concentrations and particle size distribution to detect potential changes in parent materials. Analyses were performed at the Laboratory of Soil Analysis (Arras, France). Seven paired sites were finally kept (Table S1), as their REE and grain size skeleton patterns did not differ between land uses considering the analytical uncertainties (see supplementary information, SI, part 3 for more details) and thus could be considered as having the same parent material. Bulk density measurements were performed using the volumetric cylinder method in cultivated areas and the excavation method in forested areas because the root density prevented the use of the cylinder. When bulk density could not be measured (e.g., at site 1166), it was estimated using the pedotransfer function proposed by Alexander (1980), which relates bulk density to soil organic carbon (SOC) content. To compare the forested and cultivated sites, composite values (0–25 cm) were calculated for the forested sites considering the thickness of the two sampled horizons (0–5 cm and 5–25 cm) and their respective bulk densities.

2.2. Samples characterisation
2.2.1. Pedological analysis
Air dried samples were analysed for pedological characteristics at the Soil Analysis Laboratory of INRAE (Arras, France). The particle-size distribution was obtained by wet sieving and the pipette method (NF X 31–107). The particle size fraction contents are hereafter denominated < 2 μm, 2–20 μm, 20–50 μm, 50–200 μm, 200–2000 μm. The < 2 μm fraction CEC (CEC<2μm) was calculated following equation (1).

\[
CEC_{2\mu m} = \frac{((CEC_{Soc} + SOC) \times 1000)}{(SOC + 2 < 2 \mu m)}
\]  

where SOC and < 2 μm are the contents in SOC and in the < 2 μm fraction, respectively. We used 200 cmol-kg⁻¹ as an estimate of CECsoc (Baize, 2000) of both the ploughed horizon of the cultivated site and for the 5–25 cm horizon of the forested plots and 100 cmol-kg⁻¹ as an estimate of CECsoc of the 0–5 cm horizon of the forested plots that contains a greater fraction of particulate organic matter with a lower CEC (Balesdent, pers. comm., 2018).

Total major elements concentrations in soil, including Si (SiTot), were also analysed at the Soil Analysis Laboratory of INRAE (Arras, France) by ICP-MS analysis after HF tri-acid dissolution (Altot, Fetot, Natom, Coatot, Mgtot, Ktot, Mntot) or alkaline fusion (SiTot, NF ISO 10694). Si in crystalline silicates plus part of the phytoliths equals (Sitot + Sid). We extracted by these three methods and Fe and Al extracted by the latter two were measured using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). Both Si< and Si> were extracted and measured at the Soil Analysis Laboratory of INRAE (Arras, France).

The different soil Si forms were then estimated considering that (i) the DSi equals the SiCaCl2; (ii) Si in SRO minerals (allophane, imogolites and poorly crystalline Fe oxides) equals (Si> - SiCaCl2); (iii) Si associated to crystalline Fe oxides or to the part of phytoliths dissolved by the extractant equals (Si< - Si<2μm); and (iv) Si in crystalline silicates plus part of the phytoliths equals (SiTot - Si>).

Error bars were estimated considering 5% uncertainty on the chemical and bulk density measurements.

2.2.3. Phytolith extraction and characterisation
Soil phytoliths were quantified, identified and their weathering state was evaluated.

BSi particles were extracted from the soils using wet digestion and heavy liquid separation (Jouquet et al., 2020; see SI part 2 for more details). No replicates have been done. Extracts, which happened to include phytoliths as well as low density particles such as micro-charcoals and amorphous silica skeletons of chrysophytes, diatoms, sponges, etc., were dried and weighed before being mounted on microscope slides to evaluate the real proportion of phytoliths versus non-phytolith particles in the extracts and, therefore, provide an estimation of the phytolith contents.

We considered that phytoliths contained 42 % of Si (Alexandre et al., 1997) and could thus estimate the soil phytolith Si pool based on the phytolith abundances in the soils.

Since cultivated plants produce morphotypes of phytoliths different from forest species (trees, shrubs, ferns, forbs), phytolith taxonomic identification was performed according to the International Committee for Phytolith Taxonomy (2019) and counting was carried out.

Lastly, the analysis of the phytolith surface is a good indicator of their weathering state (Sommer et al., 2006; Jouquet et al., 2020), we measured the proportion of corroded vs non-corroded phytoliths (for more details, see SI part 2).

2.2.4. Mineralogical characterisation of the < 2 μm fraction

Dried soils were dispersed in 200 to 300 mL of ultrapure water by rotative shaking for 22 h using plastic bottles and 20 agate balls (Ø 5 mm) (Balesdent et al. 1991). The mass of dried soil was chosen to obtain ca. 4 g of < 2 μm fraction. The suspension thus obtained was further dispersed by addition of 2 mL of Na-hexametaphosphate at 150 G L-1, mechanical shaking, and 5-min ultrasonic dispersion. The < 2 μm fraction was then sampled according to the Stokes law and the settled soil particles resuspended for a new extraction step. The process was repeated until more than 80 % of the total fraction was recovered (that is more than 3.2 g of < 2 μm fraction out of 4 g). An aliquot of the < 2 μm suspension was dried to determine the < 2 μm suspension concentration. Oriented slides were made by deposition on glass slides of 10 mg of < 2 μm particles spiked with 10 % of boehmite added as a reference for X-ray diffraction (XRD) studies. The glass slides were then analysed with a Panalytical X’pert Pro X-ray diffractometer equipped with a cobalt anti-cathode (λ = 1.79 Å) at 40 kV and 40 mA, with three treatments following Robert and Tessier (1974): air-dried (AD) and ethylene glycol (EG) solvation and heating at 490 ◦C for 4 h.

Peak areas of the main mineral phases and boehmite were measured using the Fityk software (Wojdyr, 2010). The peak area ratio with respect to boehmite was used to compare samples. Transmission electron microscope (TEM, JEOL JEM 2011) coupled to an energy-dispersive X-ray spectrometer (EDX, X-Flash Silicon Drift Detector 5030, Bruker) analysis was performed on the < 2 μm fraction of sample BS3f1 (Table S1) for checking the presence of allophanes.

2.3. Data analysis

Pedological characteristics and major element concentrations of the seven studied paired sites were analysed by principal component analysis (PCA). To identify different groups of soils from a pedological and chemical point of view, a hierarchical classification was performed on the first two factors of the PCA.

Soil characteristics of the paired sites were considered as different when the difference for a given soil characteristic exceeded the analytical uncertainties. As only one measurement by site was performed, no statistical tests could be performed to further test the statistical significance of this difference.

Significance of Pearson correlations between the SiCaCl2 concentrations and different soil parameters was estimated based on the p-values considering a threshold level of 5 %. All the statistical analyses were performed using the XLSTAT software for windows (Addinsoft).

3. Results

3.1. Seven paired sites with contrasted pedological characteristics and total concentrations of major elements

Pedological characteristics and total contents of major elements in the topsoils of the seven paired sites are reported in Tables S11 and S12. They were computed by PCA. The first two components explained 72 % of the dataset variance with 60 % for the first component (Fig. 1). The first component was correlated positively to Catot, the < 2 μm fraction, Fe tot, Al tot, Mg tot and the SOC contents, as well to pH and the CEC, and negatively to Si tot, Na tot, silt (2–20 μm and 20–50 μm fractions) and fine sand (50–200 μm fraction) contents. The second component (12 % of the variance) was correlated positively to the 2–20 μm fraction, and negatively to the 50–200 μm fraction (Fig. 1a). The PCA discriminated three groups of soils confirmed by a hierarchical clustering (Fig. 1b). The first group corresponds to calcareous Cambisols and is positively correlated with the first PCA component, which means high pH, < 2 μm fraction, Fe tot and SOC contents. The second group corresponds to soils developed on loess (Luvisols and Albeluvisols) and is negatively correlated to the first PCA component, which means high 20–50 μm fraction and Si tot contents, low pH, Fe tot and SOC contents. The third group corresponds to hypereutric Cambisols and is intermediary between the other two groups, showing more similarities with the soils developed on loess than with the calcareous Cambisols.

Although the PCA did not highlight the impact of land use, pH and Si content in SRO were higher and SOC values lower under cultivation than under forest (Fig. 2). The CEC of the < 2 μm fraction did not differ with land use in Cambisols developed on limestone but was higher under cultivation in Luvisols and Albeluvisols developed on loess (Fig. 2).

3.2. Phytoliths of grasses were dominant in the two land uses
The relative abundances of the main phytolith types grouped according to plant types and confidence intervals are given in Table 1. On average, the biogenic silica extracts contained 89 % of phytoliths (range 51–99 %), the remaining fraction consisting of 3 % of other biogenic silica particles (range 0–8 %) and of 9 % charcoal (range 0–48 %); all particles had roughly the same size. For each soil, the mass of phytoliths corrected by phytolith relative abundance (in %) (Table 1) indicates that phytolith pools in soils ranged from < 0.01 to 0.616 g 100 g−1 corresponding to 90 and up to 3970 kg Si ha−1. For comparison, 800 kg Si ha−1 was found in a rice field from Camargue, France (Desplanques et al., 2006), and values ranging from 450 to 1400 kg Si ha−1 in French forest soils (Bartoli, 1983), using a similar procedure (heavy liquid extraction).

The phytolith contents were very low in calcaric Cambisols and Albeluvisols (Fig. 2i), for which there was no clear differences due to land use. For Luvisols, we observed clearly higher phytolith contents under forest (Fig. 2i). For the hypereutric Cambisols, a clear difference in the amount of phytoliths between land uses was also observed, although not always in the same direction: for the BS2 site more phytoliths were recorded under forest, while for the 1166 site more phytoliths were observed under cultivation (Fig. 2i).

Grass phytoliths (silica short cells and various silicified epidermal tissues) represented >64 % in all forest and cultivated soil samples, except in forest samples 755-F1, 755-F2, and 1166-F1 (25 % only) (Fig. 3a). Phytoliths assigned to forest species (see Tables in SI part 2 for details) only represented 1–20 % of the total phytoliths sum, except in the forest soil sample 1166-F1 (45 %) (Fig. 3b).

The proportions of ELONGATE DENDRITIC phytoliths, mainly produced by grass inflorescences, tended to be higher in the cultivated soils of the hypereutric Cambisols (Fig. 3c). Again, in the other soils their abundance was too low to discuss any differences between land uses (Fig. 3c). These results showed that in the forest soils, except for the forest site 1166, the forest-indicator phytoliths exhibited a very low abundance relative to grass phytoliths (Fig. 3), suggesting that wild grasses were the main producers of phytoliths in forest understorey. The proportion of corroded phytoliths (ELONGATE and BLOCKY) was not different between forest and cultivated soils, except for samples from sites 1166 and BS2 where it was higher in the forest soil and in the cultivated soil respectively (Table 1).

3.3. Mineralogy of the < 2 μm fraction in the topsoils of the seven paired sites

The mineralogical composition of the < 2 μm fractions was rather similar for all forest soils (Fig. 4). All the fractions contained quartz (peak at 3.34 Å in all treatments), kaolinite (peak at 7.13 Å in both AD and EG treatments), illite (peak at 10 Å in all treatments), chlorite (peak at 14 Å in all treatments), poorly crystalline smectites and/or interlayered illite-smectite minerals (large bulge around 12–11 Å for Na-exchanged samples shifting around 14 Å with glycol with no well-marked peak; more or less marked depending on the considered sample). Soils on loess clearly contained more quartz in their < 2 μm fraction than soils on limestone as shown by their higher quartz:boehmite peak ratio (Table S13). Cultivation appeared to slightly increase the amount of smectite and interlayered minerals and the amount of illite and decrease the amount of chlorite in soils on loess and in hypereutric Cambisols (Fig. 4 b to d, and Table S13). In calcaric Cambisols, however, cultivation seemed to result in a decrease of all clay minerals, possibly due to the non-dissolution of the carbonate fraction that acts as clay cement, with no clear change in proportion between the different types of clay minerals (Fig. 4a). Transmission electron microscope (TEM) images showed the presence of discrete spherical particles with external diameter of 6 nm (Fig. 5). These spherical particles appear in the form of a disc with a white central part interpreted as being the projection of a hollow sphere.

3.4. Si pools in the topsoils of the seven paired sites assessed by chemical extractions

Whatever the soil type, more than 99 % of Si tot was contained in crystalline silicates (Si tot - Sid) (Fig. 2j). The other Si pools (Si in SRO minerals (Si So - SiCaCl2), Si associated to crystalline oxides (Sid - Sio) and Si in phytoliths) represented <0.3 % of the total soil Si. Si in SRO minerals was the most abundant of these pools in calcaric Cambisols, especially when cropped (Fig. 2g), while Si in phytoliths was the most abundant in Luvisols (Fig. 2i). Si associated to crystalline Fe oxides (Si So - SiFe) represented also a non-negligible part of the non-silicate Si pools, notably under forest (Fig. 2h).
Part of this pool may originate from amorphous silica partly dissolved by the DCB reagent (Georgiadis et al., 2013). However, the pool associated to crystalline oxides (Sia-Sia) was clearly lower than the Si content in phytoliths, indicating that the phytoliths were not entirely dissolved by DCB.

The Si CaCl2 pool represented a negligible proportion of the Si of the SIO pool (Table 1) and was larger in soils developed on limestone than in soils developed on loess (Fig. 2f). Cultivation increased both the Si CaCl2 pool, especially in soils on loess, and the SRO-Si pool, especially in soils on limestone parent material (Fig. 2g). Cultivation, however, did not seem to modify the amount of Si associated to well-crystalline iron oxides and included in crystalline silicates (Fig. 2h and j).
4. Discussion

4.1. Allophanes are responsible for the SiCaCl2 concentration in forest soils

When considering the 21 soil samples of the seven paired sites, the correlations between SiCaCl2 and other soil parameters were in a good agreement with previous studies for the following parameters:

1) positive correlations between SiCaCl2 and the < 2 μm fraction and its composition (CEC_2μm, Altot, Feot), pH, CEC (Table 2), as already observed by Caubet et al. (2020), but also between SiCaCl2 and Sio and Sid (that contains Si in see section 2.2.2). Such positive correlations of SiCaCl2 with Sio and Sid were already observed for many soil types by Yanai et al. (2016).

2) a negative correlation of SiCaCl2 with Sitot (Table 2), which can be explained by the predominance of low solubility minerals such as quartz in the total Si pool (Yanai et al., 2016; Landrée et al., 2020). However, contrary to previous studies made for very different soils, SiCaCl2 was not positively correlated with iron oxide (estimated by Fe_d contents) in the studied soils. Moreover, the Al/Si ratio observed for both forest and cultivated soils was close to 2, a typical value for allophanes (Harsh, 2005; Wada, 1989). Hence, it is likely that the Si pool consisted in SRO aluminosilicates. SRO aluminosilicates were found to be responsible for the SiCaCl2 concentration in Calcareous Cambisol and in the hypereutric Cambisol, that had a pH value close to 7 (Table S1). In this soil, reducing conditions occurring in winter and resulting in a transient high pH (Fraysse et al., 2009) may be responsible for the SiCaCl2 concentration in Calcareous Cambisol and in the hypereutric Cambisol. The absence of correlation between SiCaCl2 and phytoliths suggests that this pool is however not the main pool controlling the SiCaCl2 in temperate soils and that another pool of pedogenic origin must exist as already evoked by Vandevenne et al. (2015) and Keller et al. (2021).

Sio was very strongly correlated with Al (Fig. 6a), excluding the cultivated Calcareous Cambisol 701 that was very rich in SOC compared to the other cultivated soils (a sandy soil with very low content of SiCaCl2; de Tombeur et al., 2020) or the amount of phytoliths (estimated by Na2CO3 for Podzol and Chernozem; Li et al., 2020a) (Table 2). Li et al. (2020b) demonstrated that the extraction by Na2CO3 gave very different results from the extraction of phytoliths through heavy liquid separation. In the studied soils, the phytolith abundances estimated through heavy liquid separation were negatively correlated to the pH of forest soils (r = -0.826, p-value = 0.022). This result agrees with an increasing solubility of phytoliths with increasing pH (Fraysse et al., 2009). As a result, the amount of phytoliths in the Calcareous Cambisol and in the hypereutric Cambisol 1166, that had a pH value close to 7 (Table S1), was low. It was also the case for the Albeluvisol despite a soil pH value of 5.2 (Table S1). In this soil, reducing conditions occurring in winter and resulting in a transient high pH (Cornu et al., 2018) may be responsible for the SiCaCl2 concentration in Calcareous Cambisol and in the hypereutric Cambisol. The absence of correlation between SiCaCl2 and phytoliths suggests that this pool is however not the main pool controlling the SiCaCl2 in temperate soils and that another pool of pedogenic origin must exist as already evoked by Vandevenne et al. (2015) and Keller et al. (2021).

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Our dataset shows also a strong correlation between the < 2 μm fraction and the allophane contents (Fig. 6b), suggesting that allophanes may either be a product of clay mineral weathering or be part of the clay mineral formation, notably of the finest clays, the smectites and/or interlayered clay minerals that were shown to be present in all the soils considered (Fig. 4). Li et al. (2020a) also observed the formation of allophanes in a pot experiment as the result of weathering. When the Al/ Si ratio is above 2, which is the case in most forest soils (Table 1 and SI2), the Al content in excess is present as Al-OC complexes (Harsh, 2005). These Al-OC complexes partially preclude the formation of short range ordered alumino silicates (Harsh, 2005). SiCaCl2 was well correlated to allophane content (Fig. 7a), excluding the BS2 site for which part of the Si extracted was not contained in allophanes contrarily to all the other sites (as calculated by eq. (2)).

Therefore, allophanes are assumed to control a fraction of SiCaCl2 in soils. This agrees well with the high SiCaCl2 content observed in Andosols, which contain a large amount of imogolites and allophanes (Caubet et al., 2020). Caubet et al. (2020) concluded that SiCaCl2 was controlled by both sorption and dissolution processes, which are strongly controlled by pH for soils with < 2 μm fractions both larger than 50 g kg⁻1 and lower than 325 g kg⁻1. For Indian soils this relation is not linear but polynomial, with a stabilisation of the SiCaCl2 concentrations for pH higher than 7 (Meunier et al., 2018). We used a comparable relationship for the soils considered here excluding the BS2 and 62 forest soils (Fig. 7b). The pH value of the 62 forest plot lower than 4.5 suggests the beginning of podzolisation (Caner et al., 2010; Sauer et al., 2008; Fekiacova et al., 2017). The conifer vegetation observed on this plot (Table SI1) is compatible with the onset of such a process. This low pH also corresponds to the upper limit of the Al/Fe oxide buffer range (Stützer, 1998).

Podzolisation induces dissolution of the clay minerals, which may be responsible for the higher SiCaCl2 concentration observed with respect to the regression model presented in Fig. 7b. The above findings have the following consequences on the terrestrial Si cycle described by Struyf et al. (2010). In all soil types, 99% of Si was contained in crystalline silicates. However, in soils developed on loess almost 60% of the crystalline silicates consisted of quartz (e.g., Montagne et al., 2008 for BS3), a poorly weatherable mineral. In the calcic Cambisol, the total Si content in crystalline silicate was much lower than in soils developed on loess and was mainly contained in clay minerals and some quartz and feldspar. Despite this mineralogical difference, we concluded that the main weatherable mineral compartment contributing to SiCaCl2 consists in the clay minerals (Fig. 6). This compartment was almost twofold larger in the calcic Cambisols than in the soils on loess (Fig. 2a). The clay compartment controlled allophanes (Fig. 4b) which in turns controlled the SiCaCl2 as discussed above.

Allophanes are an easily available source of DSi as shown by dissolution rates much higher than those of phytoliths at pH lower than 9 (Raislon et al., 2021; Fraysse et al., 2009). Consequently, phytoliths did not appear to be the first source of SiCaCl2 in the considered soils, in agreement with Keller et al. (2021), who found that the clay minerals can compete with phytoliths as a main source of plant Si when the proportion of clay is high.
Reflecting the pH-dependent dissolution rate of phytoliths (Fraysse et al., 2009), the phytolith pool was lower in calcareous Cambisols (pH around 7, Table SI1) than in soils developed on loess (pH around 5, Table SI1). Consequently, the higher Si content in calcareous Cambisols compared to soils on loess could be explained by the higher amount of allophanes in calcareous Cambisol, but also, to a lesser extent, by a higher dissolution of the phytolith pool.

4.2. Impact of land use on the Si biogeochemical cycle and its various mineralogical pools

As expected, cultivation increased the soil pH (Fig. 2b) and decreased the SOC content (Fig. 2c) in all soils. For soils developed on loess, the pH was two units higher under cultivation than under forest because of liming. For calcareous Cambisols, the pH was one unit higher under cultivation than under forest because of the acidifying capacity of the forest (Fig. 2b, Table SI1). We confirm here that cultivation increases the amount of Si content for soils developed on sediments (Caubet et al., 2020; Vandevenne et al., 2015; Klotzbücher et al., 2018).

The change in pH and SOC induced by cultivation may act on the allophanes and phytoliths pools and therefore modify the terrestrial Si cycle. Based on the literature, a lower phytolith content was expected in cultivated soils compared to topsoils under forest (Guntzer et al., 2012; Vandevenne et al., 2015). This was clearly observed for Luvisols, and to a lesser extent for the BS2 hyper-eutric Cambisol (Fig. 2i). This decrease in phytoliths may be explained by both a larger dissolution of phytoliths under cultivation due to the pH increase and phytolith exportation due to harvesting. The relative abundance of phytoliths (Fig. 3) suggests that wild grasses were the main producers of phytoliths in forest undergrowth. This is in agreement with temperate trees being poor Si accumulators (Bremond et al., 2004).

Cultivation had no clear impact on the phytolith pool in the calcareous Cambisol or in the Albeluvisols, where the amounts of extracted phytoliths were very low. The proportion of corroded phytoliths (ELONGATE and BLOCK) was higher in the forest 1166 hyper-eutric Cambisol (Table 1), that also exhibits a lower amount of phytoliths than under cultivation. Differences in surface areas between grass and forest phytoliths explain the observed proportions with a higher rate of dissolution of forest phytoliths (Wilding and Dress, 1974).

However, this hypothesis is not supported by the laboratory measurements (Fraysse et al., 2009). Crop management through the restitution strategy of inedible plant parts and the crop rotation system may also lead to site fluctuation in exportation, maybe explaining the exception of the 1166 site. Indeed, crop straw recycling in agricultural soils have proven to be an efficient strategy for limiting desilication (Puppe et al., 2021).

By decreasing SOC (Fig. 2c), cultivation promotes the formation of allophanes that are twice as abundant under cultivation as under forest in the calcareous Cambisols and soils developed on loess (Fig. 2c and 5b). We observed Alv/Sio ratios higher than 2 in forest but close to 2 in cultivated soils (Table 1), evidencing a decrease in the Al-OC complexes that prevent allophane formation under forest as discussed above. For the cultivated soils with a pH close to 8, pH may be less favourable to Si adsorption on allophanes that are at
zero point of charges (Harsh, 2005). The high Si-Cl values may then be explained by Si adsorbed on carbonate surfaces (Caubet et al., 2020).

Struyf et al. (2010) observe that cultivation decreases the exportation of DSi at the watershed outlet. They interpret this decrease in exportation by a reduction in the silicate mineral weathering. On the contrary, our results suggest that this decrease might be due to a higher retention of Si in the soils by the increase of allophane formation under cultivation (Fig. 8).

Fig. 6. Impact of land use on the allophane amount in the pedosphere a. Al, as a function of Si(0.2-0.5 m fraction size of the < 2 mm concentration. Allophane content was calculated using Harsh's (2005) equation: % allophane = [Al(0.2-0.5 m)/Si(0.2-0.5 m)] * 100. Forest soils are reported in black and the cultivated soils in gray. Pearson correlation coefficient and p-values provided on the figure were calculated excluding the samples identified by their name (for figure a only). Forested flood correspond to composite values (0-25 cm) calculated considering the thickness of the different elements and their respective bulk densities.

Struyf et al. (2010) observe that cultivation decreases the exportation of DSi at the watershed outlet. They interpret this decrease in exportation by a reduction in the silicate mineral weathering. On the contrary, our results suggest that this decrease might be due to a higher retention of Si in the soils by the increase of allophane formation under cultivation (Fig. 8).
5. Conclusion

In temperate soils, phytoliths may not be the main Si pool contributing to bioavailable Si in contrast to tropical soils that are strongly depleted in Si and have kaolinite as dominant clay mineral. Temperate soils indeed exhibit a more complex clay mineral assemblage (smectite, illite, kaolinite and interlayered minerals). Allophanes - either precursors or dissolution products of these clay minerals - appear as the main Si pool contributing to DSi, estimated by CaCl2 extraction. This explains the correlation between Si CaCl2 and the clay fraction reported in the literature. Cultivation seems to impact soil Si pools and DSi in two ways. First, cultivation increases pH by limiting in the case of non-calcareous soils and by suppressing forest acidification. The increase in pH enhances Si sorption and phytolith dissolution. Secondly, cultivation decreases soil organic carbon, promoting the formation of allophanes. At pH lower than 4.5, other processes occur, such as podzolisation, modifying the relationship between DSI and pH. So far, there has been a lot of emphasis put on phytoliths as a source of DSI. Our work highlights the importance of allophanes as the missing link between the soil solution and the clay minerals that could explain why clay minerals may be so important, despite lower solubility rates than phytoliths.

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

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Appendix A. Supplementary data Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2022.115722.

References


D., Wanner, M., Sommer, M., 2015. The protozoic Si pool in temperate forest ecosystems—quantification, abiotic controls and interactions with earthworms. Geoderma 243-244, 196–204.

Puppe, D., Kaczorek, D., Schaller, J., Barkusky, D., Sommer, M., 2021. Crop straw recycling prevents anthropogenic desilication of agricultural soil-plant systems in the temperate zone—Results from a long-term field experiment in NE Germany. Geoderma 243-244, 196–204.


