



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

Daniel Puppe^{a,*}, Danuta Kaczorek^{a,b}, Jörg Schaller^a, Dietmar Barkusky^a, Michael Sommer^{a,c}

^a Leibniz Centre for Agricultural Landscape Research (ZALF), 15374 Müncheberg, Germany

^b Warsaw University of Life Sciences (SGGW), Department of Soil Environment Sciences, 02-776 Warsaw, Poland

^c University of Potsdam, Institute of Environmental Science and Geography, 14476 Potsdam, Germany

ARTICLE INFO

Handling Editor: Daniel Said-Pullicino

Keywords:

Sustainable crop production
Straw incorporation
Phytoliths
Silicon exports
Plant available Si

ABSTRACT

Due to the fact that silicon (Si) increases the resistance of plants against diverse abiotic and biotic stresses, Si nowadays is categorized as beneficial substance for plants. However, humans directly influence Si cycling on a global scale. Intensified agriculture and corresponding harvest-related Si exports lead to Si losses in agricultural soils. This anthropogenic desilication might be a big challenge for modern agriculture. However, there is still only little knowledge about Si cycling in agricultural systems of the temperate zone, because most studies focus on rice and sugarcane production in (sub)tropical areas. Furthermore, many studies are performed for a short term only, and thus do not provide the opportunity to analyze slow changes in soil–plant systems (e.g., desilication) over long periods. We analyzed soil and plant samples from an ongoing long-term field experiment (established 1963) in the temperate zone (NE Germany) to evaluate the effects of different nitrogen-phosphorus-potassium (NPK) fertilization rates and crop straw recycling (i.e., straw incorporation) on anthropogenic desilication in the long term. Our results clearly show that crop straw recycling not only prevents anthropogenic desilication (about 43–60% of Si exports can be saved by crop straw recycling in the long term), but also replenishes plant available Si stocks of agricultural soil–plant systems. Furthermore, we found that a reduction of N fertilization rates of about 69% is possible without considerable biomass losses. This economy of the need for N fertilizers potentially can be combined with the benefits of crop straw recycling, i.e., enhancement of carbon sequestration via straw inputs and prevention of anthropogenic desilication of agricultural soil–plant systems. Thus crop straw recycling might have the potential to act as key management practice in sustainable, low fertilization agriculture in the temperate zone in the future.

1. Introduction

Various favorable effects of silicon (Si) on plants have been reported, i.e., increased plant growth and resistance against abiotic (e.g., drought) and biotic (e.g., fungal infections) stresses (e.g., (Epstein, 1999; Ma, 2004; Puppe and Sommer, 2018)). Against this background, the International Plant Nutrition Institute (IPNI) categorizes Si as a ‘beneficial substance’ for plants (www.ipni.net). Aside from plants numerous organisms are evolutionary adapted to use monomeric silicic acid (H_4SiO_4) for the synthesis of hydrated amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) in a process called biosilicification (Ehrlich et al., 2010; Perry and Keeling-Tucker, 2000). In soils biogenic silica (BSi) formed by bacteria, fungi, protists (mainly diatoms and testate amoebae), animals (mainly

sponges), and plants can be found representing bacterial, fungal, protistic, zoogenic, and phytogenic BSi pools, respectively (Puppe, 2020).

BSi pools, especially the phytogenic ones, play an important role as source of readily or plant available Si (i.e., H_4SiO_4) in soils, because amorphous BSi is much more soluble compared to crystalline SiO_2 and silicates (Schaller et al., 2021). Si availability in turn is of special importance for agricultural biogeosystems considering the beneficial effects of Si for many crops (Haynes, 2014, 2017). Synthesized siliceous structures in plants are called phytoliths, which are mainly made of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, but also contain organic matter and various elements, e.g., aluminum, calcium, iron (Fe), manganese, phosphorus (P), and potassium (Buján, 2013; Kameník et al., 2013; Wu et al., 2014). Phytoliths are formed in living plants within cells (i.e., in the cell wall and the cell

* Corresponding author.

<https://doi.org/10.1016/j.geoderma.2021.115187>

Received 21 January 2021; Received in revised form 26 April 2021; Accepted 29 April 2021

Available online 9 May 2021

0016-7061/© 2021 Elsevier B.V. All rights reserved.

lumen) and have a specific morphology that can be used for taxonomic identification of plants (Hodson, 2016; Piperno, 2006; Sangster et al., 2001). However, next to durable (i.e., relatively stable) phytoliths, that can be frequently found in most soils, Si depositions in plants can be found in intercellular spaces or in an extracellular (cuticular) layer forming very fragile silica structures (Hodson, 2016; Sangster et al., 2001). These fragile silica structures might represent the biggest and most reactive BSi pool in soils, and thus might be the most important drivers of bio-available Si in terrestrial biogeosystems (Puppe et al., 2017). Si concentrations of plants vary considerably with about 0.1–10% Si per dry mass depending on plant species (Hodson et al., 2005). Based on their Si concentration per dry mass plants have been divided into three groups (Ma and Takahashi, 2002):

- (i) Non-accumulators or excluders (Si concentration per dry mass < 0.5%),
- (ii) Intermediate accumulators (Si concentration per dry mass 0.5–1%), and
- (iii) Accumulators (Si concentration per dry mass > 1%).

Regarding field crops especially cereal grasses of the family Poaceae (or Gramineae) are known as Si accumulators (Hodson et al., 2005). However, it should be kept in mind that the mechanisms behind the uptake, transport, and accumulation of Si in plants (active vs. passive Si transport) as well as Si induced plant resistance (mode of action of Si in plants) are not fully understood yet, and thus are under controversial discussion (see, e.g., (Coskun et al., 2018; Exley, 2015; Exley et al., 2020)).

Although the majority (>90 vol%) of the earth crust consists of SiO₂ and silicates, plant available Si is often limited in soils because Si is (i) competing with P, nitrogen (N), and carbon (C) for sorption sites at organic matter and mineral surfaces (Reithmaier et al., 2017; Schaller et al., 2019) and (ii) leached as a function of rainfall and irrigation, especially in agricultural soils (Haynes, 2019). Plant available Si in soils is ultimately controlled by the weathering stage of a soil, whereby the importance of phytoliths for plant available Si in soils has been found to increase with increasing weathering stage (Li et al., 2020). In general, soils poor in plant available Si can be characterized as highly weathered, leached, acidic, and low in base saturation. Such conditions are typical for many soils in (sub)tropical regions, where two well-known Si accumulators are grown, i.e., rice (*Oryza sativa*) and sugarcane (*Saccharum officinarum*) (see (Datnoff et al., 2001 and references therein)). For the determination of plant available Si, several extraction methods (e.g., calcium chloride, acetate/acetic acid, or citrate extractions) have been developed (see the review of (Sauer et al., 2006)). Regarding agricultural soils especially the influence of (i) adsorption/desorption reactions, (ii) leaching of Si from soils, (iii) BSi pools, and (iv) soil pH on the plant available Si fraction need a deeper understanding in general (Haynes, 2014).

Due to intensified land use (forestry, agriculture) humans directly influence Si cycling on a global scale (Struyf et al., 2010; Vandevenne et al., 2015a, 2015b). In this context, especially Si exports by harvested crops (most of them are Si accumulators) and increased erosion rates generally lead to a Si loss in agricultural soils (anthropogenic desilication, see, e.g., (Desplanques et al., 2006; Guntzer et al., 2012; Keller et al., 2012; Vandevenne et al., 2012)). Besides climate change, a growing global population, and decreasing resources (e.g., (Amundson et al., 2015; Vitousek et al., 2009; Wheeler and von Braun, 2013)), anthropogenic desilication might be one of the big challenges for modern agriculture. In fact, harvesting of field crops, for example, causes a Si loss of up to 100–500 kg Si ha⁻¹ per year depending on cultured crops (Meunier et al., 2008; Tubana et al., 2016). On a global scale about 35% of total phytogenic BSi is synthesized by field crops due to their relatively high Si concentrations as well as biomass and this proportion is going to increase with increased agricultural production within the next decades (Carey and Fulweiler, 2016).

In order to avoid (natural) limitations of plant available Si and enhance plant growth and resistance against abiotic and biotic stresses,

Si fertilization is widely used (Puppe and Sommer, 2018; Savant et al., 1999; Tubana et al., 2016). Additionally, Si fertilization might also be an effective method to mitigate anthropogenic desilication. In this context, specific Si fertilization, for example, in the form of BSi recycling (incorporation of organic siliceous materials like straw, husk, and husk ash) might be a promising and cost effective strategy for both decreasing desilication and enhancing Si supply for crops to increase yields (e.g., (Haynes, 2017; Marxen et al., 2016; Meena et al., 2014)). Moreover, the use of Si-rich biochar (Li et al., 2019; Li and Delvaux, 2019) and open straw burning in the field (Nguyen and Nguyen, 2019) have been proposed as suitable ways to supply agricultural soil–plant systems with Si. However, most studies on Si fertilization or supply focus on rice and sugarcane production in (sub)tropical areas and there is still only little knowledge about Si cycling in agricultural systems of the temperate zone. Furthermore, many studies are performed for a short term only (e.g., one cropping season), and thus do not provide the opportunity to analyze slow changes in soil properties (e.g., plant available Si) caused by management practices.

In this context, long-term field experiments (LTFEs) represent important tools for investigating changes in soil properties under different management practices and corresponding impacts on crop production and sustainability over long periods. The results obtained from LTFEs are of great importance to understand the trends and dynamics of these changes, and thus are indispensable for researchers as well as policymakers (e.g., (Debreczeni and Körschens, 2003; Sandén et al., 2018)). Regarding Si cycling in agricultural soil–plant systems, there have only few results from LTFEs been published until now. For example, (Guntzer et al., 2012) found the long-term removal of wheat straw to decrease the soil amorphous silica pool in soils at Rothamsted Research. (Yang et al., 2020) analyzed the long-term (36 years) influence of phytolith-rich straw recycling and groundwater table management on labile Si soil fractions and Si uptake by rice in subtropical China. These authors found total labile Si concentrations to increase significantly with increasing phytolith-rich straw application, whereby the largest Si fraction in soils was represented by amorphous Si assumed to originate mainly from plants (phytoliths). However, there are no studies on long-term straw recycling and its effects on Si cycling in soil–plant systems of the temperate zone to the best of our knowledge. In our study we analyzed soil and plant samples from an ongoing LTFE (established 1963 in a randomized block design: plots of low, medium, and high mineral nitrogen-phosphorus-potassium (NPK) fertilization rates, plots with crop straw recycling in addition to NPK fertilization, control plots) in NE Germany to answer the following questions:

- (i) Can we observe a significant desilication (indicated by a decrease in plant available Si in soils) of agricultural systems in the temperate zone in the long term?
- (ii) Is this potential desilication affected by NPK fertilization rates?
- (iii) Is this potential decrease of plant available Si in soils reflected in Si concentrations of the grown plants (e.g., wheat as Si accumulator)?
- (iv) Can we prevent potential anthropogenic desilication by crop straw recycling?

The answers to these questions will help us to obtain a deeper understanding of Si cycling in agricultural biogeosystems in the temperate zone and to assess the potential of Si for a more environmentally friendly and sustainable production of resilient crops. This kind of production is intended, for example, by the “Farm to Fork Strategy”, an important component of the European Green Deal, which aims to overcome climate change and environmental degradation (Commission, 2019).

2. Materials and methods

2.1. Study site and sampling

The examined LTFE “V140” (52°31′01″N, 14°07′19″E) at ZALF was established in a full randomized block design in 1963 to analyze the effects of different mineral and organic fertilizers on yields and soil fertility (Barkusky, 2009; Barkusky et al., 2020). The experimental site is managed according to “Good Agricultural Practice”. The soil is classified as Albic Luvisol (Arenic, Neocambic) (World reference base for soil resources, 2014) with argic horizons in depths of 80–120 cm (Bt1) and 120–160 cm (Bt2), soil texture is dominated by sand (Table A1). The climate is characterized by a mean annual precipitation of 555 mm and a mean annual temperature of 8.9 °C (ZALF weather station, 1981–2010). The experimental setup includes different treatments, i.e., (i) NPK fertilization in steps of five rates related to N (plots NPK 1–5), (ii) organic fertilization (manure or straw plots), and (iii) control plots, with 8 field repetitions per treatment (168 single plots in total, see Fig. 1). Aboveground plant biomass (yield) per plot is captured every year. For our study we selected plots of low (NPK 1, 0–50 kg N ha⁻¹ y⁻¹ depending on crops, resulting in a mean fertilization rate of about 30 kg N ha⁻¹ y⁻¹), medium (NPK 3, 40–150 kg N ha⁻¹ y⁻¹, mean fertilization rate of about 98 kg N ha⁻¹ y⁻¹), and high (NPK 5, 80–250 kg N ha⁻¹ y⁻¹, mean fertilization rate of about 166 kg N ha⁻¹ y⁻¹) mineral NPK fertilization rates. Additionally, plots with crop straw recycling (incorporation of 4.0 t dry mass (DM) ha⁻¹ every second year generally using chopped straw of the harvested cereal crop, Table 1) in addition to NPK fertilization (NPK 1 + Straw, NPK 3 + Straw, NPK 5 + Straw), and control plots (no NPK fertilization, no crop straw recycling) in 4 field repetitions per treatment were analyzed (Fig. 1). Soil samples were regularly taken by the staff of the Experimental Station of ZALF and analyzed (e.g., pH, phosphate concentrations) in the Central Laboratory of ZALF (Barkusky,

2009; Barkusky et al., 2020) (Fig. A1). We used retained soil samples from 1976 (i.e., samples taken 13 years after the beginning of the experiment) and 1998 (i.e., samples taken 35 years after the beginning of the experiment) and additionally took soil samples in 2018 (i.e., 55 years after the beginning of the experiment) for our analyses (see 2.2.). In addition, samples of winter wheat (2018) were analyzed to detect potential effects on Si concentrations in Si accumulating crops (see 2.2. as well).

2.2. Soil and plant analyses

Soil samples were air dried and sieved and the fine earth fraction (<2 mm) was used for laboratory analyses. Soil pH was measured based on the (DIN ISO, 1039) in 0.01 M CaCl₂ suspensions at a soil-to-solution ratio of 1:5 (w/v) after a 60 min equilibration period using a glass electrode. Calcium chloride (CaCl₂) was used to extract the easily soluble or mobile Si fraction, i.e., the plant available Si fraction (Si present in the soil solution, i.e., silicic acid (H₄SiO₄) in most soils). For extraction, two-gram samples of soils were placed in 50 mL plastic centrifuge tubes with 20 mL of a 0.01 M CaCl₂ solution. Samples were agitated continuously on a reciprocating shaker for 16 h (Haysom and Chapman, 1975; de Lima Rodrigues et al., 2003). All soil analyses were performed at the minimum of two lab replicates per sample.

Phytoliths were extracted from soil samples as follows: (i) 10 g of dry soil material (<2 mm) was weighed, (ii) organic matter was oxidized using H₂O₂ (30%), HNO₃ (65%), and HClO₄ (70%) at 80 °C until reaction subsides, (iii) carbonates and Fe oxides were dissolved by boiling the sample in HCl (10%) for 30 min, (iv) the < 2 µm granulometric fraction was removed by dispersion of the remaining solid phase with a sodium hexametaphosphate solution (2%, 6–12 h), (v) samples were centrifuged (1,000 rpm, 2–3 min) and decanted, (vi) phytoliths were separated by shaking with 30 mL of sodium polytungstate (Na₆(H₂W₁₂O₄₀)·H₂O) with a density of 2.3 g cm⁻³ and subsequent centrifugation (3,000 rpm, 10 min), (vii) the supernatant was carefully pipetted and filtered using 5 µm Teflon filters (this step was repeated three times), (viii) the filter residue was washed with distilled water, bulked, dried at 105 °C, and weighed. Purity of the isolated phytoliths was checked via polarized light microscopy (Nikon ECLIPSE LV100 microscope). Phytolith morphotypes were characterized according to (Madella et al., 2005) and (Neumann et al., 2019).

Plant samples (winter wheat) were washed with distilled water to remove adhering soil minerals and oven-dried at 45 °C for 48 h. Subsequently, plant samples were separated into straw, grain, and husk for further analyses. The different plant materials were milled using a knife mill (Grindomix GM 200, Retsch) in two steps: (i) 4,000 rpm for 1 min and (ii) 10,000 rpm for 3 min. Sample aliquots of approximately 100 mg were digested under pressure in PFA digestion vessels using a mixture of 4 mL distilled water, 5 mL nitric acid (65%) and 1 mL hydrofluoric acid (40%) at 190 °C using a microwave digestion system (Mars 6, CEM). A second digestion step was used to neutralize the hydrofluoric acid with 10 mL of a 4% boric acid solution at 150 °C. All plant analyses were performed in three lab replicates per sample.

Si concentrations in soil and plant extracts were measured via ICP-OES (ICP-iCAP 6300 Duo, Thermo Fisher Scientific Inc.) using internal standards. To avoid Si contaminations, only plastic equipment was used during the entire procedures.

2.3. Calculation of Si inputs and outputs

Potential minimal and maximal Si inputs per year were calculated for the corresponding cultivated crop by multiplication of its (i) minimal and (ii) maximal Si concentration (in % each) with the rate of crop straw recycling (4.0 t DM ha⁻¹ every second year) (see Table 1). Subsequently, we calculated cumulative sums for (i) minimal and (ii) maximal Si inputs of the period 1963–2018. Si outputs (i.e., gross Si outputs) per year were calculated by multiplication of the corresponding aboveground biomass

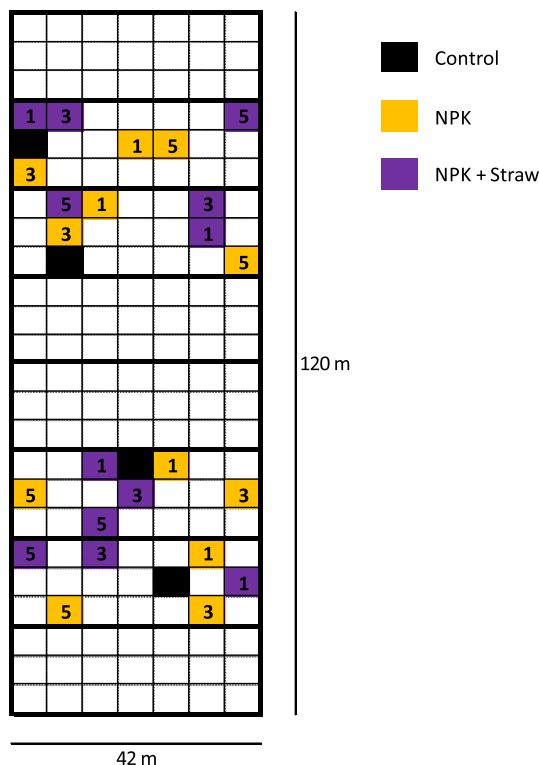


Fig. 1. Experimental setup of the long-term field experiment V140 at ZALF. Plots used for the current study are highlighted in black (control plots), orange (NPK plots), and purple (NPK + Straw plots). The numbers indicate the NPK fertilization rate: 1 = Low NPK fertilization rate, 3 = Medium NPK fertilization rate, 5 = High NPK fertilization rate.

Table 1

Overview of cultivated crops at the LTFE V140 in the period 1963–2018. Crop straw is applied every second year (when cereal crops are grown) after harvest using the straw of the harvested cereal crop.

Year	Crop	Binomial	Plant family	Si content (%) [*]		Straw recycling (4.0 t DM ha ⁻¹)
				Min.	Max.	
1963	Silage maize	<i>Zea mays</i>	Poaceae	0.6	1.1	No
1964	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
1965	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1966	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
1967	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1968	Summer wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1969	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1970	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1971	Silage maize	<i>Zea mays</i>	Poaceae	0.6	1.1	No
1972	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
1973	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1974	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1975	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1976	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1977	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1978	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1979	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1980	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1981	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1982	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1983	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1984	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1985	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1986	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1987	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1988	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1989	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1990	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
1991	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
1992	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1993	Sugar beet	<i>Beta vulgaris</i>	Amaranthaceae	–	–	No
1994	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
1995	Silage maize	<i>Zea mays</i>	Poaceae	0.6	1.1	No
1996	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
1997	Linseed	<i>Linum usitatissimum</i>	Linaceae	0.05	0.05	No
1998	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
1999	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
2000	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
2001	Field pea	<i>Pisum sativum</i> subsp. <i>arvense</i>	Fabaceae	0.1	0.1	No
2002	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
2003	Silage maize	<i>Zea mays</i>	Poaceae	0.6	1.1	No
2004	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
2005	Linseed	<i>Linum usitatissimum</i>	Linaceae	0.05	0.05	No
2006	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
2007	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
2008	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
2009	Pea	<i>Pisum sativum</i>	Fabaceae	0.1	0.1	No
2010	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes
2011	Silage maize	<i>Zea mays</i>	Poaceae	0.6	1.1	No
2012	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
2013	Linseed	<i>Linum usitatissimum</i>	Linaceae	0.05	0.05	No
2014	Winter rye	<i>Secale cereale</i>	Poaceae	0.2	1.7	Yes
2015	Potato	<i>Solanum tuberosum</i>	Solanaceae	–	–	No
2016	Summer barley	<i>Hordeum vulgare</i>	Poaceae	0.3	6.2	Yes
2017	Field pea	<i>Pisum sativum</i> subsp. <i>arvense</i>	Fabaceae	0.1	0.1	No
2018	Winter wheat	<i>Triticum aestivum</i>	Poaceae	0.1	11.3	Yes

^{*} Data taken from the compilation published by (Hodson et al., 2005).

of the cultivated crop (t ha⁻¹ DM) with its (i) minimal and (ii) maximal Si concentration (in % each). Afterwards, cumulative sums for (i) minimal and (ii) maximal Si outputs of the period 1963–2018 were calculated. Net Si outputs were calculated by subtracting (minimal, maximal) Si inputs from (minimal, maximal) Si (gross) outputs. Subsequently, we calculated cumulative sums for (i) minimal and (ii) maximal net Si outputs of the period 1963–2018.

2.4. Statistical analyses

Statistical significances were evaluated by means of the Kruskal-

Wallis analysis of variance (ANOVA) and relationships were analyzed via Spearman's rank correlation using the software package SPSS Statistics (version 22.0.0.0, IBM Corp.).

3. Results

3.1. Harvest-related Si outputs at the long-term field experiment V140

Cumulative sums of minimal and maximal annual Si outputs were considerably higher at NPK and NPK + Straw plots compared to control plots (Fig. 2). Under low (NPK1) and medium (NPK3) NPK fertilization

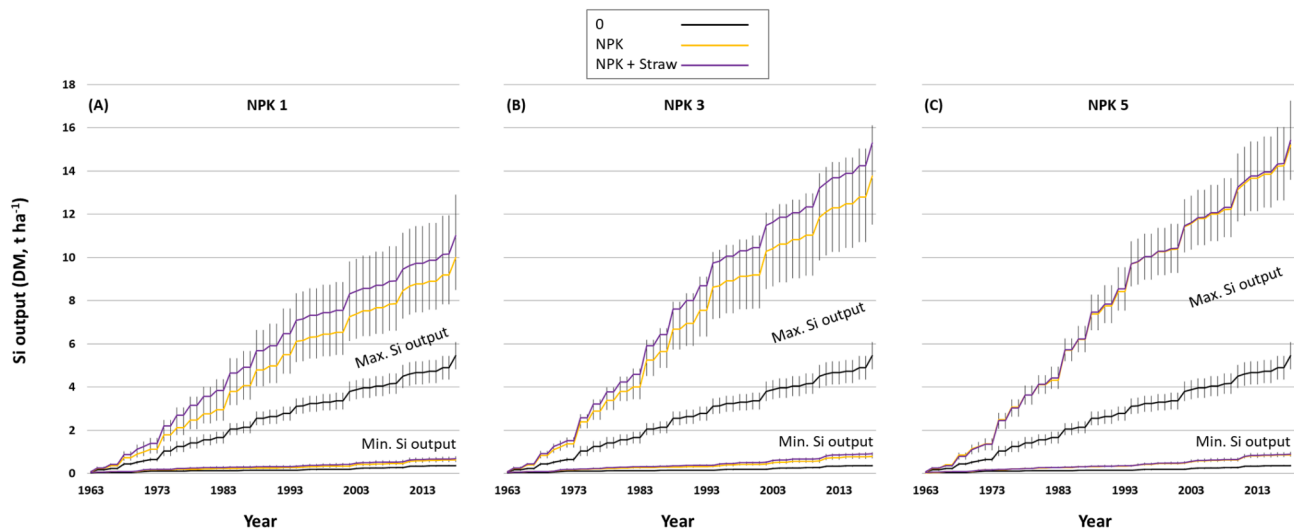


Fig. 2. Cumulative sums of minimal (3 lower lines) and maximal (3 upper lines) annual Si outputs (Means \pm SD, $n = 4$) at the LTFE V140 in the period 1963–2018. Data for (A) low (NPK1), (B) medium (NPK3), and (C) high (NPK5) fertilization rates are displayed.

rates NPK + Straw plots were characterized by slightly higher Si outputs compared to NPK plots. In contrast, Si outputs in the high (NPK5) NPK fertilization treatment were almost equal at NPK and NPK + Straw plots. Si outputs in medium (NPK3) and high (NPK5) NPK fertilization treatments were comparable and higher than Si outputs in the low (NPK1) fertilization treatment. An overview of (i) annual Si outputs (ranges and means of min. and max. Si outputs) and (ii) maximal Si outputs per year of individual cereal crops, i.e., maize, barley, wheat, and rye, can be found in the appendix (Table A2, Fig. A2).

Cumulative sums of minimal and maximal annual net Si outputs clearly revealed crop straw recycling effects (Fig. 3). Under all NPK fertilization rates (i.e., NPK1, NPK3, and NPK5) NPK + Straw plots were characterized by considerably lower net Si outputs compared to NPK plots. Under low fertilization rates (NPK1) net Si outputs at NPK + Straw plots were even lower than net Si outputs at control plots. Net Si outputs at NPK and NPK + Straw plots in medium (NPK3) and high (NPK5) fertilization rate treatments were comparable and considerably higher than net Si outputs in the low (NPK1) fertilization rate treatment. The difference ($\Delta_{\text{net Si output}}$) between cumulative sums of annual net Si outputs of NPK plots and corresponding NPK + Straw plots increased

with time (Fig. A3). Calculated deltas ($\Delta_{\text{net Si output}}$) represent the potential savings on Si outputs by crop straw recycling. At plots under low fertilization rates (NPK1) $\Delta_{\text{net Si output}}$ reached about 0.2 and 6.2 t ha⁻¹ DM (1963–2018) assuming minimal or maximal Si output, respectively. Under medium fertilization rates (NPK3) $\Delta_{\text{net Si output}}$ was about 0.1 and 5.6 t ha⁻¹ DM assuming minimal or maximal Si output, respectively. Under high fertilization rates (NPK5) $\Delta_{\text{net Si output}}$ reached about 0.2 and 6.9 t ha⁻¹ DM assuming minimal or maximal Si output, respectively.

3.2. Si concentrations of plant materials of winter wheat

Si concentrations of analyzed plant materials increased in the order grain (range: 0.2–0.4 mg g⁻¹), straw (6.3–10.7 mg g⁻¹), and husk (9.5–23.2 mg g⁻¹) (Fig. 4). Statistically significant differences between the plots were found for straw and husk samples, whereby these differences were more pronounced in husk samples. This means that differences between the plots were more pronounced with increasing Si concentrations in plant materials. While Si concentrations of husk samples were highest in control plots, Si concentrations of husk samples tended to decrease with NPK fertilization rate. Si concentrations of husk

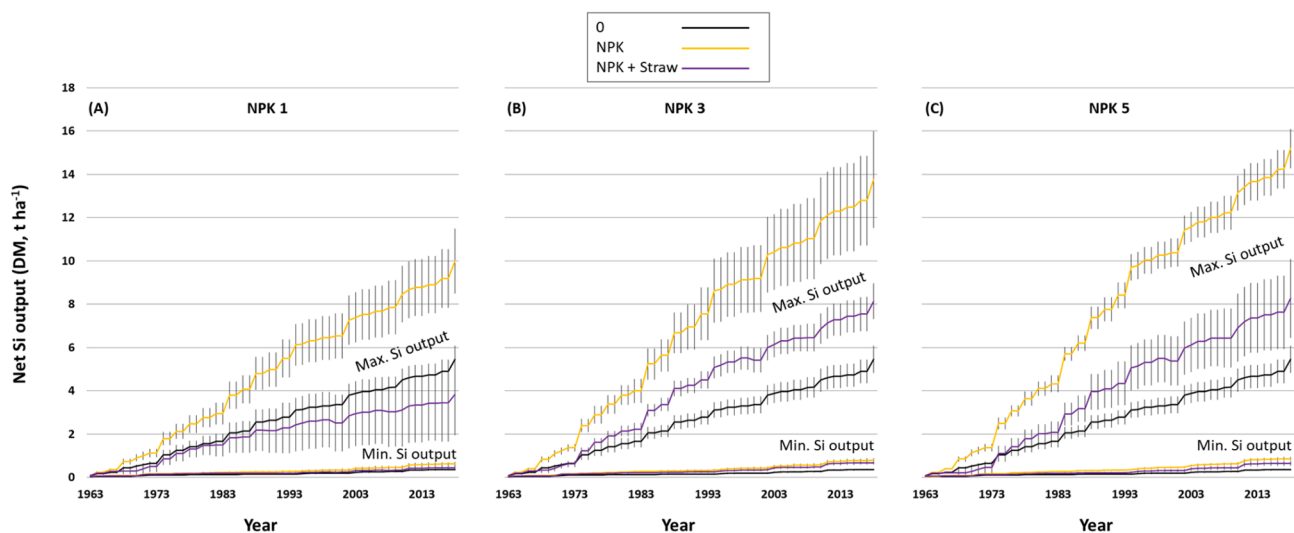


Fig. 3. Cumulative sums of minimal (3 lower lines) and maximal (3 upper lines) annual net Si outputs (Means \pm SD, $n = 4$) at the LTFE V140 in the period 1963–2018. Data for (A) low (NPK1), (B) medium (NPK3), and (C) high (NPK5) fertilization rates are displayed.

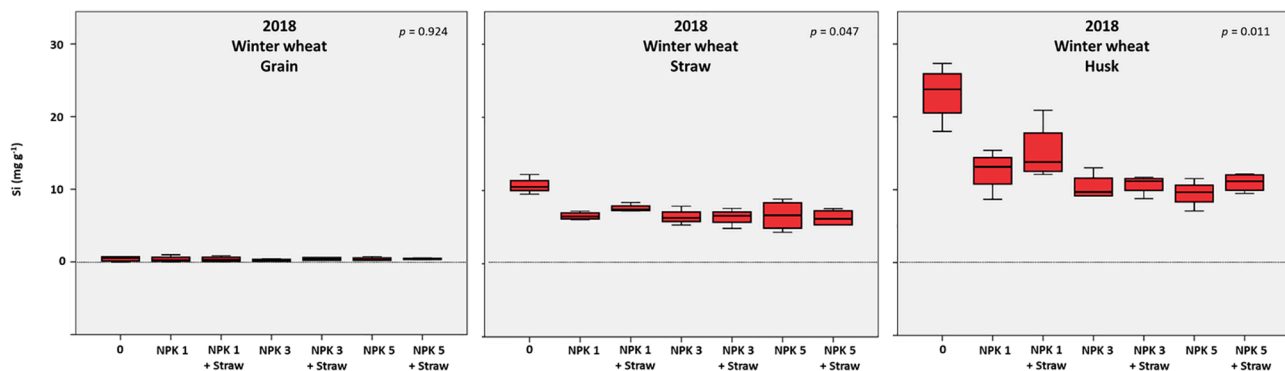


Fig. 4. Boxplots of Si concentrations of grain (left), straw (center), and husk (right) samples of *Triticum aestivum* cultured at the LTFE V140 in 2018. Differences between the experimental plots were evaluated using the Kruskal-Wallis ANOVA ($n = 4$).

samples were slightly higher at NPK + Straw plots compared to NPK plots. We found no relationships between Si concentrations of plant materials and plant available Si in soils (see 3.3): grain Si vs. plant available Si ($r_s = -0.036$, $p = 0.939$), straw Si vs. plant available Si ($r_s = 0.143$, $p = 0.760$), and husk ($r_s = 0.429$, $p = 0.337$).

3.3. Plant available Si and phytoliths in soils

Plant available Si in soils considerably increased with time: 1976 (range: 5.1–7.6 mg kg⁻¹, mean: 6.3 mg kg⁻¹), 1998 (5.9–8.4 mg kg⁻¹, mean: 7.2 mg kg⁻¹), and 2018 (8.3–9.9 mg kg⁻¹, mean: 9.2 mg kg⁻¹) (Fig. 5). However, statistically significant differences between the treatments (0, NPK, NPK + Straw) were found only in samples of 1976 with highest concentrations of plant available Si in control plots and lowest concentrations in NPK5 + Straw plots. This pattern of decreasing plant available Si concentrations with increasing NPK fertilization rates was also given for samples of 1998 (although statistically not significant). In contrast, plant available Si in soil samples of 2018 was found to be very similar in the different treatments (0, NPK, NPK + Straw) with a smaller difference between minimal and maximal values (min.: 8.3 mg kg⁻¹, max.: 9.9 mg kg⁻¹, difference: 1.6) compared to 1998 (min.: 5.9 mg kg⁻¹, max.: 8.4 mg kg⁻¹, difference: 2.5) and 1976 (min.: 5.1 mg kg⁻¹, max.: 7.6 mg kg⁻¹, difference: 2.5). Differences in plant available Si in soils between control, NPK, and NPK + Straw plots in a given year were only statistically significant for NPK5 in 1976 (Fig. A4). In general, concentrations of plant available Si in soils tended to decrease with increasing plant biomass ($r_s = -0.410$, $p = 0.065$). Plant biomass for every single year can be found in the appendix (Fig. A5).

Regarding the individual treatments the observed increase in plant available Si with time was statistically significant for NPK3 + Straw and NPK5 + Straw plots (Fig. 6). However, this increase also tended ($p < 0.1$) to be statistically significant for all other treatments (NPK1, NPK1 +

Straw, NPK3, and NPK5 plots) except control plots.

Phytolith concentrations in soils increased with time: 1976 (range: 1.2–2.1 mg g⁻¹, mean: 1.6 mg g⁻¹), 1998 (1.1–2.1 mg g⁻¹, 1.6 mg g⁻¹), and 2018 (1.7–3.4 mg g⁻¹, 2.4 mg g⁻¹) (Fig. 7). Phytolith concentrations were higher than ammonium oxalate-soluble Fe concentrations (1 mg g⁻¹) in the upper 30 cm of soils (Ap horizon), but lower compared to dithionite-soluble Fe (2.6 mg g⁻¹) in the Ap horizon (Table A1). Due to relatively high standard deviations there were no distinct differences between phytolith concentrations in soils of NPK and NPK + Straw plots, although there seemed to be a trend to higher phytolith concentrations in NPK + Straw plots compared to NPK plots (i.e., in seven times out of nine, see Fig. 7). Highest phytolith concentrations were unexpectedly (no crop straw recycling, lowest plant biomass) recorded at control plots in 2018. Most phytoliths were classified as elongate, polylobate, short (saddle, rondel), and cross morphotypes, which are typical for grass (Poaceae) phytoliths (Fig. 8A, B). Aside from phytoliths, some diatom frustules and sponge spicule fragments were also observed (Fig. 8B).

Plant available Si in soils was strongly related to soil pH and phytolith concentrations in soils, and tended ($p < 0.1$) to be significantly correlated with N_t and P_{DL} (Table 2).

4. Discussion

4.1. Anthropogenic desilication of agricultural systems in the temperate zone in the long term

In general, the calculated potential Si outputs in our study showed a wide range with maxima up to about 1,500 kg ha⁻¹ per year (calculated for winter wheat with a Si concentration of 11.3%, cf. Table 1). However, depending on the measured Si concentration in wheat plants (cultured 2018), actual Si outputs at V140 have to be considered smaller than potential maximal values. In fact, Si concentrations in wheat

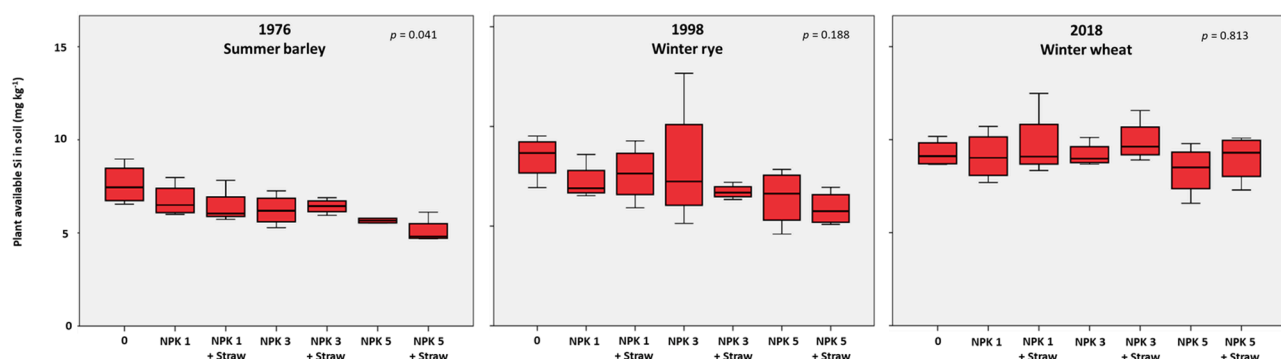


Fig. 5. Boxplots of plant available Si in soils from the LTFE V140 taken in 1976 (left), 1998 (center), and 2018 (right). Differences between the experimental plots were evaluated using the Kruskal-Wallis ANOVA ($n = 4$).

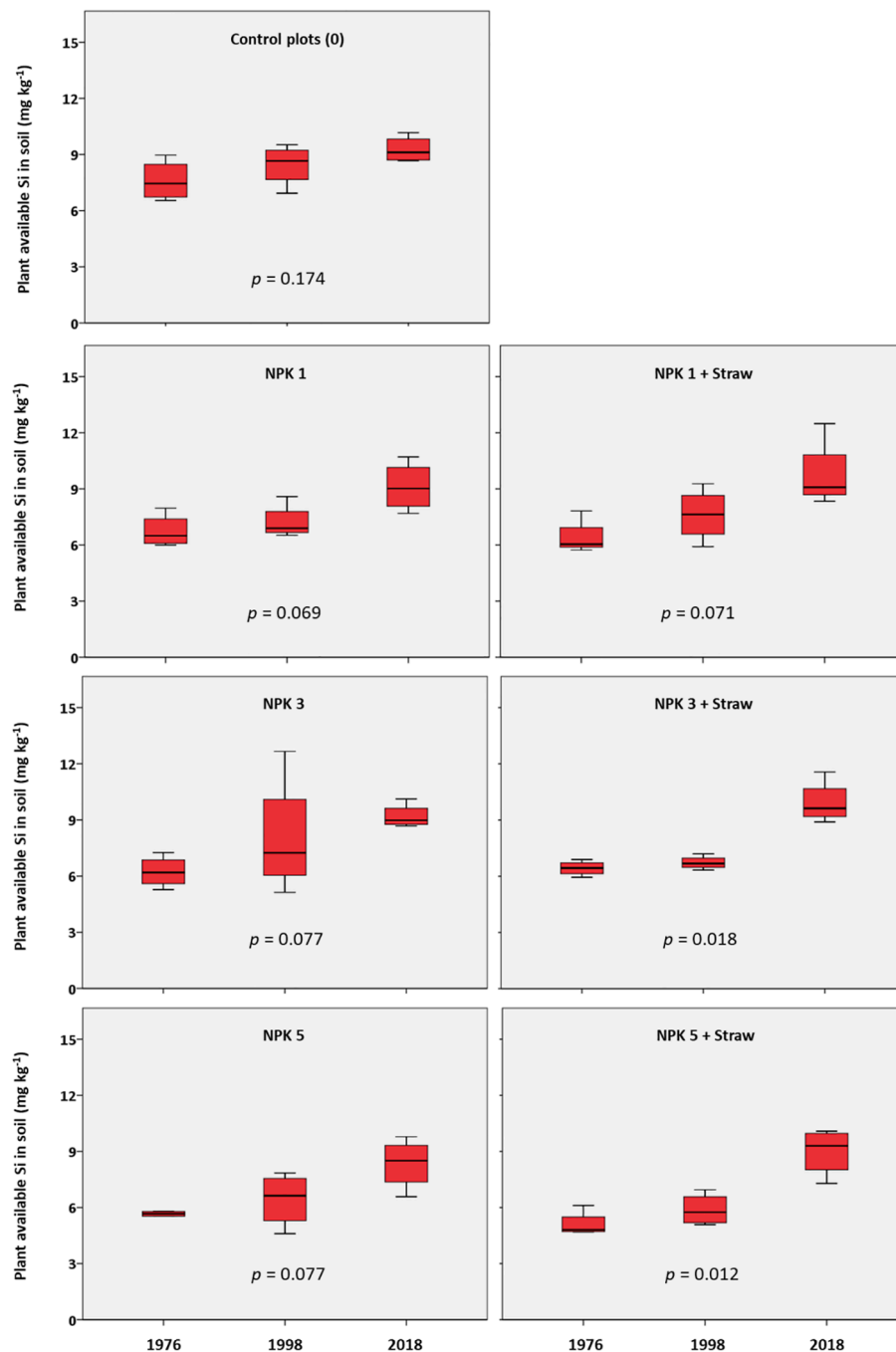


Fig. 6. Boxplots of plant available Si in soils of the different treatments at the LTFE V140 in the years 1976, 1998, and 2018. Differences between the years within a treatment (control plots (0), mineral fertilizer plots (NPK), and mineral fertilizer plots that were additionally supplied with crop straw (NPK + Straw)) were evaluated using the Kruskal-Wallis ANOVA ($n = 4$).

aboveground biomass ranged between 0.4 and 0.8% (mean 0.5%) depending on experimental treatment (control > NPK1 > NPK1 + Straw > NPK3 + Straw > NPK5 + Straw > NPK5 > NPK3), and thus are about four to eight times higher than published minimal Si concentrations of wheat (0.1%, (Hodson et al., 2005)). Accordingly, we can reasonably assume an actual mean Si output of about 66 kg ha^{-1} for winter wheat in the year 2018 at our study site. This value is in the range of previously reported Si uptakes (which can be assumed to equal Si outputs by harvesting) for wheat in the temperate zone (i.e., $20\text{--}113 \text{ kg Si ha}^{-1} \text{ y}^{-1}$, see Table 1 in (Keller et al., 2012)). Compared to Si uptakes of rice ($270\text{--}500 \text{ kg Si ha}^{-1} \text{ y}^{-1}$, (Keller et al., 2012) $\text{kg Si ha}^{-1} \text{ y}^{-1}$; (Savant et al., 1996) and sugarcane ($379 \text{ kg Si ha}^{-1} \text{ y}^{-1}$, (Savant et al., 1999)), these values are

considerably lower. Contrary to natural ecosystems (Si uptake of $2\text{--}127 \text{ kg Si ha}^{-1} \text{ y}^{-1}$, (Keller et al., 2012), where large amounts of Si are recycled year by year (e.g., (Sommer et al., 2013)), the annual Si exports in agricultural soil–plant systems are mostly not compensated. This is clearly underlined by our results: annual net Si outputs were always considerably higher at plots without straw recycling compared to plots with straw recycling. That implies a successful compensation of harvest-related Si exports by crop straw recycling (see subsection 4.4 for a more detailed discussion of this aspect) (Fig. 9).

(Guntzer et al., 2012) analyzed archived soil (selected samples from the years 1881–2000) and plant (selected samples from the years 1872–2000) samples of the long-term “Broadbalk winter wheat

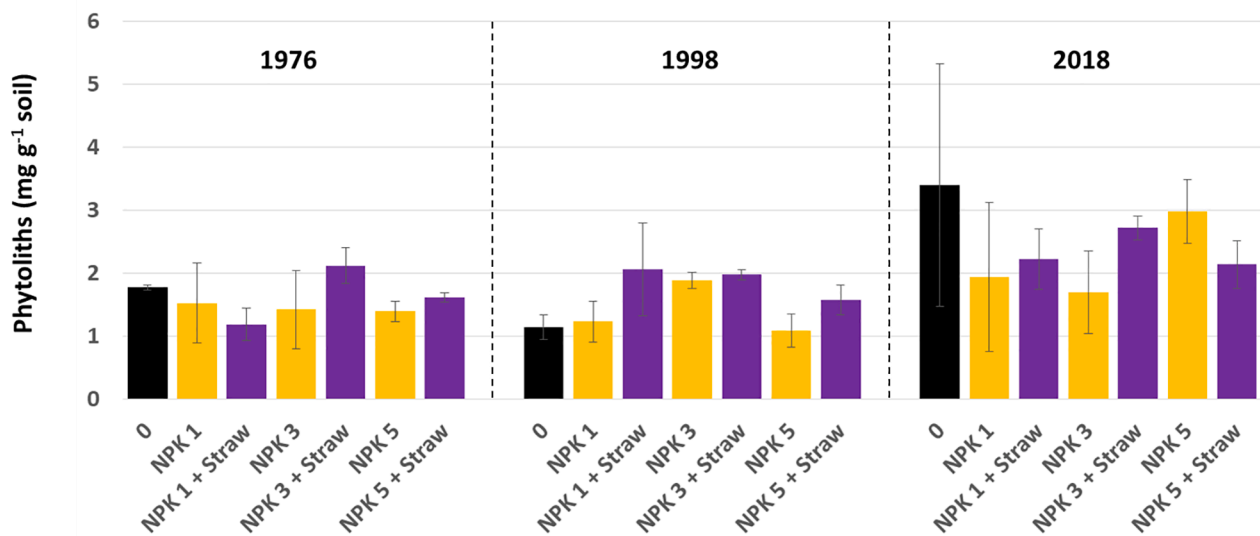


Fig. 7. Phytolith concentrations (means \pm SD, $n = 2$ for soil samples from 1976 and 1998 each, $n = 4$ for soil samples from 2018) in soils of the different treatments at the LTFE V140 in the years 1976, 1998, and 2018. Black, orange, and purple bars represent control plots (0), mineral fertilizer plots (NPK), and mineral fertilizer plots that were additionally supplied with crop straw (NPK + Straw), respectively. 1 = low NPK fertilization rate, 3 = medium NPK fertilization rate, 5 = high NPK fertilization rate.

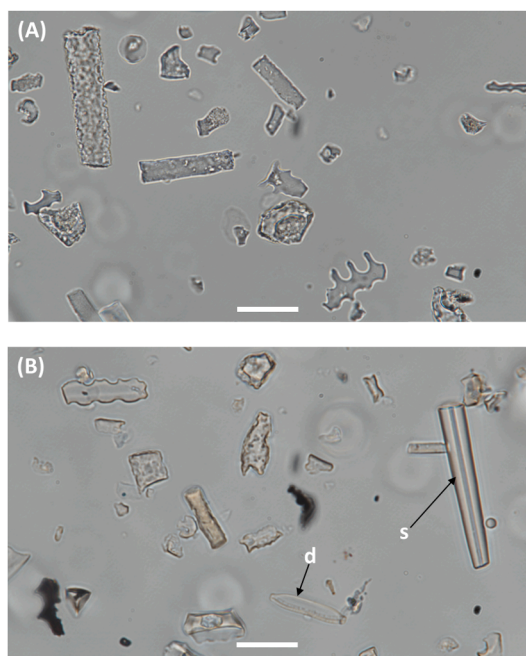


Fig. 8. Micrographs (light microscopy, magnification 400x) of phytoliths found in soils of V140. Scale bars in (A) and (B) are 25 μm . d = diatom frustule, s = sponge spicule fragment.

experiment" at Rothamsted Research (Harpenden, UK). They found that the long-term removal of wheat straw considerably decreased amorphous silica pools in soils. However, a distinct relationship between this decrease and a corresponding decrease in Si concentrations of crop straw was not observable. In fact, Guntzer and colleagues (2012) found such a relationship only for the samples taken before 1944. After this year Si concentrations in straw tended to increase. From their results (Guntzer et al., 2012) concluded increased soil pH due to periodic liming to increase amorphous silica (i.e., phytoliths) dissolution, and thus to represent the main driver of increased Si uptake by the cultivated wheat plants. This is underpinned by a recent study of (Caubet et al., 2020),

who ascribed an increase of calcium chloride extractable Si in cultivated soils (perennial and annual crops) in France to liming. However, it has to be kept in mind that Si availability in (agricultural) soils is determined by a complex interaction of factors, and thus liming effects on Si availability follow no general rule, i.e., there are studies showing negative and other studies reporting positive correlations between pH and Si availability (see the review of (Haynes, 2019)). In this context, the source (lithogenic/pedogenic, biogenic, adsorbed, or fertilizer Si) of potentially available Si and the evaluation period (weeks, years, or decades) of pH effects are key factors for soil pH-Si availability relationships.

4.2. Effects of NPK fertilization rates on anthropogenic desilication

Our results show that NPK fertilization rates control plant biomass, and thus harvest-related Si exports. Cumulative sums of, e.g., maximal Si exports increased from about 10 t ha⁻¹ DM (1963–2018) to 14 and 15 t ha⁻¹ DM under low (NPK1), medium (NPK3), and high (NPK5) fertilization rates, respectively. The corresponding potential savings on Si exports by crop straw recycling were relatively high and reached about 6 t ha⁻¹ DM (1963–2018) for low (NPK1) and medium (NPK3) fertilization rates. Under high fertilization rates (NPK5) Δ_{net} Si output was about 7 t ha⁻¹ DM. Due to the fact that values of Δ_{net} Si output increase with time, crop straw recycling becomes the more effective the longer straw recycling is applied. Our study shows that about 43–60% of Si exports can be saved by crop straw recycling in the long term. This is also reflected by increasing phytolith concentrations in soils with time. Said phytoliths were classified as elongate, polylobate, short, and cross morphotypes, which are typical for grass phytoliths (Madella et al., 2005; Neumann et al., 2019), and thus directly can be assigned to the crops cultured at V140. Higher plant biomass generally leads to higher Si exports, which in turn lead to decreasing plant available Si concentrations in soils with time. NPK + Straw plots often showed higher biomass compared to NPK plots indicating synergistic effects of NPK and Si supply. This is in line with studies on, e.g., rice production, where Si fertilization has been found to increase yields by enhancing N fertilization efficacy (Savant et al., 1996). Similarly, (Thomsen and Christensen, 2004) found that long-term (1981–1999) incorporation of barley straw increased yields and total N uptake in winter wheat. These findings are corroborated by pot experiments with winter wheat, which indicated an increase in aboveground plant biomass and nitrogen use

Table 2

Relationships (Spearman's rank correlation) between selected soil properties and phytoliths. Significant correlations are marked with asterisks (* indicates $p < 0.05$, ** indicates $p < 0.01$).

		Soil pH	N _t (g kg ⁻¹)	C _t (g kg ⁻¹)	P _{DL} (mg kg ⁻¹)	K _{DL} (mg kg ⁻¹)	Phytoliths (mg g ⁻¹)
N _t (g kg ⁻¹)	<i>r_s</i>	-0.167	1.000				
	<i>p</i>	0.069					
	<i>n</i>	119	133				
C _t (g kg ⁻¹)	<i>r_s</i>	-0.060	0.682**	1.000			
	<i>p</i>	0.516	0.000				
	<i>n</i>	119	133	140			
P _{DL} (mg kg ⁻¹)	<i>r_s</i>	0.663**	0.008	0.137	1.000		
	<i>p</i>	0.000	0.929	0.127			
	<i>n</i>	119	126	126	127		
K _{DL} (mg kg ⁻¹)	<i>r_s</i>	0.047	0.282**	0.046	0.302**	1.000	
	<i>p</i>	0.609	0.001	0.611	0.001		
	<i>n</i>	119	126	126	127	127	
Phytoliths (mg g ⁻¹)	<i>r_s</i>	0.526*	0.556**	0.140	0.270	0.242	1.000
	<i>p</i>	0.014	0.009	0.544	0.236	0.290	
	<i>n</i>	21	21	21	21	21	21
Plant available Si (mg kg ⁻¹)	<i>r_s</i>	0.899**	0.432	-0.139	0.431	0.271	0.599**
	<i>p</i>	0.000	0.050	0.548	0.051	0.235	0.004
	<i>n</i>	21	21	21	21	21	21

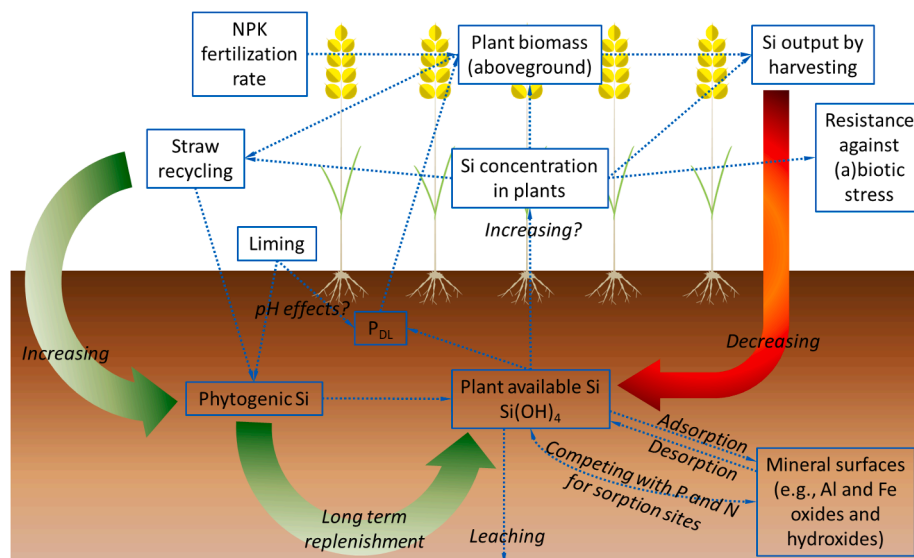


Fig. 9. Long-term anthropogenic desilication (red arrow) of agricultural soil-plant systems in the temperate zone and its prevention by crop straw recycling (green arrows).

efficiency driven by enhanced Si supply (Neu et al., 2017).

(Klotzbücher et al., 2020) analyzed the Si mobility in soils depending on sorption competition with highly competitive compounds (i.e., dissolved organic matter and phosphates). From their results they concluded a weaker binding strength of Si (as compared to P and dissolved organic matter) to Fe oxides leading to Si mobilization by the input of P and dissolved organic matter. It should be kept in mind that the laboratory experiments of (Klotzbücher et al., 2020) were performed under acidic conditions (pH 4) resulting in a potentially decreased binding strength of Si due to slowed polymerization of H_4SiO_4 (cf. (Schaller et al., 2020)). According to these findings it can be assumed that NPK fertilization as well as organic matter input by crop straw recycling should increase Si mobilization in soils resulting in potentially higher Si accumulation in plant biomass. (Li et al., 2020), for example, found combined Si-P fertilizers to increase concentrations of plant available Si in soils leading to higher biomass and phytolith concentrations of rice plants. However, in our study we found (i) no significant differences between the different experimental plots regarding plant available Si in soils of 2018 and (ii) Si concentrations in plant material (i.e., straw and husk) of winter wheat to be very similar at NPK3, NPK3 + Straw, NPK5,

and NPK5 + Straw plots. Thus we found no evidence for a relationship between plant available Si in soils and corresponding Si uptake by plants driven by higher NPK fertilization rates and potential corresponding Si-P interactions in soils in the long term (see also subsections 4.3 and 4.4). However, due to the fact that we solely analyzed plant materials from 2018 such a relationship might manifest in future studies focusing on long-term Si uptake rates of crops under different NPK fertilization rates. As Si-P interactions in the soil-plant system are driven by complex biogeochemical processes that are still not fully understood (e.g., (Schaller et al., 2019)), further studies are needed to enlighten this aspect.

Generally, the results of (Guntzer et al., 2012) (see subsection 4.1 for details) indicate that Si concentrations in crops tend to increase with increasing Si supply in the long term. In this context, it is of great interest to which degree Si uptake of cultured plants is determined by their phylogenetic position, the mode of Si uptake, and environmental factors like temperature or Si availability (e.g., (Prychid et al., 2004; Hodson et al., 2005; Cooke and Leishman, 2012; Coskun et al., 2018)). Taking into account that (i) Si concentrations in analyzed plant materials (i.e., straw and husk) of winter wheat were very similar and (ii) differences in

plant biomass at NPK3, NPK3 + Straw, NPK5 and NPK5 + Straw plots were negligible in our study (Fig. A6), we reasonably can assume Si exports at medium (NPK3, NPK3 + Straw) and high (NPK5, NPK5 + Straw) fertilization rates to be about the same size. However, as we found an increase of plant available Si in soils with time these Si exports at V140 were not only compensated by straw supply, but stocks of plant available Si were also replenished by straw recycling in the long term. Furthermore, the yield (plant biomass) data of V140 show that a reduction of N fertilization rates of about 69% (N rate of NPK1 vs. N rate of NPK3, which is commonly applied as regulated by the national Fertilizer Ordinance) is possible without considerable biomass losses (Fig. A7). This economy of the need for N fertilizers can be combined with the benefits of crop straw recycling (NPK1 + Straw), i.e., enhancement of C sequestration via straw inputs (cf. (Barkusky et al., 2020)) and prevention of anthropogenic desilication of agricultural soil–plant systems (this study).

4.3. Relationship between Si concentration of wheat and plant available Si in soils

Concentrations of plant available Si in soils of V140 increased with time (1976: 5.1–7.6 mg kg⁻¹, 1998: 5.9–8.4 mg kg⁻¹, and 2018: 8.3–9.9 mg kg⁻¹). While said concentrations in soil samples from 1976 were comparable to plant available Si in topsoils of agricultural sites in the temperate zone (about 5 mg kg⁻¹ in the upper 30 cm, (Kaczorek et al., 2019)), concentrations of plant available Si in soils from 2018 reached values comparable to the low range of plant available Si in soils of undisturbed ecosystems like forests under temperate conditions (e.g., 10–40 mg kg⁻¹, (Cornelis et al., 2011) mg kg⁻¹; (Puppe et al., 2015) mg kg⁻¹; (Kaczorek et al., 2019)). It can be assumed that this increase of plant available Si in soils is also reflected in corresponding Si concentrations of crops (cf. (Guntzer et al., 2012)). However, this assumption has to remain unproven in our study due to the lack of plant samples from 1976 (as well as 1998). Regarding plant samples from 2018 concentrations of plant available Si in soils were not correlated to Si concentrations of wheat parts, i.e., grain, straw, and husk. Such a relationship has been reported in some studies, which considered several study sites with relatively large gradients in plant available Si, conducted in (sub) tropical regions where sugarcane and rice are cultivated. (Miles et al., 2014), for example, analyzed 28 sites located throughout the sugarcane-growing areas of South Africa and found a close correlation between plant available Si in soils (0.01 M CaCl₂ as extractant, range of plant available Si in soils: about 10–95 mg kg⁻¹) and Si concentrations in sugarcane leaves. Regarding rice production (Korndörfer et al., 2001) analyzed 28 field experiments in the Everglades Agriculture Area representing a wide range of available Si in soils. They found plant available Si in these soils (0.5 M acetic acid as extractant, range of plant available Si in soils: about 5–85 mg L⁻¹) to be correlated with Si concentrations in rice straw.

Our results corroborate studies that did not observe (or only partly found) a relationship between plant available Si in soils and Si concentrations in plants. For example, (Klotzbücher et al., 2018) found no relationship between plant available Si in soils (herein concentration of dissolved Si in soil solution) and Si concentrations in rice straw in one (i. e., the drier one) of two analyzed cropping seasons in a field experiment in Southern Vietnam. However, they found such a correlation in the second cropping season, i.e., the wetter one. From their results (Klotzbücher et al., 2018) speculated climatic differences to be responsible for their observation (cf. (de Tombeur et al., 2020)) and concluded field experiments to be inconsistent with results from laboratory studies regarding relationships between plant available Si in soils and Si uptake by plants (e.g., (Gocke et al., 2013; Marxen et al., 2016)). This is underpinned by (Keeping, 2017), who found that the uptake of Si by sugarcane in a shade house pot experiment did neither reflect the concentration of plant available Si in soils nor the Si concentration of used Si sources (calcium silicate slag, fused magnesium (thermo) phosphate,

volcanic rock dust, magnesium silicate, and granular potassium silicate).

In general, the ambiguous results discussed above reveal the complexity of soil–plant Si interactions and as long as we do not better understand the factors that determine plant availability of Si in soils and Si uptake by plants (uptake mechanisms, phylogenetic and environmental factors) these interactions remain arcane. According to (Haynes, 2014) there are three key factors that control plant availability of Si: (i) the Si concentration in soil solution, (ii) the reserve in the solid phase as Si source (e.g., amorphous pedogenic and biogenic silicates, crystalline phyllosilicates, residual Si fertilizers), and (iii) the Si adsorption capacity or retention capability of the soil. As all of these factors are the result of complex biogeochemical interactions, and thus differ from one soil to another, a general understanding of plant availability of Si in different soils and its uptake by plants represents a hard-set challenge especially for soil–plant systems in the temperate zone. This is because (younger) soils in the temperate zone are mostly not highly weathered as it is the case for (sub)tropical (older) soils showing a characteristically low Si availability (Sommer et al., 2006), and thus biogeochemical Si cycling might be characterized by more potential interactions between the various Si pools and fractions in soils of the temperate zone.

Furthermore, inconsistent results of previous studies might not only result from differences in soils but also from the use of different extractants for the determination of plant available Si. (Crusciol et al., 2018) showed that correlations between plant available Si and Si in sugarcane were depending on soil texture and extractant (CaCl₂, deionized water, KCl, Na-acetate buffer at pH 4.0, and acetic acid). In fact, there is no common standard procedure for the evaluation of plant available Si in soils because these procedures have been developed for specific plants in specific climates, i.e., mainly sugarcane and rice in (sub)tropical zones (cf. (Sauer et al., 2006)). What we need now is detailed research on methods for a reliable determination of Si availability in soils of the temperate zone. In this context, a combination of (i) different information on the Si status of soils (e.g., concentration of extractable plant available Si, quantity and quality of solid biogenic and pedogenic Si phases, retention of plant available Si in soils, influence of climate and vegetation) and (ii) laboratory and (long-term) field experiments (e.g., identifying of required concentrations of plant available Si in different soils for an optimal Si supply of specific crops) might be the most promising approach to enlighten the complex interactions in biogeochemical Si cycling.

4.4. Prevention of anthropogenic desilication by crop straw recycling

In our study Si outputs via harvesting did not lead to a decrease of plant available Si in soils. Instead, the reverse is true and we found plant available Si in soils to increase with time (which is also reflected by increasing phytolith concentrations with time). We thus assign this increase directly to straw recycling as our data showed a positive relationship between soil phytoliths (originating mainly from the applied straw) and plant available Si in soils. Moreover, we found only relatively low concentrations of ammonium oxalate-soluble Fe (i.e., Fe mainly from pedogenic amorphous silicates and organic complexes) in the Ap horizon of V140. As these concentrations were always lower than phytolith concentrations, we reasonably assume phytoliths to represent the main source of plant available Si in our study. In this context, it should be kept in mind that the phytoliths extracted from soil samples do not reflect the actual (total) phytolith input by crop straw recycling, because phytolith extraction is limited to a specific fraction of phytoliths (i.e., relatively stable phytoliths > 5 µm) (see discussion in (Kaczorek et al., 2019)). Furthermore, phytoliths are characterized by differences in physicochemical properties (e.g., specific surface areas, dissolution signs, and differences on molecular levels) detectable via, e.g., infrared spectroscopy, confocal laser scanning and scanning electron microscopy (Sommer et al., 2013; Puppe and Leue, 2018; Kaczorek et al., 2019)). However, in our study we focused on harvest-related Si exports, corresponding effects of long-term Si losses on agricultural soil–plant systems,

and potential prevention by straw recycling, which is why we did not perform such detailed, time-consuming spectroscopic and microscopic phytolith analyses.

Surprisingly, the increase of plant available Si in soils was not limited to plots with straw recycling but occurred in all plots, and thus was also observable in control plots and plots without straw recycling. However, only in the plots with medium and high NPK fertilization rates and straw recycling (i.e., NPK3 + Straw and NPK5 + Straw) the observed increase in plant available Si in soils was statistically significant. We ascribe these observations to the fact that (i) all plots of V140 were regularly limed potentially leading to increased dissolution of amorphous silica in these plots (cf. (Guntzer et al., 2012)) and (ii) crop straw recycling directly increased plant available Si in NPK + Straw plots. From our results we conclude that straw recycling does not only prevent anthropogenic desilication, but also replenishes plant available Si in soils with time (Fig. 9).

In general, our results are corroborated by the findings of (Yang et al., 2020), who analyzed the long-term (36 years) influence of phytolith-rich straw recycling (three treatments: (i) NPK only, (ii) NPK + low straw rate (1/3 of total N fertilization), (iii) NPK + high straw rate (2/3 of total N fertilization)) and groundwater table management on labile Si soil fractions (determined by sequential chemical extraction using (i) CaCl_2 , (ii) acetic acid, (iii) H_2O_2 , (iv) NH_4 -oxalate, and (v) Na_2CO_3) and Si uptake by rice in subtropical China. These authors found total labile Si concentrations to increase significantly with increasing phytolith-rich straw application, whereas the largest Si fraction in soils was represented by Na_2CO_3 -Si, i.e., amorphous Si assumed to originate mainly from plants (phytoliths). While (Yang et al., 2020) found no significant differences between the three treatments (NPK, NPK + low straw rate, NPK + high straw rate) regarding plant available Si in soils (extracted via CaCl_2), Si concentrations in cultured rice plants increased significantly with increasing straw recycling.

The results of (Yang et al., 2020) and our results on hand clearly indicate the potential of straw recycling to compensate harvest-related Si losses from agricultural soil-plant systems, and thus to mitigate anthropogenic desilication in these systems. If we assume a linear increase of plant available Si in the analyzed soils, concentrations of plant available Si in NPK + Straw plots would double within 60–87 years reaching values of about 10–13 mg Si kg^{-1} soil between 2036 and 2063 (Fig. A8), thus resulting in plant available Si stocks of the order of the ones in natural ecosystems, e.g., forests, in the temperate zone (Puppe et al., 2015). Consequently, straw recycling might be the most promising strategy for the replenishment of plant available Si stocks in the temperate zone that were exhausted by industrial agriculture in the 19th (Second Agricultural Revolution, e.g., (Thompson, 1968)) and 20th century (Third Agricultural Revolution, e.g., (Pellegrini and Fernández, 2018)).

Moreover, straw recycling might be also a promising way to enhance the water holding capacity of agricultural soils (Schaller et al., 2020), which is especially urgent against the background of increased drought events in some regions of the world due to climate change (Liu et al., 2018; Hari et al., 2020). Regular (annual) long-term incorporation of crop straw has also been found to be effective in soil erosion alleviation (Peng et al., 2016) and the enhancement of C sequestration (Song et al., 2016; Li et al., 2018; Barkusky et al., 2020; Berhane et al., 2020). In addition, our data indicate that straw recycling might have positive effects on mobilization and utilization of plant available P in soils as Si and P compete for equivalent adsorption sites in soils. This is in accordance to the findings of studies on Si-P interactions in (agricultural) soils (e.g., (Ma and Takahashi, 1990; Schaller et al., 2020)). Straw-derived P released by microbial decomposition and P occluded in phytoliths released by phytolith dissolution might also play a role in this context (Trinh et al., 2017; Yang et al., 2019). As plant available Si concentrations increased relatively slow in our study (doubling within 60–87 years) we reasonably assume P losses due to a potential over-mobilization and consequential leaching of phosphates to be low. Our

results do not show a significant relationship between the concentrations of plant available Si and K in soils. Si fertilization might have positive effects on the K uptake by crops. However, corresponding results published so far are ambiguous (see, e.g., (Puppe and Sommer, 2018 and references therein)), and thus further research is needed to enlighten Si-K interactions in soils and plants.

Finally, straw incorporation might be a potential alternative to open burning of straw in the field, which is still a common practice in many countries worldwide, although it has been widely criticized due to health (smog) and climate change (emissions of CO_2) concerns (e.g., (Gustafsson et al., 2009)). However, the ban of open straw burning has been discussed controversially (e.g., (Nguyen, 2020)). Potential risks of crop straw incorporation include greenhouse gas emissions (microbial decomposition) and aggravation of plant pest infestation (Li et al., 2018). Future studies should focus on unraveling the mechanisms behind these aspects in different soil-plant systems to (i) find and evaluate solution strategies (e.g., implementation of innovative soil tillage practices like ditch-buried straw return, (Yang et al., 2019)) to mitigate potential negative effects of crop straw recycling and (ii) establish regulations for purposeful crop straw recycling rates, and thus for sustainable, low fertilization agriculture.

4.5. Open questions

In order to put the field regarding the potential of straw recycling for sustainable crop production forward the following key questions have to be resolved in future studies:

(i) How can we reliably test agricultural soils on the need for Si supply?

We urgently need standardized tests for quantification of plant available Si in agricultural soils. Due to the fact that several tests are used by researchers worldwide (reviewed by (Sauer et al., 2006)), it is difficult to determine reliable lower limits for plant available Si in different soils, and thus for a need for Si supply (see the review of (Schaller et al., 2021)).

(ii) How much Si has to be accumulated in different plants at the minimum to obtain stress resistance?

Although we know that Si accumulation in plants increases their resistance against abiotic and biotic stress, we do not know how much Si actually has to be accumulated to obtain this resistance. For sugarcane and rice production critical tissue Si values of 0.5–0.7% and 3–6% are stated in literature, respectively (Haynes, 2017 and references therein). However, there are no critical tissue Si values for other Si accumulating crops in literature to the best of our knowledge. Thus we urgently need field and laboratory experiments to examine said Si values for different crops. Only with this knowledge a targeted enhancement of crop resistance via Si supply will be possible and corresponding reductions in the use of pesticides and fertilizers can be optimized.

(iii) Which crop straw recycling rates are needed for different crops?

Only if we know how much Si in a given soil is plant available (see question (i) above) and how much Si has to be accumulated by the cultured crop to become stress resistant (see question (ii) above), we can define corresponding crop straw recycling rates. However, these rates will be not only dependent on soil Si availability and the Si need of the cultured crop, but also on, e.g., soil properties and microbiomes, agricultural practice (e.g., liming), climate conditions, and specific national regulations. Furthermore, differences in the release of Si from crop straw driven by, e.g., phytogenic Si concentrations of straw and straw-soil interactions have to be considered as well (Ma and Takahashi, 1989, 1991; Wickramasinghe and Rowell, 2006). Thus, much more work is required to (i) understand the complex interactions of the factors above for biogeochemical Si cycling in agricultural soil-plant systems and (ii) implement crop straw recycling in existing farming systems.

5. Conclusions

Our results show that crop straw recycling prevents anthropogenic desilication and replenishes plant available Si stocks of agricultural soil–plant systems in the temperate zone. Plant available Si in agricultural soils would reach levels of plant available Si known from natural ecosystems within 60–87 years, if we assume a linear increase. Furthermore, our results indicate that yields at low (NPK1) and medium (NPK3) fertilization plots are statistically indistinguishable, and thus a reduction of N fertilization rates of about 69% (N rate of NPK1 vs. N rate of NPK3) is possible. This economy of the need for N fertilizers could be combined with the benefits of crop straw recycling (NPK1 + Straw), i.e., enhancement of C sequestration via straw inputs and prevention of anthropogenic desilication of agricultural soil–plant systems. Our study reveals that about 43–60% of Si exports can be saved by crop straw recycling in the long term. Si supply by crop straw recycling has the potential to act as a key management practice in sustainable, low fertilization agriculture in the future. In this context, the ultimate goal should be the restoration of natural Si recycling processes in agricultural ecosystems to the extent deemed possible.

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.

Acknowledgements

First of all many thanks to Christian Buhtz and René Ende (working group ‘Si Biogeochemistry’, ZALF) for their excellent laboratory work. Further, we would like to thank Kristina Holz (head of the Central Laboratory, ZALF) and her team, especially Ellen Janiszewski, for ICP-OES analyses. We thank Sven Äge Schnabel (Experimental Station, ZALF) for his support of our sampling campaign. Samples of winter wheat (2018) were kindly provided by the Experimental Station of ZALF. DP was funded by the Deutsche Forschungsgemeinschaft (DFG) under grant PU 626/2-1 (*Biogenic Silicon in Agricultural Landscapes (BiSIAL) – Quantification, Qualitative Characterization, and Importance for Si Balances of Agricultural Biogeosystems*). Last but not least many thanks to two anonymous reviewers, whose insightful comments on our manuscript considerably improved its quality.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2021.115187>.

References

- Amundson, R., Berhe, A.A., Hopmans, J.W., Olson, C., Sztein, A.E., Sparks, D.L., 2015. Soil and human security in the 21st century. *Science* 348, 1261071.
- Barkusky, D., 2009. Müncheberger Nährstoffsteigerungsversuch, V140. Ministerium für Ländliche Entwicklung, Umwelt und Verbraucherschutz, Landesamt für Verbraucherschutz, Landwirtschaft und Flurneuordnung (ed.): Dauerfeldversuche in Brandenburg und Berlin-Beiträge für eine nachhaltige landwirtschaftliche Bodenbenutzung. MLUL, Brandenburg, Germany, 103–109.
- Barkusky, D., Joschko, M., Reinhold, J., 2020. C-Sequestrierung – Was kann die Landwirtschaft leisten? Dauerfeldversuche sind unverzichtbar. *LOP* 06 (2020), 14–23.
- Berhane, M., Xu, M., Liang, Z., Shi, J., Wei, G., Tian, X., 2020. Effects of long-term straw return on soil organic carbon storage and sequestration rate in North China upland crops: A meta-analysis. *Glob. Change Biol.* 26, 2686–2701.
- Buján, E., 2013. Elemental composition of phytoliths in modern plants (Ericaceae). *Quat. Int.* 287, 114–120.
- Carey, J.C., Fulweiler, R.W., 2016. Human appropriation of biogenic silicon - the increasing role of agriculture. *Funct. Ecol.* 30, 1331–1339.
- Caubet, M., Cornu, S., Saby, N.P.A., Meunier, J.D., 2020. Agriculture increases the bioavailability of silicon, a beneficial element for crop, in temperate soils. *Sci. Rep.* 10, 1–11.
- Cooke, J., Leishman, M.R., 2012. Tradeoffs between foliar silicon and carbon-based defences: evidence from vegetation communities of contrasting soil types. *Oikos* 121, 2052–2060.
- Cornelis, J.T., Titeux, H., Ranger, J., Delvaux, B., 2011. Identification and distribution of the readily soluble silicon pool in a temperate forest soil below three distinct tree species. *Plant Soil* 342, 369–378.
- Coskun, D., Deshmukh, R., Sonah, H., Menzies, J.G., Reynolds, O., Ma, J.F., Kronzucker, H.J., Bélanger, R.R., 2018. The controversies of silicon's role in plant biology. *New Phytol.* 221, 67–85.
- Crusciol, C.A.C., De Arruda, D.P., Fernandes, A.M., Antonangelo, J.A., Alleoni, L.R.F., Do Nascimento, C.A.C., Rossato, O.B., McCray, J.M., 2018. Methods and extractants to evaluate silicon availability for sugarcane. *Sci. Rep.* 8, 1–14.
- Datnoff, L.E., Snyder, G.H., Korndörfer, G.H. (Eds.), 2001. *Silicon in Agriculture*, vol. 8. Elsevier, Amsterdam, The Netherlands.
- Debreczeni, K., Körschens, M., 2003. Long-term field experiments of the world. *Arch. Agron. Soil Sci.* 49, 465–483.
- de Lima Rodrigues, L., Daroub, S.H., Rice, R.W., Snyder, G.H., 2003. Comparison of three soil test methods for estimating plant-available silicon. *Commun. Soil Sci. Plant Anal.* 34, 2059–2071.
- de Tombeur, F., Vander Linden, C., Cornélis, J.T., Godin, B., Compère, P., Delvaux, B., 2020. Soil and climate affect foliar silicification patterns and silica-cellulose balance in sugarcane (*Saccharum officinarum*). *Plant Soil* 452, 529–546.
- Desplanques, V., Cary, L., Mouret, J.C., Trolard, F., Bourrié, G., Grauby, O., Meunier, J.-D., 2006. Silicon transfers in a rice field in Camargue (France). *J. Geochem. Explor.* 88, 190–193.
- DIN ISO 1039: Bodenbeschaffenheit: Bestimmung des pH-Wertes, Deutsches Institut für Normung, Beuth, Berlin, 1997.
- Ehrlich, H., Demadis, K.D., Pokrovsky, O.S., Koutsoukos, P.G., 2010. Modern views on desilicification: biosilica and abiotic silica dissolution in natural and artificial environments. *Chem. Rev.* 110, 4656–4689.
- Epstein, E., 1999. Silicon. *Annu. Rev. Plant Biol.* 50, 641–664.
- Commission, E., 2019. A European Green Deal: striving to be the first climate-neutral continent. accessed May 25th, 2020. https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en.
- Exley, C., 2015. A possible mechanism of biological silicification in plants. *Front. Plant Sci.* 6, 853.
- Exley, C., Guerriero, G., Lopez, X., 2020. How is silicic acid transported in plants? *Silicon* 12, 2641–2645.
- Gocke, M., Liang, W., Sommer, M., Kuzyakov, Y., 2013. Silicon uptake by wheat: effects of Si pools and pH. *J. Plant Nutr. Soil Sci.* 176, 551–560.
- Guntzer, F., Keller, C., Poulton, P.R., McGrath, S.P., Meunier, J.-D., 2012. Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk, Rothamsted. *Plant Soil* 352, 173–184.
- Gustafsson, Ö., Kruså, M., Zencak, Z., Sheesley, R.J., Granat, L., Engström, E., Praveen, P.S., Rao, P.S.P., Leck, C., Rodhe, H., 2009. Brown clouds over South Asia: biomass or fossil fuel combustion? *Science* 323, 495–498.
- Hari, V., Rakovec, O., Markonis, Y., Hanel, M., Kumar, R., 2020. Increased future occurrences of the exceptional 2018–2019 Central European drought under global warming. *Sci. Rep.* 10, 1–10.
- Haynes, R.J., 2014. A contemporary overview of silicon availability in agricultural soils. *J. Plant Nutr. Soil Sci.* 177, 831–844.
- Haynes, R.J., 2017. The nature of biogenic Si and its potential role in Si supply in agricultural soils. *Agric. Ecosyst. Environ.* 245, 100–111.
- Haynes, R.J., 2017. Significance and role of Si in crop production. *Adv. Agron.* 146, 83–166.
- Haynes, R.J., 2019. What effect does liming have on silicon availability in agricultural soils? *Geoderma* 337, 375–383.
- Haysom, M.B.C., Chapman, L.S., 1975. Some aspects of the calcium silicate trials at Mackay. *Proc. Aust. Sugar Cane Technol.* 42, 117–122.
- Hodson, M.J., 2016. The development of phytoliths in plants and its influence on their chemistry and isotopic composition. Implications for palaeoecology and archaeology. *J. Archaeol. Sci.* 68, 62–69.
- Hodson, M.J., White, P.J., Mead, A., Broadley, M.R., 2005. Phylogenetic variation in the silicon composition of plants. *Ann. Bot.* 96, 1027–1046.
- IUSS Working Group WRB, 2015. World reference base for soil resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. *World Soil Resources Reports No. 106*. FAO, Rome.
- Kaczorek, D., Puppe, D., Busse, J., Sommer, M., 2019. Effects of phytolith distribution and characteristics on extractable silicon fractions in soils under different vegetation – An exploratory study on loess. *Geoderma* 356, 113917.
- Kamenik, J., Mizera, J., Randa, Z., 2013. Chemical composition of plant silica phytoliths. *Environ. Chem. Lett.* 11, 189–195.
- Keeping, M.G., 2017. Uptake of silicon by sugarcane from applied sources may not reflect plant-available soil silicon and total silicon content of sources. *Front. Plant Sci.* 8, 760.
- Keller, C., Guntzer, F., Barboni, D., Labreuche, J., Meunier, J.D., 2012. Impact of agriculture on the Si biogeochemical cycle: input from phytolith studies. *Compt. Rendus Geosci.* 344, 739–746.
- Klotzbücher, A., Klotzbücher, T., Jahn, R., Van Chien, H., Hinrichs, M., Sann, C., Vetterlein, D., 2018. Effects of Si fertilization on Si in soil solution, Si uptake by rice, and resistance of rice to biotic stresses in Southern Vietnam. *Paddy Water Environ.* 16, 243–252.
- Klotzbücher, T., Treptow, C., Kaiser, K., Klotzbücher, A., Mikutta, R., 2020. Sorption competition with natural organic matter as mechanism controlling silicon mobility in soil. *Sci. Rep.* 10, 1–11.

- Korndörfer, G.H., Snyder, G.H., Ulloa, M., Powell, G., Datnoff, L.E., 2001. Calibration of soil and plant silicon analysis for rice production. *J. Plant Nutr.* 24, 1071–1084.
- Li, Z., Delvaux, B., 2019. Phytolith-rich biochar: A potential Si fertilizer in desiccated soils. *GCB Bioenergy* 11, 1264–1282.
- Li, H., Dai, M., Dai, S., Dong, X., 2018. Current status and environment impact of direct straw return in China's cropland – A review. *Ecotoxicol. Environ. Saf.* 159, 293–300.
- Li, Z., Unzué-Belmonte, D., Cornelis, J.T., Vander Linden, C., Struyf, E., Ronsse, F., Delvaux, B., 2019. Effects of phytolith-rich rice-straw biochar, soil buffering capacity and pH on silicon bioavailability. *Plant Soil* 438, 187–203.
- Li, Z., Cornelis, J.T., Vander Linden, C., Van Ranst, E., Delvaux, B., 2020. Neoformed aluminosilicate and phytogenic silica are competitive sinks in the silicon soil–plant cycle. *Geoderma* 368, 114308.
- Li, Z., Guo, F., Cornelis, J.T., Song, Z., Wang, X., Delvaux, B., 2020. Combined silicon-phosphorus fertilization affects the biomass and phytolith stock of rice plants. *Frontiers. Plant Sci.* 11.
- Liu, W., Sun, F., Lim, W.H., Zhang, J., Wang, H., Shioyama, H., Zhang, Y., 2018. Global drought and severe drought-affected populations in 1.5 and 2 °C warmer worlds. *Earth System. Dynamics* 9, 267.
- Ma, J.F., 2004. Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. *Soil Sci. Plant Nutr.* 50, 11–18.
- Ma, J., Takahashi, E., 1989. Release of silicon from rice straw under flooded conditions. *Soil Sci. Plant Nutr.* 35, 663–667.
- Ma, J., Takahashi, E., 1990. Effect of silicon on the growth and phosphorus uptake of rice. *Plant Soil* 126, 115–119.
- Ma, J., Takahashi, E., 1991. Availability of rice straw Si to rice plants. *Soil Sci. Plant Nutr.* 37, 111–116.
- Ma, J.F., Takahashi, E., 2002. Soil, Fertilizer, and Plant Silicon Research in Japan. Elsevier, Amsterdam, The Netherlands.
- Madella, M., Alexandre, A., Ball, T., 2005. International code for phytolith nomenclature 1.0. *Ann. Bot.* 96, 253–260.
- Marxen, A., Klotzbücher, T., Jahn, R., Kaiser, K., Nguyen, V.S., Schmidt, A., Schädler, M., Vetterlein, D., 2016. Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system. *Plant Soil* 398, 153–163.
- Meena, V.D., Dotaniya, M.L., Coumar, V., Rajendiran, S., Kundu, S., Rao, A.S., 2014. A case for silicon fertilization to improve crop yields in tropical soils. *Proc. Natl. Acad. Sci. India B Biol. Sci.* 84, 505–518.
- Meunier, J.-D., Guntzer, F., Kirman, S., Keller, C., 2008. Terrestrial plant-Si and environmental changes. *Mineral. Mag.* 72, 263–267.
- Miles, N., Manson, A.D., Rhodes, R., van Antwerpen, R., Weigel, A., 2014. Extractable silicon in soils of the South African sugar industry and relationships with crop uptake. *Commun. Soil Sci. Plant Anal.* 45, 2949–2958.
- Neu, S., Schaller, J., Dudel, E.G., 2017. Silicon availability modifies nutrient use efficiency and content, C: N: P stoichiometry, and productivity of winter wheat (*Triticum aestivum* L.). *Sci. Rep.* 7, 1–8.
- Neumann, K., Stromberg, C.A., Ball, T., Albert, R.M., Vrydaghs, L., Cummings, L.S., 2019. International code for phytolith nomenclature (ICPN) 2.0. *Ann. Bot.* 124, 189–199.
- Nguyen, M.N., 2020. Worldwide bans of rice straw burning could increase human arsenic exposure. *Environ. Sci. Technol.* 54, 3728–3729.
- Nguyen, A.T., Nguyen, M.N., 2019. Straw phytolith for less hazardous open burning of paddy straw. *Sci. Rep.* 9, 1–6.
- Pellegrini, P., Fernández, R.J., 2018. Crop intensification, land use, and on-farm energy-use efficiency during the worldwide spread of the green revolution. *Proc. Natl. Acad. Sci.* 115, 2335–2340.
- Peng, X., Zhu, Q.H., Xie, Z.B., Darboux, F., Holden, N.M., 2016. The impact of manure, straw and biochar amendments on aggregation and erosion in a hillslope Ultisol. *Catena* 138, 30–37.
- Perry, C.C., Keeling-Tucker, T., 2000. Biosilicification: the role of the organic matrix in structure control. *J. Biol. Inorg. Chem.* 5, 537–550.
- Piperno, D.R., 2006. *Phytoliths: A Comprehensive Guide for Archaeologists and Paleoecologists*. Rowman and Littlefield, New York, NY, USA.
- Prychid, C.J., Rudall, P.J., Gregory, M., 2004. Systematics and biology of silica bodies in monocotyledons. *Bot. Rev.* 69, 377–440.
- Puppe, D., 2020. Review on protozoic silica and its role in silicon cycling. *Geoderma* 365, 114224.
- Puppe, D., Leue, M., 2018. Physicochemical surface properties of different biogenic silicon structures: Results from spectroscopic and microscopic analyses of protistic and phytogenic silica. *Geoderma* 330, 212–220.
- Puppe, D., Sommer, M., 2018. Experiments, uptake mechanisms, and functioning of silicon foliar fertilization — A review focusing on maize, rice, and wheat. *Adv. Agron.* 152, 1–49.
- Puppe, D., Ehrmann, O., Kaczorek, D., Wanner, M., Sommer, M., 2015. The protozoic Si pool in temperate forest ecosystems: a quantification, abiotic controls and interactions with earthworms. *Geoderma* 243–244, 196–204.
- Puppe, D., Höhn, A., Kaczorek, D., Wanner, M., Wehrhan, M., Sommer, M., 2017. How big is the influence of biogenic silicon pools on short-term changes in water-soluble silicon in soils? Implications from a study of a 10-year-old soil-plant system. *Biogeosciences* 14, 5239–5252.
- Reithmaier, G.M.S., Knorr, K.H., Arnhold, S., Planer-Friedrich, B., Schaller, J., 2017. Enhanced silicon availability leads to increased methane production, nutrient and toxicant mobility in peatlands. *Sci. Rep.* 7, 1–8.
- Sandén, T., Spiegel, H., Stüger, H.-P., Schlatter, N., Haslmayr, H.-P., Zavattaro, L., Grignani, C., Bechini, L., D'Hose, T., Molendijk, L., Pecio, A., Jarosz, Z., Guzmán, G., Vanderlinden, K., Giráldez, J.V., Mallast, J., ten Berge, H., 2018. European long-term field experiments: knowledge gained about alternative management practices. *Soil Use Manag.* 34, 167–176.
- Sangster, A. G., Hodson, M. J., & Tubb, H. J., 2001. Silicon deposition in higher plants. In: *Studies in Plant Science*, Vol. 8, pp. 85–113. Elsevier.
- Savant, N.K., Snyder, G.H., Datnoff, L.E., 1996. Silicon management and sustainable rice production. *Adv. Agron.* 58, 151–199.
- Savant, N.K., Korndörfer, G.H., Datnoff, L.E., Snyder, G.H., 1999. Silicon nutrition and sugarcane production: a review. *J. Plant Nutr.* 22, 1853–1903.
- Sauer, D., Saccone, L., Conley, D.J., Herrmann, L., Sommer, M., 2006. Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry* 80, 89–108.
- Schaller, J., Faucher, S., Joss, H., Obst, M., Goeckede, M., Planer-Friedrich, B., Pfeiffer, S., Gilfedder, B., Elberling, B., 2019. Silicon increases the phosphorus availability of Arctic soils. *Sci. Rep.* 9, 449.
- Schaller, J., Frei, S., Rohn, L., Gilfedder, B.S., 2020. Amorphous Silica Controls Water Storage Capacity and Phosphorus Mobility in Soils. *Front. Environ. Sci.* 8, 94.
- Schaller, J., Cramer, A., Carminati, A., Zarebanadkouki, M., 2020. Biogenic amorphous silica as main driver for plant available water in soils. *Sci. Rep.* 10, 1–7.
- Schaller, J., Puppe, D., Kaczorek, D., Ellerbrock, R., Sommer, M., 2021. Silicon cycling in soils revisited. *Plants* 10, 295.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes — a review. *J. Plant Nutr. Soil Sci.* 169, 310–329.
- Sommer, M., Jochheim, H., Höhn, A., Breuer, J., Zagorski, Z., Busse, J., Barkusky, D., Meier, K., Puppe, D., Wanner, M., Kaczorek, D., 2013. Si cycling in a forest biogeosystem — the importance of transient state biogenic Si pools. *Biogeosciences* 10, 4991–5007.
- Song, Z., McGrouther, K., Wang, H., 2016. Occurrence, turnover and carbon sequestration potential of phytoliths in terrestrial ecosystems. *Earth Sci. Rev.* 158, 19–30.
- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., Conley, D. J., Batelaan, O., Frot, E., Clymans, W., Vandevenne, F., Lancelot, C., Goos, P., Meire, P., 2010. Historical land use change has lowered terrestrial silica mobilization. *Nat. Commun.* 1, 129.
- Thompson, F.M.L., 1968. The second agricultural revolution, 1815–1880. *Econ. History Rev.* 21, 62–77.
- Thomsen, I.K., Christensen, B.T., 2004. Yields of wheat and soil carbon and nitrogen contents following long-term incorporation of barley straw and ryegrass catch crops. *Soil Use Manag.* 20, 432–438.
- Trinh, T.K., Nguyen, T.T., Nguyen, T.N., Wu, T.Y., Meharg, A.A., Nguyen, M.N., 2017. Characterization and dissolution properties of phytolith occluded phosphorus in rice straw. *Soil Tillage Res.* 171, 19–24.
- Tubana, B.S., Babu, T., Datnoff, L.E., 2016. A review of silicon in soils and plants and its role in US agriculture: history and future perspectives. *Soil Sci.* 181 (9/10), 393–411.
- Vandevenne, F., Struyf, E., Clymans, W., Meire, P., 2012. Agricultural silica harvest: have humans created a new loop in the global silica cycle? *Front. Ecol. Environ.* 10, 243–248.
- Vandevenne, F.I., Delvaux, C., Hughes, H.J., André, L., Ronchi, B., Clymans, W., Barao, L., Govers, G., Meire, P., Struyf, E., 2015a. Landscape cultivation alters d30Si signature in terrestrial ecosystems. *Sci. Rep.* 5, 7732.
- Vandevenne, F.I., Barao, L., Meire, P., Struyf, E., Ronchi, B., Govers, G., Kelly, E.F., 2015b. Silicon pools in human impacted soils of temperate zones. *Global Biogeochem. Cycles* 29. <https://doi.org/10.1002/2014GB005049>.
- Vitousek, P.M., Naylor, R., Crews, T., David, M.B., Drinkwater, L.E., Holland, E., Johnes, P.J., Katzenberger, J., Martinelli, L.A., Matson, P.A., Nizigheba, G., Ojima, D., Palm, C.A., Robertson, G.P., Sanchez, P.A., Townsend, A.R., Zhang, F.S., 2009. Nutrient imbalances in agricultural development. *Science* 324, 1519–1520.
- Wheeler, T., von Braun, J., 2013. Climate change impacts on global food security. *Science* 341, 508–513.
- Wickramasinghe, D.B., Rowell, D.L., 2006. The release of silicon from amorphous silica and rice straw in Sri Lankan soils. *Biol. Fertil. Soils* 42, 231–240.
- Wu, Y., Yang, Y., Wang, H., Wang, C., 2014. The effects of chemical composition and distribution on the preservation of phytolith morphology. *Appl. Phys. A* 114, 503–507.
- Yang, H., Zhou, J., Feng, J., Zhai, S., Chen, W., Liu, J., Bian, X., 2019. Ditch-buried straw return: A novel tillage practice combined with tillage rotation and deep ploughing in rice-wheat rotation systems. *Adv. Agron.* 154, 257–290.
- Yang, X., Song, Z., Qin, Z., Wu, L., Yin, L., Van Zwieten, L., Song, A., Ran, X., Yu, C., Wang, H., 2020. Phytolith-rich straw application and groundwater table management over 36 years affect the soil-plant silicon cycle of a paddy field. *Plant Soil* 454, 343–358.