REGULAR ARTICLE

Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk, Rothamsted

Flore Guntzer · Catherine Keller ·
Paul R. Poulton · Steve P. McGrath ·
Jean-Dominique Meunier

Abstract

Aims Most cereals accumulate Si in their shoots. Soil bioavailability of Si may be a constraint on the beneficial role of silica in cereals but it is not yet well supported by field data. The aim of this study is to evaluate the long-term impact of wheat straw exports on the pool of soil phytoliths, which, it is suggested, represents the most labile and renewable pool of soil Si.

Methods We measured the amorphous Si (ASi) in soils from several experiments at Rothamsted Research (UK), which provided long-term soil data back to the middle of the 19th century, using two alternative extraction techniques: Na_2CO_3 (referred to as AS_{nc}) or zinc bromide extraction (referred to as ASi_{zb}).

Results All samples showed a similar range of AS_{nc} and ASi_{zb} but low values (0.1–3.4 mg g^{-1} DW) compared to published data on natural ecosystems. In the Broadbalk experiment, a decrease over time in ASi in the topsoil samples is in good agreement with the hypothesis that cropping and exports of straw leads to depletion of soil phytoliths. A decrease in Si concentration in straw samples was observed between 1883 and 1944. From 1944 to the present, Si concentration increased irregularly in the straw, probably as the result of liming, which enhanced the dissolution of the remaining phytoliths through increasing pH. In the reforested Geescroft field the higher phytolith concentration in the modern topsoil samples is in good agreement with a re-building of phytolith storage from litter input in an acidic environment.

Conclusions Our results therefore support the hypothesis that export of wheat straw leads to a decrease in bioavailable Si.

Keywords Phytolith · Silicon · Bioavailability · Cereals · Sustainability

F. Guntzer · C. Keller (✉) · J.-D. Meunier (✉)
CEREGE CNRS/Aix-Marseille Université,
Europôle Méditerranéen de l'Arbois,
13545 Aix-en-Provence, cedex 4, France
e-mail: keller@cerege.fr
e-mail: meunier@cerege.fr

P. R. Poulton · S. P. McGrath
Rothamsted Research,
Harpenden, Herts AL5 2JQ, UK

Introduction

Although not generally considered as an essential element, Si is often beneficial for crops such as wheat and rice (Jones and Handreck 1967; Epstein 1999; Datnoff et al. 2001). More than a decade ago, Savant et al. (1997b) suggested that intensive rice cultivation where straw is removed may deplete plant available silica, which could be a factor for explaining yield decline. However, no recent studies have been

published to support this hypothesis, which remains of utmost interest considering the question of the sustainability of food production.

The silicon concentration in plants depends primarily on the concentration of silicic acid in the soil solution (Ding et al. 2005; Henriet et al. 2008; Jones and Handreck 1965) and is not correlated with the total Si concentration of the soil (Brenchley and Maskell 1927; Savant et al. 1997a). However, correlations were observed between the Si concentration in rice and the percentage of clay in soils (Cheng 1982), and between the Si concentration in rice or banana and the stock of weatherable minerals (Henriet et al. 2008; Makabe et al. 2009). The weatherability of silicate minerals, including phytoliths which are particles of amorphous opaline silica (Piperno 1987), depends on environmental factors such as temperature and pH as well as the physico-chemical characteristics of the minerals which can be evaluated by thermodynamic and kinetic data (White and Brantley 1995; Heaney et al. 1994). The dissolution of phytoliths is minimal at pH=3 and increases with increasing pH (Fraysse et al. 2006). Their dissolution is one order of magnitude faster than that of primary clays or silicates (Fraysse et al. 2006, 2009) especially in the pH range of most soil types, indicating that plant Si biocycling may be the most important source of available Si to plants.

In plants, silica is mostly present in the shoots where it accumulates as phytoliths and, in natural ecosystems, most of the Si taken up by plants returns to the soil as phytoliths through litterfall. The distribution of phytoliths through the soil profile is similar to that of carbon and shows a rapid decrease with depth (Alexandre et al. 1999; Bartoli 1981; Saccone et al. 2007, 2008). A simple mass-balance calculation performed in rice fields in Camargue (France) has shown that the stock of easily weatherable Si would be depleted within a decade if the soil phytoliths were the only source of available Si for the plants (Desplanques et al. 2006).

In order to test the hypothesis that the stock of phytoliths, and more generally plant-available Si, is decreasing in cultivated areas, analysis of amorphous silica contents is required on contrasting systems, i.e. with low and high Si exports where biomass outputs have been quantified over a long period. Several experiments at Rothamsted Research (Harpenden, UK) are particularly well suited to test such a

hypothesis (Rothamsted Research 2006). The Broadbalk winter wheat experiment, which started in 1843, allows us to monitor a wheat field, which has been continuously cultivated for several centuries, through measurement of soil available silicon as well as plant Si content between 1844 and 2000. In addition, the Broadbalk and the Geescroft Wildernesses allow for the study through time of fields which were previously arable but which were left uncultivated more than a century ago and have reverted to woodland. They may document the recovery of the phytoliths stock with time under natural conditions.

Materials and methods

Materials

Broadbalk field: the winter wheat experiment

The Broadbalk soil is a Chromic Luvisol with properties shown in Table 1, which is thought to have been in arable cropping for centuries prior to 1843. Annual rainfall is approximately 704 mm per year (Rothamsted Research 2006). The first experimental crop of winter wheat was sown in autumn 1843 and harvested in 1844 (Rothamsted Research 2006). Every year since then, wheat (*Triticum aestivum* L.) has been sown and harvested on all, or part of, the experiment. Yields of grain and straw have been recorded and samples of plants and soil taken periodically and kept for chemical analyses.

Even though many treatments underwent changes in fertilisers and manures over the years, all samples used here are from plot 8, on which the fertilizer treatment has scarcely changed, consisting of N, P, K, Mg and Na (Table 2), with intermittent additions of chalk from the 1950s to maintain a stable soil pH (Rothamsted Research 2006). The whole field (including what became the Wilderness) was heavily chalked before the experiment began.

We took archived topsoil samples consisting of the ploughed layer (0–23 cm) from 1881, 1893, 1944 and 2000 and samples of the soil profile from the years 1893 and 2000, with samples taken of every 23 cm depth (0–23, 23–46, 46–69, 69–91 cm). Plants (grain and straw) from the most frequently grown cultivars were sampled at the same dates as the soils when possible and at various dates in between (Table 3).

Table 1 Broadbalk winter wheat experiment: general soil characteristics (after Avery and Catt 1995)

Depth (cm)	Bulk density g cm^{-3}	Sand 60 μm–2 mm mg g^{-1}	Silt 2–60 μm mg g^{-1}	Clay<2 μm mg g^{-1}	Loss on ignition mg g^{-1}	Organic carbon mg g^{-1}	CaCO$_3$ equiv. mg g^{-1}	Extr. Fe$_2$O$_3$ mg g^{-1}	pH (H$_2$O)
0–23	1.514	160	650	190	46	6	3	22	8.1
23–41	1.498	100	650	250	38	4	2	29	8.0
41–66	1.451	30	580	390	49	4	?	29	7.9
66–94	?	50	550	400	49	?	?	32	7.9

Broadbalk and Geescroft Wildernesses

The Broadbalk and Geescroft Wildernesses are two areas of regenerating woodland (Poulton et al. 2003). Broadbalk Wilderness is 0.2 ha at the west end of the Broadbalk winter wheat experiment which was left unharvested after 1882. Within a few years, wheat disappeared completely. Half of the area was left untouched, and is now a regenerating woodland dominated by ash (*Fraxinus excelsior*), sycamore (*Acer pseudoplatanus*) and hawthorn (*Crataegus monogyna*). Similarly, the Geescroft Wilderness is a 1.3 ha site which has been untouched since 1886. It is now also a regenerating woodland dominated by oak (*Quercus robur*) and ash (*Fraxinus excelsior*). The main difference between the two Wildernesses is the pH. Although the Broadbalk Wilderness was heavily chalked in the years *before* the main wheat experiment started in 1843; it has not received chalk since but, in 1999, topsoil pH was still 7.2. Geescroft field did not receive the same large dressings of chalk prior to any experiments and so the topsoil pH declined from 7.1 in 1883 to 4.4 in 1999 (Poulton et al. 2003).

Samples of the two Wilderness areas have been taken very infrequently. We took samples from two soil profiles collected in 1999 in both woodlands and labeled as "hole 1" and "hole 4" for both sites;

samples of litter were also sampled at Geescroft. The Broadbalk soil sample from 1881 (i.e. taken the year before the area that became the Wilderness was abandoned) can be thought as being equivalent to the Broadbalk "Wilderness" soil prior to the development of the woodland. However the whole soil profile was not sampled in 1881. Thus, in order to establish whether there was a change in ASi distribution along the soil profile associated with the establishment of the woodland, we compared the 1893 field soil profile (plot 8) that we considered as representative of the soil profile of the Wilderness before the woodland, with the 1999 Broadbalk Wilderness profiles. We also used the mixed samples of the soil profile from Geescroft collected in 1883, a few years before the arable experiment was stopped.

Analytical methods

We used two techniques which provided us with estimations of the fraction of Si derived from amorphous silica particles: 1) a non-destructive technique based on heavy liquid extraction using zinc bromide (Kelly 1990; Alexandre et al. 1997) and, 2) a destructive technique using sodium carbonate, which allows for the quantification of the proportion of amorphous Si from crystalline silicates Si (DeMaster

Table 2 Fertiliser treatments on plot 8 of the Broadbalk winter wheat experiment

Treatments until 1967	Treatments from 1968	Treatments from 1985
144 kg N as ammonium sulphate	144 kg N as calcium ammonium nitrate	144 kg N as ammonium nitrate
35 kg P as single superphosphate	35 kg P as single superphosphate	35 kg P as triple superphosphate since 1988
90 kg K as potassium sulphate	90 kg K as potassium sulphate	90 kg K as potassium sulphate
16 kg Na as sodium sulphate	16 kg Na as sodium sulphate until 1973	35 kg Mg as kieserite every 3rd year
11 kg Mg as magnesium sulphate	11 kg Mg as magnesium sulphate until 1973 then 35 kg as kieserite every 3rd year	

Table 3 Years of harvest and cultivar grown on plot 8 of the Broadbalk winter wheat experiment that were analysed for their Si content (Rothamsted Research 2006)

Year	Cultivar	Section	Samples analysed
1872	Red Rostock	8b	Grain and straw
1892	Red Club	8b	Straw
1893	Red Club	8b	Grain
1916	Squarehead's Master	8 top	Grain and straw
1944	Red Standard	8/01	Grain and straw
1957	Squarehead's Master	8Ib	Grain and straw
1970	Cappelle Desprez	081	Grain and straw
1982	Flanders	081	Grain and straw
1985	Brimstone	081	Grain and straw
1988	Squarehead's Master/Brimstone	082	Straw
1989	Squarehead's Master/Brimstone	083	Straw
1990	Squarehead's Master/Brimstone	087	Straw
1993	Apollo	081	Grain and straw
2000	Hereward	081	Grain and straw

1981; Saccone et al. 2007). Both methods are able to measure the amorphous silica particles of biogenic origin (such as diatom phytoliths) as well as those of nonbiogenic origin (such as volcanic opaline cement). The fractions extracted with the non-destructive method were weighed and mounted on slices for optical microscope inspection (Leica DM RXP) in order to characterise their state of conservation and to detect the presence of non-phytolith amorphous silica particles. We calculated the content of Si in phytoliths after checking that the extract analysed was only composed of phytoliths, and assuming that the water content of phytoliths is 10% (Bartoli 1981), which gave a proportion of 42% of Si in the fraction extracted by zinc bromide. Three or four replicates of each sample were performed with the sodium carbonate procedure while the heavy liquid extraction was conducted only once per sample due to limited amounts of available material. In the following, Si from Na_2CO_3 extraction is referred to as ASi_{nc} and Si from zinc bromide ($ZnBr_2$) extraction is referred to as ASi_{zb}. Both ASi_{nc} and ASi_{zb} are given in mg g^{-1} dry weight of soil.

Silicon in plants was measured using a Tiron digestion. The procedure, previously developed for amorphous silica in soils (Biermans and Baert 1977), was adapted for plants (Guntzer et al. 2010). Thirty milliliters of a 0.1 mol l^{-1} Tiron solution buffered at pH=10.5 was added to 50 mg of ground plant material in polypropylene tubes. The tubes were placed in a water bath during 2 h at 85°C and horizontally shaken with the cap loosely closed to prevent evaporation. The tubes were then cooled and 10 ml were sampled and added to 10 ml of 30% H_2O_2 in order to destroy Tiron before Si analysis by ICP-OES.

Results

Broadbalk wheat experiment

ASi_{nc} and ASi_{zb} values ranged respectively from 0.6 to 3.4 and from 0.1 to 1.4 mg g^{-1} Si DW in topsoil samples (Fig. 1a, b and c) with lower values for ASi_{zb}. Both ASi_{nc} and ASi_{zb} concentrations decreased between 1893 and 1944 (Fig. 1a). In the 1893 profile samples, ASi_{nc} significantly increased with depth (Fig. 1b) except between the 0–23 and the 23–46 cm-layers. A similar trend was observed in the 2000-ASi_{nc} profile despite larger uncertainties for the 46–69 cm-layer. The same trend is also observed for the ASi_{zb} at both dates (Fig. 1c) but only if surface and deeper samples are compared because intermediate samples have the lowest values. Microscopic inspection showed that well preserved phytoliths were rare, most of them were either broken or weathered (Fig. 2a, b, c). However, the amorphous silica fraction extracted by zinc bromide was essentially composed of phytoliths, intact, weathered or broken, with no obvious Si amounts of abiotic origin. Soil pH also showed a decrease between 1881 and 1966, and then an increase until 1994 (Fig. 1a).

Fig. 1 Concentrations of ASi_{nc} and ASi_{zb} in the Broadbalk winter wheat experiment between 1881 and 2000: **a** ASi_{nc} and ASi_{zb} in surface soil samples (0–23 cm depth) compared to soil pH; sd for ASi_{nc} = replicate of the same sample, $n=3$ or 4 except for 1893 mean of 4 samples, and 2000 mean of 2 samples from sections 0 and 1; **b** ASi_{nc} in the 1893 and 2000 soil profiles; sd = replicate of the same sample, $n=3$ or 4; ASi_{zb} **c** ASi_{zb} in the 1893 and 2000 soil profiles
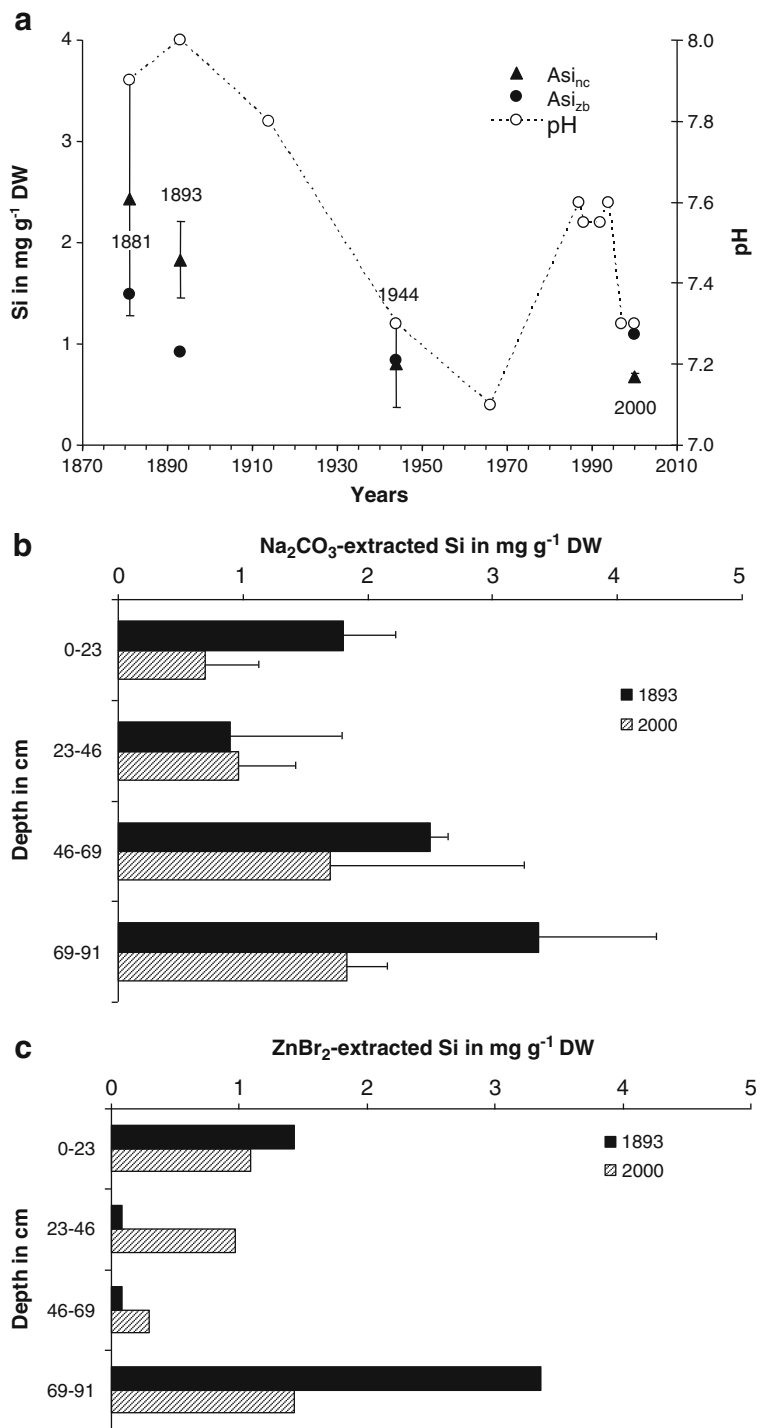
For all cultivars, the Si concentration in grain was below detection limit (0.4 mg g^{-1} DW, data not shown), while the Si concentration in straw ranged from 2.0 to 14.6 mg g^{-1} DW (Fig. 3a and b). Variation in Si concentrations in straw with time showed two trends, before and after 1944 (Fig. 3a): from 1872 to 1944 Si concentrations in straw decrease, while after 1944 (Fig. 3b) they tend to be larger than those
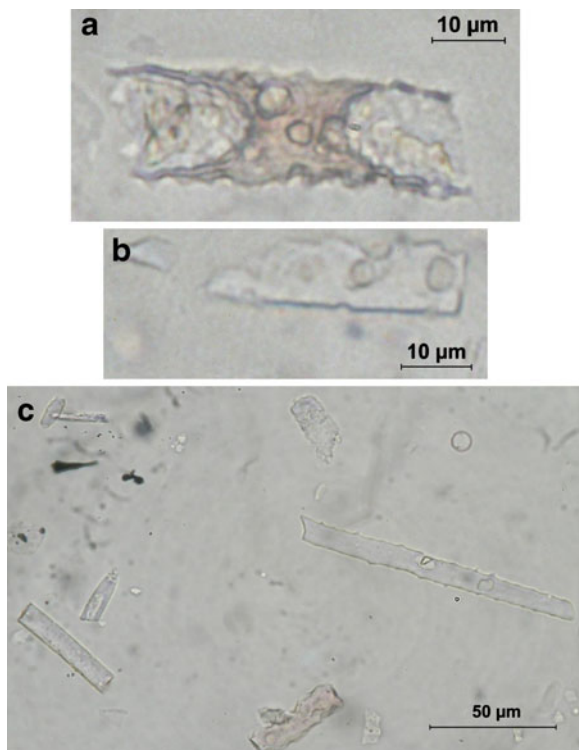
Fig. 2 Micrographs of phytoliths taken with optical microscope: **a** from the 0–23 cm layer at Broadbalk winter wheat experiment (plot 8) collected in 1881 showing a weathered surface; **b** from the 0–23 cm layer of the Geescroft field collected in 1883, showing a weathered surface; **c** from the 0–23 cm layer of the Geescroft Wilderness collected in 1999, characterised by a larger size and smooth surfaces

measured in samples collected before 1944 and, this increase is uneven with two peaks in 1957 and 1989 (Fig. 3b). It is notable that the same cultivar (cv Squarehead's Master) showed Si concentrations respectively three and five times smaller in 1916 than in 1956 and 1989. Two cultivars were grown on the same plot in 1988–1990 (Table 3), and their Si concentrations followed the same changes with time, with concentrations in Brimstone straw being always larger than in Squarehead's Master straw. These were short and long straw varieties, respectively.

Broadbalk and Geescroft Wildernesses

ASi_{nc} concentrations in the soil samples from the Broadbalk and the Geescroft Wildernesses ranged respectively from less than 0.5 mg g^{-1}–4.3 mg g^{-1} and from less than 0.5 mg g^{-1} to 4.6 mg g^{-1} (Fig. 4a and b), with minima and maxima not being found at the same depth in both profiles. In the 1999 Broadbalk Wilderness profiles ASi_{nc} concentration increased with increasing depth, almost similar to what is observed in the 1893-Broadbalk wheat field profile (Fig. 4a). In the Geescroft profiles, ASi_{nc} concentration showed two different trends with increasing depth (Fig. 4b): 1) an increase for the 1883-profile similar to that observed for the modern and old Broadbalk field profiles and, 2) a decrease for the modern soils (1999, holes 1 and 4).
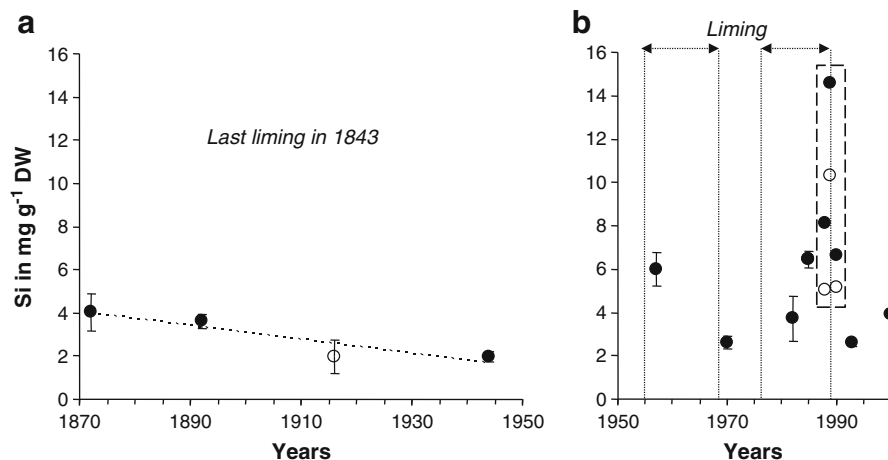

Fig. 3 Si concentrations in the straw of the main cultivars (closed circles) cropped between 1872 and 2000 on the Broadbalk winter wheat experiment (plot 8) (sd = replicate of the same sample, $n=2$). Cultivars are presented in Table 3. **a** Concentrations measured between 1872 and 1950; **b** concentrations measured between 1950 and 2000; open circle indicates the three years (1988, 1989 and 1990) during which Squarehead's Master was grown alongside Brimstone cv)

Fig. 4 Concentrations of ASi_{nc} (Na_2CO_3-extracted Si) (sd = replicate of the same sample, $n=3$ or 4) ASi_{zb} in soil profiles from: **a** the Broadbalk Wilderness (1999) compared to Broadbalk field (1893). Topsoil for the 1893 profile: mean of 4 individual samples (4 holes); **b** the Geescroft Wilderness (1883: mean of 4 individual samples (4 holes) and 1999: holes 1 & 4)
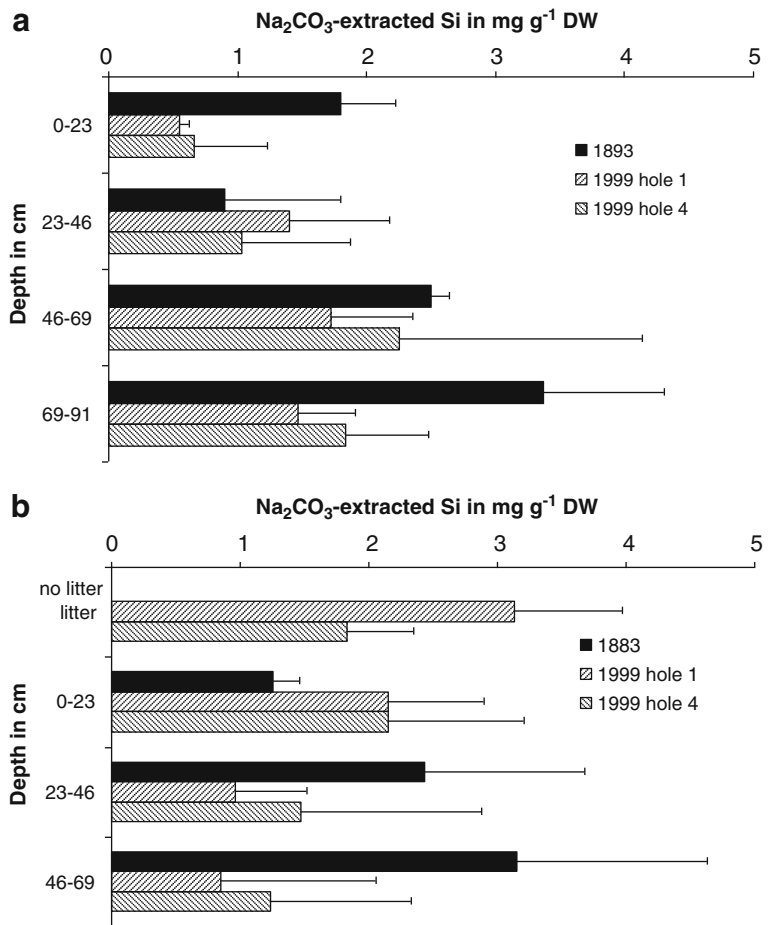
ASi_{zb} concentrations in the Broadbalk Wilderness modern samples ranged from 0.2 mg g^{-1} to 1.1 mg g^{-1} (Fig. 5a) but the distribution with depth showed slight differences when compared to ASi_{nc} concentrations, with 1) a decreasing ASi_{zb} concentration with depth for the Broadbalk Wilderness (modern soil samples) as compared to the ASi_{nc} profiles and, 2) the lowest values at intermediate depths for the 1893-Broadbalk Wilderness and a very large concentration in the 69-91-cm-layer. Microscopic inspection showed that the phytoliths from Broadbalk Wilderness had the same characteristics as the ones found in the wheat field samples, with only a few well preserved phytoliths and no visible abiotic silicic materials.

At Geescroft, ASi_{zb} concentrations ranged from 0.2 mg g^{-1} to 4.6 mg g^{-1} (Fig. 5b). They decreased with depth in both the 1893 and the modern soil profiles (litter excluded). Under the microscope, the phytoliths from the 1883 field surface sample look similar to phytoliths of the Broadbalk field and

Wilderness, that was mostly broken or weathered (Fig. 2a and b) while the phytoliths from the 1999-Wilderness litter samples presented well preserved morphotypes, and only very few had weathered surfaces or were broken (Fig. 2c).

Discussion

Wheat belongs to the monocot group, which is known to contain plants that accumulate Si and hence produce phytoliths (Hodson et al. 2005). However, literature on Si content in wheat straw is still limited. Although we did not analyse the whole plant, the straw content is likely to be larger than the mean Si concentration of the whole plant and thus will give a maximal concentration, because grain does not contain a significant amount of Si (in our case below detection limit that is <0.04%, data not shown), the bran has a negligible weight and root concentrations

Fig. 5 Concentrations of ASi_{zb} (phytolith Si) in soil profiles from **a** the Broadbalk field (1893) and Wilderness and **b** the Geescroft Wilderness (1883 and 1999, holes 1 & 4)
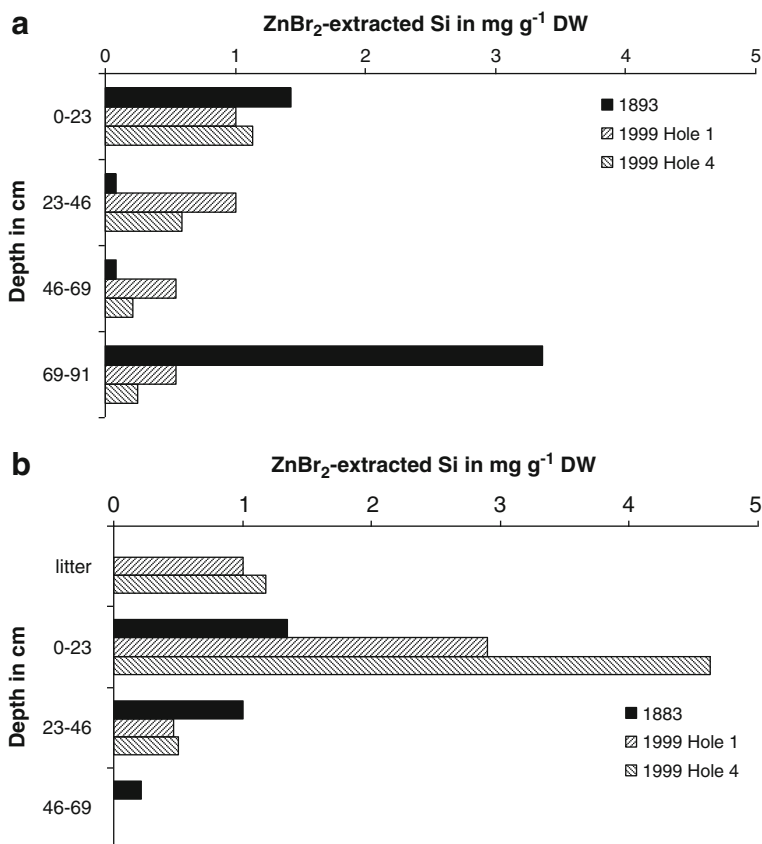
are always lower than shoot concentrations (Sangster et al. 2001; Tuna et al. 2008). With Si concentrations in straw mostly below 10 mg g^{-1} DW for the nine cultivars analysed (Fig. 3), with an average of 5.4± 3.3 mg g^{-1} Si when calculated on a total of 16 straw samples sampled between 1872 and 2000, the Broad-balk samples have lower concentrations than those generally found. Ma and Takahashi (2002) report an average wheat Si concentration of 14.4 mg g^{-1} DW (whole shoot) on a Japanese soil, while Rodgers-Gray and Shaw (2004) reported concentrations ranging from 9 to 31 mg g^{-1} on four UK soils with 2 different cultivars, and values up to 20–43 mg g^{-1} on the same cultivars when silica is added as fertiliser. As it is unlikely that all nine cultivars analysed are weak Si accumulators, bioavailable Si is assumed to be low in the Broadbalk field, which is in accordance with the ASi concentrations measured in the surface soil samples (Fig. 1a).

In the Broadbalk experiment, a decrease of ASi in the surface samples through time (Fig. 1a) is in good agreement with the hypothesis that cultivation with

export of straw leads to depletion of soil phytolith stocks. The initial soil sampled in 1881 contained already a low ASi concentration as compared to topsoil samples from temperate forests and grasslands analysed by Saccone et al. (2007). The low Si concentrations in the Broadbalk topsoil samples sampled at that time may be explained either by depletion in soil phytoliths before the beginning of the Broadbalk experiment due to previous agricultural practices, or by cropping not favourable to phytolith production (Bartoli 1981). Indeed, before 1843 the field is thought to have been in mixed arable cropping (since at least 1623) and straw removed for animal bedding. Turnips, barley, peas, wheat and oats preceded the first crop of experimental wheat (Lawes and Gilbert 1864). The whole field was heavily chalked before 1843 and, in addition, lime has been intermittently applied since 1955 on the arable part of Broadbalk (Fig. 3b). Liming increases soil pH (Fig. 1a) and thus may have increased the dissolution rate of phytoliths present in the soil (Fraysse et al. 2006). Indeed, larger Na_2CO_3-extracted Si concen-

trations are associated with larger pH values (Fig. 1a). An ASi_{nc} measurement performed on topsoil sampled on the grassland strip adjacent to the field experiment gave 3.2 mg g^{-1} Si, which is larger than all measurements performed on the continuous wheat experiment, indicating more Si input through vegetation turnover.

The assumption of decrease in bioavailable soil Si with time should be correlated with a decrease in Si concentrations in plants. This assumption is in agreement with the results obtained with the archived straw samples collected before 1944. After 1944, Si concentrations in straw tended to increase and ASi in soil samples was slightly larger in 2000. This increase has been observed due to inputs of bioavailable Si through irrigation as observed in the Camargue (Desplanques et al. 2006), but no irrigation was applied on the Broadbalk field. Periodic liming increased pH and the related increasing rate of phytolith dissolution (Fraysse et al. 2006) could explain the increase in plant Si uptake (Fig. 3b and c). However the changes of cultivars with time might also explain the changes observed, as they vary in their ability to take up Si (e.g. Tuna et al. 2008): for example in the Broadbalk experiment Squarehead's Master cv was grown alongside Brimstone cv in 1988, 1989 and 1990 (Table 3) and showed the same trend but Brimstone straw contained between 30 and 60% more Si than Squarehead's Master (Fig. 3b). A significant increase in Si concentration between 1916 and 1957 and onwards for the same cultivar, Squarehead's Master points (Fig. 3a and b), however, to a change in Si bioavailability in the soil. In addition, the parallel trend for Si concentrations in Brimstone and Squarehead's Master cv straw between 1988 and 1990 indicates that factors such as agronomic practices (both were 1st wheats after a 2-year break (fallow, potatoes), climate and soil status also control Si concentrations in straw. We thus suggest that the larger ASi dissolution rate due to an increase or stabilisation of soil pH may promote Si uptake by wheat, as suggested by the general increase in straw Si concentrations when periodical liming was applied (Fig. 3b).

Combining Si concentrations in straw and the yield at Broadbalk throughout the years (1881–2000), a simple calculation shows that since our first soil sample was taken in 1881, approximately 1.98 t Si ha^{-1} has been extracted from the soil by wheat, which is less than 20 kg ha^{-1} $year^{-1}$. Amounts of Si exported calculated between 1881 and 2000 from ASi concen-trations in the topsoil (Fig. 1a) differ depending on whether ASi_{nc} or ASi_{zb} values are used. ASi_{nc} values give usually larger outputs than ASi_{zb} because ASi_{nc} values might not only include Si in phytoliths but also non-biogenic amorphous Si. Indeed, when ASi_{nc} values are taken, amounts exported from topsoils are three times larger (ca. 5.8 t Si between 1881 and 2000) than values calculated from straw (ca. 2 t Si for the same period of time) while they are slightly lower or within the same range when ASi_{zb} values are used indicating that other mechanisms than plant uptake might significantly modify ASi stocks in soil. The rate at which Si can be depleted from the soil by plant uptake was found to reach 500 kg ha^{-1} $year^{-1}$ under a rice paddy field (Makabe et al. 2009), but the rate of removal of Si by wheat has not previously been investigated. With an average mean Si concentration of 14.4 mg g^{-1} DW in wheat whole shoot as measured by Ma and Takahashi (2002) and a mean straw yield of 4–9 t DW ha^{-1} $year^{-1}$ (ADEME/ITCF 1998), Si uptake of a wheat crop would be approximately 94 kg ha^{-1} $year^{-1}$ (or slightly larger if grain yield is also taken into account), that is slightly lower than that of rice or sugarcane, and larger than uptake calculated for this continuous wheat experiment.

However, in 1881, ASi_{zb} accounted for 21.4 tha^{-1} in the soil, taken as a whole. The export of straw would account for a decrease of approximately 10% of the ASi stock over a period of just 100 years if we consider amorphous silica as the only source of silicon for plants. This is probably slightly overestimated because some straw always returns to the soil and thus contributes to replenishment of the ASi stock. The ASi stock through the whole profile decreased to approximately 30% of the initial content between 1893 and 2000 but, as standard deviations are high for some of the samples, this decrease could be explained solely by wheat uptake.

The assumption of a depletion of bioavailable soil Si might also be related to a yield decline as suggested by Savant et al. (1997b) for rice. Based on the selected samples analysed there is a good correlation for plot 8 between Si concentration in straw and both the grain and straw yields (Fig. 6) except for straw before 1968. After 1968 highly productive cultivars with shorter straw (Table 3) were used alternatively with old cultivars and their behaviour as far as Si is concerned might be different.
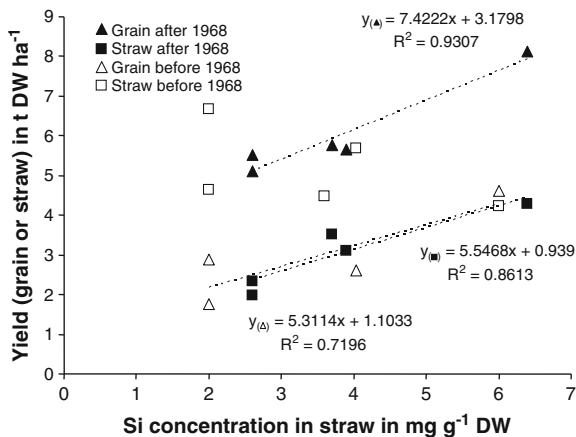
Fig. 6 Correlation between straw Si concentration (% DW) and yields of grain and straw harvested on the Broadbalk field (t ha^{-1}) obtained on plot 8. Yields of grain and straw from section 081 are used for samples after 1968 while results from section 080 are used for samples before 1968. A distinction is made between samples collected before and after 1968 because after 1968 high yielding cultivars were used

Another important finding is the distribution of ASi in the soil profiles. If we compare the Broadbalk field ASi_{zb} profiles to natural ecosystems, we see an opposite trend. In a natural environment, the silicon absorbed by the roots of the plants (mainly transformed into phytoliths in the leaves) goes back to the surface as plant residues. Phytoliths accumulate at the surface, especially in acidic soils where they dissolve more slowly, while at depth, the phytolith concentration decreases dramatically (Bartoli 1981; Sommer et al. 2006). In addition, at the surface, phytoliths are temporarily trapped in the litter being decomposed whereas at depth most of them are dissolved.

In all the profiles studied at Broadbalk and Geescroft under cultivation (1883), the ASi concentration increases with depth (Fig. 1b and c and, profile 1883 in Fig. 4b). This distribution can be explained by the export of the wheat for more than a century, and that plant Si was not returned (apart from that in roots and the remaining straw) to the soil. Alternatively, this distribution could be explained by the translocation of the remaining phytolith particles down the profile (Fishkis et al. 2010a, b) and stopped by a discontinuity at depth. However, soil description and particle size analysis of the Broadbalk soil (Avery and Catt 1995) do not indicate the presence of such a layer. This further suggests a progressive depletion of ASi starting in topsoil and progressing down the soil profile.

Measurements of bioavailable Si in a soil profile under a cultivated field was performed by Ma and Takahashi (2002). They report soluble Si concentrations (measured by acetate buffer) in a paddy field increasing with depth, with a trend similar to that of the ASi profiles at Broadbalk. Though they interpreted these results as a pH effect (soil pH having the same distribution), this could be due to the uptake of Si by rice. Furthermore, as for the Broadbalk field until 1944, they monitored a decrease in bioavailable Si through the years, associated with a decrease of both Si in the plants and soil pH. We suggest that in this case two effects are combined: 1) annual straw exports reduce the amount of phytolith inputs to the soil and, 2) pH decrease that may happen in cultivated fields (before 1944 in our case, Fig. 1a), slows down the rate of phytolith dissolution in agreement with the experimental results of Fraysse et al. (2006), which in turn leads to a decrease in plant Si concentration.

In the woodland samples, we expected that phytoliths would start accumulating in surface horizons. However in Broadbalk Wilderness, no increase in surface ASi concentrations is observed (Fig. 5a). In addition, a decrease in ASi concentrations is observed at depth, especially between 69 and 91 cm which indicates a further absorption of ASi by the woodland. One explanation is that the soil was already depleted in bioavailable Si before the development of the forest, as indicated by the low both ASi_{nc} and ASi_{zb} concentration measured in the 1893-topsoil sample (Figs. 4a and 5a). Therefore the trees have grown in a Si depleted environment. Under woodland, there might be a wide discrepancy in ASi values if measured at the top or at the bottom of the 0–23 cm layer from which we can only get a mean value of, whereas in the field ploughing homogenises the first 23 cm of soil. Saccone et al. (2007) found that Na_2CO_3-extractable ASi decreased from 52.5 mg g^{-1} to 1.8 mg g^{-1} in the first 21 cm of a natural forest soil, while the 0–23 cm layer at Broadbalk Wilderness gives a 0.5 mg g^{-1} mean value in 1999 (Fig. 4a). This result is thus in good agreement with the hypothesis of a Si-depleted soil and the potential increase at the surface might be diluted within the 0–23 cm depth. A finer soil sampling within the first 23 cm would help to clarify that point. Another explanation is that because of the high pH that prevails in this soil, phytoliths are dissolved too fast and Si is either

leached or taken up by trees to allow a measureable replenishment of the surface phytolith pool.

The ASi_{nc} profiles from the Geescroft acidic woodland soil samples show the opposite trend between the 1883 and 1999 that fits well with the hypothesis: the larger phytolith concentration in the modern surface samples is in a good agreement with a re-building of phytolith stock from litterfall (Fig. 5b). ASi_{zb} shows also lower values in 1883 than in 1999 but data are lacking at the bottom of the 1999 profiles, which would have allowed better interpretation. Because the pH of Geescroft Wilderness is acidic enough to prevent rapid phytolith dissolution (Fraysse et al. 2006), we can measure a net increase in the top layer, contrary to Broadbalk Wilderness. This is in accordance with the good conservation of the phytoliths observed in the 1999 samples, in which the phytoliths were not broken or weathered, contrary to all the other samples (Fig. 2c).

The concentration profile of ASi in the 1999 Geescroft Wilderness (Figs. 4b and 5b) is similar to the one found in a natural ecosystem (Bartoli 1981; Sommer et al. 2006). However, though the first layer of soil regenerated itself in terms of phytoliths (Fig. 5b), the acidity of the soil makes them probably less available than on Broadbalk. Indeed, the extracting pH of Na_2CO_3 is 10 while soil pH in 1999 at Geescroft Wilderness was 4.4. This should be verified by measuring the Si concentration in the above ground vegetation. In that case, the ASi_{nc} and ASi_{zb} measures are more an estimation of the potential rather than the effective bioavailable Si.

Conclusion

The results obtained on a long-term cultivated field provide us with major findings on the impact of Si-accumulating plants on the biogeochemical cycle of Si. The concentration of amorphous silica is lower in cultivated soils compared to natural ecosystems where plant Si is not exported. Systems in which the straw is exported from the field do not sustain high Si concentrations in wheat. The soil ASi pool decreases with time and is depleted particularly in surface soil, contrary to natural ecosystems. An additional pH decrease observed in unlimed fields may further decrease ASi solubility and hence bioavailability. This study should be extended to other long-term

cultivated fields with Si accumulator crops to validate the results at a global scale.

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