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Role of phytolith occluded carbon of cereales plants for climate change mitigation

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Abstract: Phytolith-occluded carbon (PhytOC) is highly stable, and constitutes an important source of long-term C storage in agrosystems. This stored carbon is resistant to the processes of oxidation of carbon compounds. In our research phytolith content in barley (Estonia) and oat (Poland) grain and straw was assessed at field trials, with Si as a liquid immune stimulant OPTYSIL and compost fertilisation. We showed that cereals can produce relatively high amounts of phytoliths. PhytOC plays a key role in carbon sequestration, particularly for poor, sandy Polish and Estonian soils. The phytolith content was always higher in straw than in grain regardless of the type of cereals. The phytolith content in oat grains varied from 18.46 to 21.28 $mg \cdot g^{-1}$ DM, and in straw 27.89–38.97 $mg \cdot g^{-1}$ DM. The phytolith content in barley grain ranged from 17.24 to 19.86 $mg \cdot g^{-1}$ DM, and in straw from 22.06 to 49.08 $mg \cdot g^{-1}$ DM. Our results suggest that oat ecosystems can absorb from 14.94 to 41.73 kg e-$CO_2 \cdot ha^{-1}$ and barley absorb from 0.32 to 1.60 kg e-$CO_2 \cdot ha^{-1}$. The accumulation rate of PhytOC can be increased 3-fold in Polish conditions through foliar application of silicon, and 5-fold in Estonian conditions. In parallel, the compost fertilisation increased the phytolith content in cereals.

Keywords: carbon sequestration, cereals, climate change, compost, phytolith occluded carbon, silicon

INTRODUCTION

Climate change is one of the major environmental issues of the modern world. Global CO_2 emissions for 2022 increased by 1.5% relative to 2021, reaching $36.1 \cdot 10^{13}$ kg CO_2 (Liu Z. *et al.* 2023). New strategies for mitigating climate change are sought to reduce the concentration of CO_2 in atmosphere through carbon sink. Plants play a critical role in the global carbon cycle and are key to climate change mitigation and adaptation. Therefore carbon sequestration in terrestrial ecosystems is a stable carbon sink and can play significant role in mitigate long-term climate warming (Song, McGrouther and Wang, 2016; Song *et al.* 2017; Liu L. *et al.* 2023).

Phytoliths are microscopic amorphous silica bodies that form inside tissues of living plants (e.g., cell walls, cell lumina, and intercellular spaces). They are present in most plants (Sharma, Kumar and Kumar, 2019). Each phytolith shows a different structure and is characteristic of a given plant species. This makes them useful in archaeological studies where radiocarbon dating of phytoliths by means of ^{14}C is commonly applied. The phytolith content in plant parts varies from <0.5% DM for the majority of dicotyledons to >15% DM in *Gramineae* (Parr *et al.*, 2010). Differences in phytolith contents between monocotyledonous and dicotyledonous plants primarily result from their ability to take up and accumulate silica (Guo *et al.*, 2015). Even plants of the same species can differ in the phytolith amount produced, depending on the climate and soil conditions, including the silicon (Si) availability in the substrate (Guo *et al.*, 2015; Rehman *et al.*, 2023). During the development of phytoliths in plant tissues, from 0.2 to 5.8% of organic carbon is occluded inside the phytolith forming phytolith-occluded carbon (PhytOC) (Parr and Sullivan, 2005; Parr *et al.*, 2010).

Parr and Sulivan (2011) proposed a detailed methodology for extracting phytoliths from plants. Further research showed that the structure of phytoliths itself is complex, since next to Si, phytoliths additionally contain carbon and nitrogen, as well as other macro- and microelements. Nitrogen content in phytoliths has been previously reported by Jones and Beavers (1963), showing it occurs in low amounts. Hodson *et al.* (2008) confirmed for wheat that the nitrogen content in phytoliths varied from 0.01 to 0.06% N, depending on the plant parts.

After plant decomposition, phytoliths and phytolith-occluded carbon (PhytOC) may accumulate in soils. Due to high durability of phytoliths, PhytOC can persist in the soil over centuries, or even millennia (Parr *et al.*, 2010), depending on the morphological and chemical structure of the respective phytoliths and the environmental conditions (Nguyen *et al.*, 2019).

Based on the example of the C–Si bond (E = 369 kJ·mol^{-1}; binding length – 1.87Å), it can be expected that the bond is durable in the natural environment. This is supported by a number of arguments. The first one is the binding energy. In the case of bond C–Si, the binding energy is higher than for bond C–N. This means that breaking a longer bond requires greater energy. Another argument is the fact that N and Si atoms have different sizes. The larger the atom, the greater the electron number, and as a result the longer the bond. The third argument is the presence of a free electron pair on the nitrogen atom. The free electron pair improves the reactivity of the compound. Higher reactivity of the compound with durable bonds results in a greater ability to form new groups with different binding lengths and energies. The fourth argument is the reference of elements to the scale of electronegativity on the Pauling scale. Chemical bonds are shifted in the particle towards the more electronegative atom. Based on the example of bond C–Si, the bond will be shifted in favour of the carbon atom (electronegativity of C – 2.5, electronegativity of Si – 1.8) (Handke, 2008). A similar dependency concerns bond C–N where the bond is shifted towards the nitrogen atom (electronegativity of C – 2.5, of N – 3.0).

In recent years, increasingly more attention is paid to potential mitigation of climate change by phytoliths. The process involves durable carbon occlusion on phytoliths. The bond of silicon with carbon is highly resistant to the processes of microbiological biodegradation. Therefore, carbon occlusion on phytoliths naturally allows for an increase in the pool of soil organic carbon by cultivation of agricultural crops.

Soil accumulates from 400 to 1000 times more PhytOC than plant biomass. According to Parr and Sullivan (2005), up to approximately 82% of carbon in some soils may be derived from the decomposition of plants from before 2000 years ago. This suggests that PhytOC can play an important role in long-term carbon sequestration and reduction of CO_2 emission in the atmosphere (Song *et al.*, 2016; Song *et al.*, 2022).

Many papers have evidenced that PhytOC shows high potential for sequestration of considerable amounts of atmospheric CO_2. Based on Parr, Sullivan and Quirck (2009), the PhytOC content in sugar cane varies from 0.12 to 0.36 Mg e-CO_2·ha^{-1}·y^{-1}. Rice is also a plant species able to bind substantial carbon amounts on phytoliths. The index of C sequestration by rice cultivars varies from 0.05 to 0.12 Mg e-CO_2·ha^{-1}·y^{-1}. Assuming the carbon accumulation rate in rice phytoliths is 0.12 Mg e-CO_2·ha^{-1}·y^{-1}, the global amount of PhytOC for rice in the studied area in China globally would reach 16.4 Tg e-CO_2 (Prajapati *et al.*, 2016). In global terrestrial biomes, total phytolith carbon sequestration has been estimated to be 156.7 ±91.6 Tg CO_2·y^{-1} (Song *et al.*, 2017).

It is evident that cultivation of crops producing high phytolith amounts can contribute to the mitigation of climate change through the reduction of CO_2 emission to the atmosphere. The content of organic carbon resistant to mineralisation processes in the soil can also be increased, thereby improving the volume of the sorption complex and water capacity of soils. With an increase in Si availability in the substrate, higher accumulation of phytoliths in plant biomass is observed. Therefore, fertilisation with silicon can increase CO_2 sequestration through an increased PhytOC amount in plants (Rehman, Malik and Rashid, 2023).

The presence of phytoliths in cereal plants is well documented (Prabha *et al.*, 2022; Wenjuan *et al.*, 2022; Rehman, Malik and Rashid, 2023). The variability of silica accumulation in oat in the conditions of variable fertilisation, however, has not been investigated so far.

Management of the ecosystems to maximise PhytOC production may further enhance the global phytolith carbon sink and contribute to the mitigation of rapid atmospheric CO_2 increase and climate warming (Song, McGrouther and Wang, 2016; Song *et al.*, 2017).

Accordingly, the objectives of this research were as follows:
- to study the phytolith and PhytOC content in barley and oat in differentiated fertilisation conditions,
- to explore the potential of C biosequestration within phytoliths in cereales.

MATERIALS AND METHODS

Field experiments were established both in Poland and Estonia (Fig. 1). The Polish experiment was set up in April 2022 at the Experimental Station in Skierniewice (51°57'535N, 20°9'254E). It was established on Luvisol soil (IUSS Working Group WRB, 2015) with each experimental plot being 15 m^2 in three replicates. The Estonian experiment was implemented in 2021 at the Agricultural Research Centre in Matapera, Viljandi, Estonia (58°20'06.0"N, 25°32'34.8"E). Plots were established on Dystric

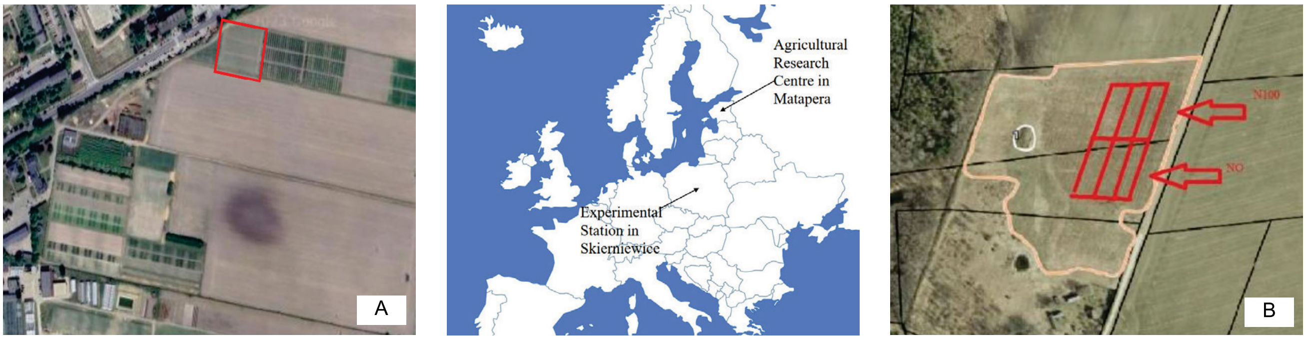

Fig. 1. Location of experimental field in Poland (A) and Estonia (B); source: own elaboration

Planosol soil (IUSS Working Group WRB, 2015), with four replicates (20 m^2 each) for all treatments. The initial soil properties are presented in Table 1.

Table 1. Characteristic of soil physico-chemical properties

Parameter	Poland	Estonia
Soil texture (%)	sand 76, silt 8, clay 16	sand 60.9, silt 29.5, clay 9.6
TOC ($g \cdot kg^{-1}$)	8.40	10.80
TON ($g \cdot kg^{-1}$)	0.76	nd
pH	4.75	5.70
P available ($mg \cdot kg^{-1}$)	38.57	49.60
K available ($mg \cdot kg^{-1}$)	70.60	96.50
Mg available ($mg \cdot kg^{-1}$)	26.10	135.00

Explanations: TOC = total organic carbon, TON = total organic nitrogen, nd = not determined.
Source: own elaboration.

The soil pH was determined in 1M KCl by the potentiometric method on an automatic pH meter (ISO 10390:2021). Total soil N was determined by the Kjeldahl method (ISO 11261:1995). Total soil carbon was determined by means of the Vario Max analyser CHNS (ISO 10694:1995). Available phosphorus and potassium were determined by the Egner–Riehm method (PN-R-04023) and magnesium by Schachtschabel method (PN-R-04020:1994+Az1:2004).

The atmospheric conditions were collected from the weather station localised in Experimental Field in Skierniewice. Mean annual temperature in 2022 reached 9.6°C, and was higher than mean temperature from the multiannual period (1921–2022) by as much as 1.6°C (Fig. 2). Mean temperature in the remaining months of the growing season of oat exceeded the mean temperature from the multiannual period. Mean total precipitation in 2022 reached 605 mm, and exceeded the mean value of the multiannual period by as much as 78 mm. In the growing period (July, August), mean monthly precipitations were higher than the mean value on the 1921–2022 period, providing good conditions for the growth and development of plants.

At the Estonian trial site the climate conditions can be described as continental. The precipitation total was 592.3 mm, being lower than in Poland (Fig. 2). Like in Skierniewice, the most humid month was July, with 125 mm rainfall. Mean air temperature reached 6.6°C, and was as much as three degrees lower than in Skierniewice. On average, temperatures in the period of plant vegetation (months May–September) were from 1.4 to 4.0°C lower in comparison to the Polish experiment.

Spring oat 'Symphony' and spring barley 'Fantex' were sown in Poland and Estonia, accordingly.

The Polish experiment covered the following fertiliser combinations: control, NPK, NPK + Se, NPK + Si, $compost_{170}$, $compost_{170}$ + Se, $compost_{170}$ + Si, $compost_{120}$ + Nmin, $compost_{120}$ + Nmin + Se, $compost_{120}$ + Nmin + Si. Mineral

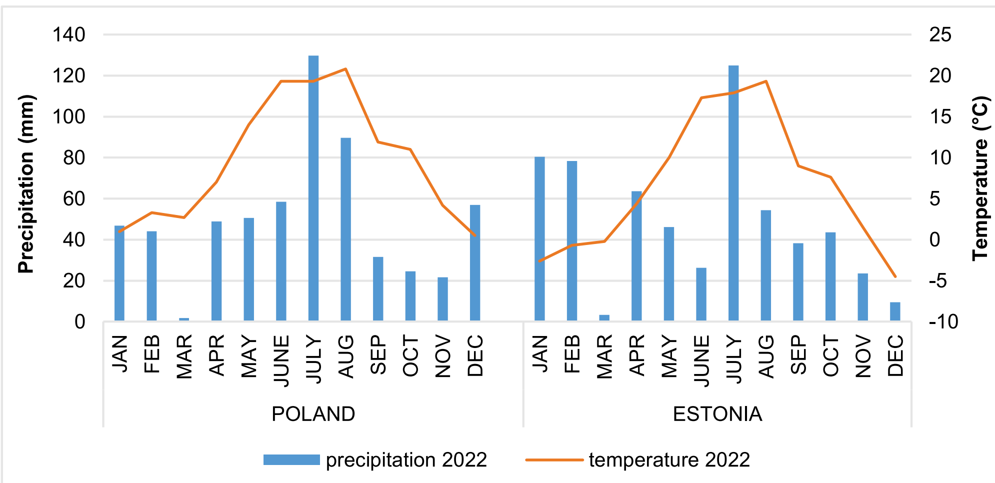

Fig. 2. Weather conditions at the experimental station in Skierniewice, Poland and at the experimental station in Matapera, Viljandi, Estonia; source: own elaboration

fertilisation was applied at the following doses: 100 kg N·ha^{-1} – $CO(NH_2)_2$, 35 kg P·ha^{-1} – $Ca(H_2PO_4)_2$, and 100 kg K·ha^{-1} – KCl. The compost was applied at a dose corresponding to 170 and 120 kg N·ha^{-1}.

The Estonian experiment consisted the following treatments: N_0 (control), N_0 + Si, N_0 + Si + Se, N_{100}, N_{100} + Si, N_{100} + Si + Se, compost$_{170}$, compost$_{170}$ + Si, compost$_{170}$ + Si + Se. Mineral fertilisation was applied as follow: N_{100} – 20 kg·ha^{-1} (ASN 26) and 500 kg·ha^{-1} (14-14-21 NPK YaraMila).

In both experiments, compost and mineral fertilisation was applied before sowing, selenium was applied in the form of Na_2SeO_4 as foliar fertilisation at a dose of 5.00 g Se·ha^{-1} (BBCH[1] 18), and silicon was applied as foliar fertilisation at a dose 139.8 g Si·ha^{-1} as OPTYSIL (INTERMAG Sp. z o.o., Poland) at three plant development stages: I: phase 3 of leaves (BBCH 18), II: beginning of stem shooting (BBCH 35), III: end of the flowering phase (BBCH 72).

The compost used in both field trials was produced through composting four organic waste substances, namely municipal sewage sludge, municipal green waste, sawdust, and spent mushroom substrate. The chemical characteristics of compost pellets were as follows pH 6.7, Corg – 158.7, N – 12.8, S – 1.49, P – 11.05, Na – 1.02, Ca – 84.6, Mg – 5.4 and K – 10.7 g·kg^{-1} DM.

After harvest the plant samples (grain and straw) were dried at a temperature of 50°C, and then ground in a laboratory mill (Retsch) at 5000 rpm.

Carbon and nitrogen contents in grain and straw were determined using a CHNS Vario Cube analyser Macro. Contents of phytoliths and PhytOC were determined in grain and straw samples according to Paar and Sullivan (2011). Statistical analyses were conducted with the Statgraphics 5.1 software. The data were subject to variance analysis at a significance level of $p = 0.05$.

The related calculations were done as per Song *et al.* (2022).

1. The PhytOC content (mg·g^{-1} DM) was calculated using following equation:

$$\text{PhytOC content of organ} = \text{phytolith content} \cdot \text{C-content in phytoliths} \quad (1)$$

where: phytolith content = the weight of phytolith in unit organ (mg·g^{-1} DM), C-content in phytoliths = the weight of C in-unit phytolith (mg·g^{-1} DM).

2. Phytolith production flux is the total phytolith production in the crop above-ground biomass per ha per year (kg·ha^{-1}·y^{-1}), was calculated using following equation:

$$\text{Phytolith production flux} = \text{phytolith content} \cdot \text{ANPP} \quad (2)$$

where: phytolith content = the content of phytoliths in crop aboveground biomass (mg·g^{-1} DM), ANPP = the above-ground net primary productivity of the crop (kg·ha^{-1}·y^{-1}).

3. PhytOC production flux is the annual PhytOC production by above-ground biomass (kg CO_2·ha^{-1}·y^{-1}),

$$\text{PhytOC production flux} = \text{phytolith production flux} \cdot 44/12 \quad (3)$$

where: phytolith production flux (kg·ha^{-1}·y^{-1}) can be calculated from Equation (2), PhytOC content = the content of PhytOC in phytoliths (mg·g^{-1} DM), 44/12 = the mass transfer coefficient of CO_2/C.

RESULTS

The applied mineral and organic fertilisation caused significant changes in the content of phytoliths in cereales in both the experiments conducted in Poland and Estonia.

For oat in the Polish experiments, the phytolith content in grain varied from 18.46 to 21.28 mg·g^{-1} DM (Tab. 1). The phytolith content in straw was multiple times higher, varying from 27.89 to 38.97 mg·g^{-1} DM. The applied fertilisation significantly influenced the phytolith content in the plant parts. In treatments with foliar Si fertilisation, the phytolith content was always significantly higher as compared to the other treatments. The highest contents of phytoliths in grain was observed on compost$_{170}$ + Si treatment and straw occurred for the compost$_{170}$ + Si treatment. The phytolith content was correlated with the PhytOC one. The lowest content of PhytOC in grain was determined in the control treatment with no fertilisation (8.13 mg C·g^{-1} phytolith), and the highest (13.66 mg C·g^{-1} phytolith) for the NPK + Si treatment. For the straw, the lowest content occurred in the compost$_{170}$ + Se treatment (12.11 mg C·g^{-1} phytolith), and the highest one for the NPK + Si treatment (18.91 mg C·g^{-1} phytolith). This PhytOC content was used to compute its equivalent in kg e-CO_2·ha^{-1}. For grain, the amount corresponded to 2.23–3.88 kg e-CO_2·ha^{-1}, and for straw to 12.69–37.85 kg e-CO_2 ha^{-1}, respectively. The total equivalent of carbon accumulated in durable bonds (grain + straw) varied, depending on treatments, from 14.94 to 41.73 kg e-CO_2·ha^{-1} (Tab. 2).

For spring barley in the Estonian experiments, the phytolith contents in grain were considerably lower as compared to those for oat in Polish field trial; it varied from 17.24 to 19.86 mg·g^{-1} DM (Tab. 2). The phytolith content in straw was higher and ranged from 22.06 to 49.08 mg·g^{-1} DM. The phytolith content significantly depended on the treatments. The highest phytolith content in grain was determined for the N_0 + Si treatment, and in straw for the compost$_{170}$ + Si treatment. The phytolith content was correlated with the PhytOC one. The lowest PhytOC content for grain occurred for the N_{100} + Si + Se treatment (0.43 mg C·g^{-1} phytolith), and the highest (1.25 mg C·g^{-1} phytolith) for the N_0 + Si + Se treatment. For straw, the lowest PhytOC content was found for the compost170 treatment (1.30 mg C·g^{-1} phytolith), and the highest one for the N_0 + Si + Se treatment (3.54 mg C·g^{-1} phytolith). For grain, the PhytOC content corresponded to 0.10–0.28 kg e-CO_2·ha^{-1}, and for straw to 0.20–1.41 kg e-CO_2·ha^{-1}, respectively. The total equivalent of carbon accumulated in durable bonds (grain + straw) depended on treatments, and ranged from 0.32 to 1.60 kg e-CO_2·ha^{-1}.

[1] The BBCH-scale is used to identify the phenological development stages of plants. The first digit of the scale refers to the principal growth stage. The second digit refers to the secondary growth stage which corresponds to an ordinal number or percentage value. Post-harvest or storage treatment is coded as 99. Seed treatment before planting is coded as 00. The abbreviation BBCH derives from the names of the originally participating stakeholders: "Biologische Bundesanstalt, Bundessortenamt und CHemische Industrie".

Table 1. Content of phytoliths and phytolith-occluded C (PhytOC) in oat grain and straw cultivated at the Skierniewice experiment, Poland

Treatment	Content in										
	grain					straw					grain + straw – estimated PhytOC yield ($kg\ e\text{-}CO_2 \cdot ha^{-1}$)
	phytoliths ($mg \cdot g^{-1}$ DM)	C occluded on phytoliths			estimated PhytOC yield ($kg\ e\text{-}CO_2 \cdot ha^{-1}$)	phytoliths ($mg \cdot g^{-1}$ DM)	C occluded on phytoliths			estimated PhytOC yield ($kg\ e\text{-}CO_2 \cdot ha^{-1}$)	
		$mg \cdot g^{-1}$ phytolith	$mg \cdot g^{-1}$ DM	in yield kg			$mg \cdot g^{-1}$ phytolith	$mg \cdot g^{-1}$ DM	in yield kg		
Control	19.43a	8.13a	0.16a	0.67a	2.47a	27.89b	12.47a	0.35a	4.77c	17.50b	19.96b
NPK	19.24a	12.26	0.23d	0.66a	2.42a	31.23d	15.30b	0.48c	4.20b	15.40b	17.83a
NPK + Se	19.59a	9.52a	0.19b	0.75b	2.76b	28.38c	14.69b	0.42b	5.48d	20.09c	22.84b
NPK + Si	20.13ab	13.66d	0.28e	1.06d	3.88d	38.97f	18.91d	0.74e	10.32g	37.85f	41.73e
$Compost_{170}$	19.28a	9.17a	0.18a	0.64a	2.35a	30.29cd	13.18b	0.40a	4.47b	16.41b	18.76b
$Compost_{170}$ + Se	18.46a	10.56b	0.20b	0.61a	2.24a	31.47d	12.11a	0.38a	3.46a	12.69a	14.94a
$Compost_{170}$ + Si	21.28b	8.69a	0.18a	0.61a	2.23a	34.20e	14.21b	0.49c	5.82e	21.35d	23.58c
$Compost_{120}$ + Nmin	19.88a	11.24c	0.22c	0.92c	3.37c	31.07d	16.70c	0.52d	8.27f	30.33e	33.70d
$Compost_{120}$ + Nmin + Se	18.63a	10.30b	0.19b	0.65a	2.39a	28.61b	17.47c	0.50c	5.51d	20.19c	22.58b
$Compost_{120}$ + Nmin + Si	20.06ab	9.25a	0.18a	0.62a	2.28a	32.91d	14.58b	0.48c	5.61e	20.57c	22.85b

Explanations: values denoted by the same letter, were not significantly differentiated at the level of p = 0.05; DM = dry mass.
Source: own study.

Table 2. Content of phytoliths and phytolith-occluded C (PhytOC) in spring barley cultivated at the Matapera experiment, Estonia

Treatment	Content in										
	grain					straw					grain + straw – estimated PhytOC (kg e-CO_2·ha^{-1})
	phytoliths (mg·g^{-1} DM)	C occluded on phytoliths			estimated PhytOC yield (kg e-CO_2·ha^{-1})	phytoliths (mg·g^{-1} DM)	C occluded on phytoliths			estimated PhytOC yield (kg e-CO_2·ha^{-1})	
		mg·g^{-1} phytolith	mg·g^{-1} DM	in yield kg			mg·g^{-1} phytolith	mg·g^{-1} DM	in yield kg		
N_0	19.35d	0.52	0.010a	0.034a	0.12b	25.08a	2.13b	0.05a	0.06a	0.20a	0.32a
N_0 + Si	19.86e	0.90d	0.018c	0.058b	0.21e	38.47e	3.18d	0.12c	0.21d	0.76c	0.98c
N_0 + Si + Se	19.10d	1.25e	0.024d	0.072c	0.26f	33.44c	3.54e	0.12c	0.23e	0.84d	1.11d
N_{100}	17.24a	0.62c	0.011a	0.052b	0.19d	36.55d	3.28d	0.12c	0.39f	1.41e	1.60e
N_{100} + Si	17.39a	0.90d	0.016b	0.076c	0.28g	29.10b	2.53c	0.07b	0.23e	0.84d	1.12d
N_{100} + Si + Se	17.55ab	0.43a	0.008a	0.039ab	0.14c	22.06a	2.65c	0.06a	0.15c	0.54b	0.69b
$Compost_{170}$	18.69c	0.57b	0.011a	0.034a	0.12b	34.06c	1.30a	0.04a	0.06a	0.21a	0.34a
$Compost_{170}$ + Si	19.12d	0.50a	0.010a	0.027a	0.10a	49.08f	2.47c	0.12c	0.15c	0.57b	0.66b
$Compost_{170}$ + Si + Se	19.18d	0.46a	0.009a	0.025a	0.09a	38.56e	2.05b	0.08b	0.10b	0.36a	0.45a

Explanations as in Tab. 1.
Source: own study.

DISCUSSION

Our study evidenced that oat responds well to foliar Si application by increasing the phytolith content and PhytOC. Significant higher phytolith contents (in the Polish experiment) were determined in oat straw as compared to oat grain. In the Estonian experiment with barley changes in the phytolith content due to fertilisation were considerably lower. Regardless of the field trial, the highest phytolith contents were always recorded for crops fertilised with Si immune stimulant OPTYSIL. Similar results were obtained by Majumdar and Prakash (2020) showing straw management in a rice field affected Si circulation in the environment. Long-term rice cultivation at the same site and leaving straw in the soil promoted the phytolith accumulation in the soil. Rice straw contains as much as 86% of Si absorbed by the plants. Parr *et al.* (2009) pointed out the strong correlation between the content of phytoliths in the leaf and stem material of wheat, bamboo as well as sugar cane, and the PhytOC content. Similar dependencies were observed by Malik *et al.* (2021) determining a positive correlation between the contents of silica and phytoliths as well as between phytolith and PhytOC contents. Fertilisation with silicon caused an additional increase in the analysed indices in the cultivation of wheat in comparison to the control treatment (a four-fold increase in comparison to treatments fertilised with silicon). Anjum and Nagabovanalli (2021) pointed out that rice cultivars with a longer growing period (>140 days) accumulate significantly higher amounts of phytoliths and PhytOC in straw in comparison to cultivars with a shorter growing period (125 days). Such tendencies were also confirmed by Davamani *et al.* (2022). They determined that the content of phytoliths and PhytOC in all studied oil palms significantly differed and increased with age. The highest amounts of phytoliths were found in 15-year-old palms and the lowest in 4-year-old palms. According to Qi *et al.* (2021) the phytolith and PhytOC contents in the biomass of desert steppe of typical dry steppe and typical wet steppe in China significantly differed between species. The dominant species of grasses and sedges were characterised by relatively high content of phytoliths and their content was consider-ably higher in the underground parts (86.44. 58.73 and 76.94 $g \cdot kg^{-1}$ respectively) than above-ground parts (16.68. 17.94 and 15.85 $g \cdot kg^{-1}$ respectively). Similar dependencies were obtained for PhytOC of 1.11, 0.72 and 1.02 $g \cdot kg^{-1}$ respectively in the underground biomass of three types of steppe and 0.68, 0.48, and 0.59 $g \cdot kg^{-1}$ respectively in above-ground parts.

Oat is a cereal with the highest nutritional requirements for silicon, which is why the amount of phytoliths produced is greater compared to barley. Plants having higher Si uptake levels than water are classified as active (e.g., rice, wheat, and barley), whereas those with similar rates are classified as passive (e.g., oat) and those with lower uptake rates are classified as rejective (Kaur and Greger, 2019).

Our results show that the phytolith and PhytOC contents decreases cultivar dependent both in grain and straw of cereales depending on latitude. This is confirmed by Wenjuan *et al.* (2022) who showed a strong positive effect of climatic factors related to temperature and precipitation on the production of phytoliths and PhytOC. Based on these authors, the characteristics of distribution of phytoliths and PhytOC in wheat straw and soil showed a decreasing tendency from the South to the North. They also pointed out that physicochemical soil properties such as the Si availability, total carbon (Ctot) and total nitrogen (Ntot) also affect the accumulation of phytoliths in plant parts. Other authors emphasised the phytolith accumulation in plants depending on straw management (Majumdar and Prakash, 2020), application of silicon fertilisation (Guo *et al.*, 2015). All these measures play an important role in C bio-sequestration and mitigation of climate change.

Oat cultivation would contributes to sustainable carbon sequestration in the soil. In Polish conditions (oat cultivation covers an area of approximately 500 thous. ha) the $compost_{170}$ treatment would induce a PhytOC accumulation estimated to 18.76 kg e-CO_2 $ha^{-1} \cdot y^{-1}$. Foliar Si application (NPK + Si treatment) would cause a significant (>2.5-fold) increase in carbon accumulation to 41.73 kg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$. Potential amounts of accumulated CO_2 depending on the treatments would vary from 9,380 Mg e-$CO_2 \cdot ha^{-1} \cdot year^{-1}$ (compost treat-ment) to 20,865 Mg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$ for the NPK + Si treatment. For the crops in North Europe (Estonia), the possibilities of carbon accumulation would be lower due to the much smaller cultivation area, in 2021 reaching 116.39 thous. ha (Trading Economics, no date), and lower phytolith content in grains and straw. Potential amounts of accumulated CO_2 depending on the treatments would vary from 39.5 Mg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$ (compost treatment) to 130.4 Mg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$ for the NPK + Si treatment.

The ability of crops to accumulate PhytOC in agricultural ecosystems is confirmed by Wenjuan *et al.* (2022) who estimated CO_2 accumulation in wheat crops at a level of $7.59 \cdot 10^6$ Mg, corresponding to 27.83 Tg CO_2. In wheat crops fertilised with silicon in China. Malik *et al.* (2021) determined a potential of 0.304 Mg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$. Paar *et al.* (2009) emphasised that a potential crop permitting long-lasting and durable carbon sequestration is sugar cane that is able to bind approximately 0.66 Mg e-$CO_2 \cdot ha^{-1} \cdot y^{-1}$. Lv *et al.* (2020) pointed out the vast potential of Moso bamboo (*Phyllostachys heterocycla* var. *pubescens*) for carbon sequestration and its richness in PhytOC. The Si application causes a significant increase in PhytOC. Wang and Sheng (2022) evidenced that buck-wheat is a very good plant for carbon sequestration. The average phytolith carbon sequestra-tion rate of *Fagopyrum esculentum* and *Fagopyrum tataricum* planting was $2.62 \cdot 10^{-3}$ and $1.17 \cdot 10^{-3}$ Mg CO_2 $ha^{-1} \cdot y^{-1}$ respectively.

Our study showed that foliar Si fertilisation should be applied more frequently in the future due to its influence to increase the rate of sequestration of atmospheric CO_2 as well as its contribution to an increase in resistance to stress and increase in yields of crops.

CONCLUSIONS

An addition of Si a liquid immune stimulant (OPTYSIL) has an effect on content of phytoliths and PhytOC in grain and straw of both cereal species. Our data suggest that the future amount of PhytOC in oat and barley fields can be additionally increased through adopting agricultural practices such as optimisation of Si fertilisation. The total equivalent of carbon accumulated in durable bonds (grain + straw) in barley (experiments in Estonia) varied, depending on fertilisation from 0.32 to 1.60 kg e-$CO_2 \cdot ha^{-1}$, and was much higher in oat (experiment in Poland), varying from

14.94 to 41.73 kg e-CO_2·ha^{-1}. This indicated that oat is a plant species that allocates more silicon in grains and straw than spring barley. Further research on other crop species is required to determine the equivalent of accumulated phytoliths and carbon accumulated in durable bonds and to determine its potential contribution to the mitigation of the greenhouse effect. The method of plowing in and leaving cereal straw in the field can contribute to increasing the amount of stable carbon compounds in the soil (PhytOC).

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

REFERENCES

Anjum, M. and Nagabovanalli, P.B. (2021) "Assessing production of phytolith and phytolith occluded carbon in above-ground biomass of intensively cultivated rice ecosystems in India," *Carbon Management*, 12, pp. 509–519. Available at: https://doi.org/10.1080/17583004.2021.1978552.

Davamani V. *et al.* (2022) "Phytolith-occluded carbon sequestration potential of oil palm plantation in Tamil Nadu," *ACS Omega*, 7, pp. 2809–2820. Available at: https://doi.org/10.1021/acsomega.1c05592.

Guo, F. *et al.* (2015) "Enhancing phytolith carbon seques-tration in rice ecosystems through basalt powder amendment," *Science Bulletin*, 60, pp. 591–597. Available at: https://doi.org/10.1007/s11434-015-0729-8.

Handke, M. (2008) *Krystalochemia krzemianów [Crystallochemistry of silicates]*. 2nd edn. Kraków: Uczelniane Wydawnictwa Naukowo-Dydaktyczne.

Hodson, M.J. *et al.* (2008) "Silicon, oxygen and carbon isotope composition of wheat (*Triticum aestivum* L.) phytoliths: Implications for palaeoecology and archaeology," *Journal of Quaternary Science*, 23, pp. 331–339. Available at: https://doi.org/10.1002/jqs.1176.

ISO 10390:2021. *Soil, treated biowaste and sludge – Determination of pH*. Geneva: International Organization for Standardization.

ISO 10694:1995. *Soil quality. Determination of organic and total carbon after dry combustion (elementary analysis)*. Geneva: International Organization for Standardization.

ISO 11261:1995. *Soil quality – Determination of total nitrogen modified Kjeldahl method*. Geneva: International Organization for Standardization.

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*, 106. Rome: FAO. Available at: https://www.fao.org/3/i3794en/I3794en.pdf (Accessed: August 14, 2023).

Jones, R.L. and Beavers, A.H. (1963) "Some mineralogical and chemical properties of plant opal," *Soil Science*, 96, pp. 375–379. Available at: https://journals.lww.com/soilsci/Citation/1963/12000/Some_-Mineralogical_and_Chemical_Properties_of.3.aspx (Accessed: August 14, 2023).

Kaur, H. and Greger, M. (2019) "A review on Si uptake and transport system," *Plants*, 8(4), 81. Available at: https://doi.org/10.3390/plants8040081.

Liu, L. *et al.* (2023) "Enhancement of phytolith-occluded carbon accumulation of Moso bamboo response to temperatures elevation and different fertilization," *Frontiers in Plant Science*, 14, 1144961. Available at: https://doi.org/10.3389/fpls.2023.1144961.

Liu, Z. *et al.* (2023) "Monitoring global carbon emissions in 2022," *Nature Reviews Earth & Environment*, 4, pp. 205–206. Available at: https://doi.org/10.1038/s43017-023-00406-z.

Lv, W. *et al.* (2020) "Effects of different management practices on the increase in phytolith-occluded carbon in Moso bamboo forests," *Frontiers in Plant Science*, 11, 591852. Available at: https://doi.org/10.3389/fpls.2020.591852.

Majumdar, S. and Prakash, N.B. (2020) "An overview on the potential of silicon in promoting defense against biotic and abiotic stresses in sugarcane," *Journal of Soil Science and Plant Nutrition*, 20(4), pp. 1969–1998. Available at: https://doi.org/10.1007/s42729-020-00269-z.

Malik, M.A. *et al.* (2021) "Elucidating the role of silicon in drought stress tolerance in plants," *Plant Physiology and Biochemistry*, 165, pp. 187–195. Available at: https://doi.org/10.1016/j.plaphy.2021.04.021.

Nguyen, M.N. *et al.* (2019) "Phytolith content in Vietnamese paddy soils in relation to soil properties," *Geoderma*, 333, pp. 200–213. Available at: https://doi.org/10.1016/j.geoderma.2018.07.027.

Parr, J. *et al.* (2010) "Carbon bio-sequestration within the phytoliths of economic bamboo species," *Global Change Biology*, 16, pp. 2661–2667. Available at: https://doi.org/10.1111/j.1365-2486.2009.02118.x.

Parr, J.F. and Sullivan, L.A. (2005) "Soil carbon sequestration in phytoliths," *Soil Biology and Biochemistry*, 37, pp. 117–124. Available at: https://doi.org/10.1016/j.soilbio.2004.06.013.

Parr, J.F. and Sullivan, L.A. (2011) "Phytolith occluded carbon and silica variability in wheat cultivars," *Plant and Soil*, 342, pp. 165–171. Available at: https://doi.org/10.1007/s11104-010-0680-z.

Parr, J.F. and Sullivan, L.A. (2014) "Comparison of two methods for the isolation of phytolith occluded carbon from plant material," *Plant and Soil*, 374, pp. 45–53. Available at: https://doi.org/10.1007/s11104-013-1847-1.

Parr, J., Sullivan, L. and Quirck, R. (2009) "Sugarcane phytoliths: Encapsulation and sequestration of a long-lived carbon fraction," *Sugar Tech*, 11(1), pp. 17–21. Available at: https://doi.org/10.1007/s12355-009-0003-y.

PN-R-04020:1994/Az1:2004. *Analiza chemiczno-rolnicza gleby – Oznaczanie zawartości przyswajalnego magnezu [Chemical and agricultural analysis – determination of the content available magnesium in soil]*. Warszawa: Polski Komitet Normalizacyjny.

PN-R-04022:1996/Az1:2002. *Analiza chemiczno-rolnicza gleby – Oznaczanie zawartości przyswajalnego potasu w glebach mineralnych [Chemical and agricultural analysis – Determination of the content available potassium in mineral soil]*. Warszawa: Polski Komitet Normalizacyjny.

PN-R-04023:1996. *Analiza chemiczno-rolnicza gleby – Oznaczanie zawartości przyswajalnego fosforu w glebach mineralnych [Chemical and agricultural analysis – Determination of the content* *available phosphorus in mineral soil]*. Warszawa: Polski Komitet Normalizacyjny.

Prabha, A.M. *et al.* (2022) "Silicon fertilizer – An imperative source for enhancing yield and phytolith content of maize hybrid in desilicated soil (Typic Rhodustalf)," *Ecology, Environment and Conservation*, 28(2), pp. 879–885. Available at: http://doi.org/10.53550/EEC.2022.v28i02.045.

Prajapati, K. *et al.* (2016) "Carbon occlusion potential of rice phytoliths: Implications for global carbon cycle and climate change mitigation," *Applied Ecology and Environmental Research*, 14(2), pp. 265–281. Available at: https://doi.org/10.15666/aeer/1402_265281.

Qi, L.M. *et al.* (2021) "Phytolith-occluded carbon sequestration potential in three major steppe types along a precipitation gradient in Northern China," *Ecology and Evolution*, 11, pp. 1446–1456. Available at: https://doi.org/10.1002/ece3.7155.

Rehman, I.U., Malik, M.A. and Rashid, I. (2023) "Silicon fertilization increases carbon sequestration by augmenting PhytOC production in wheat," *Journal of Soil Science and Plant Nutrition*, 23, pp. 1149–1155. Available at: https://doi.org/10.1007/s42729-022-01110-5.

Sharma, R., Kumar, V. and Kumar, K. (2019) "Distribution of phytoliths in plants: A review," *Geology, Ecology and Landscapes*, 3 (2), pp. 123–148. Available at: https://doi.org/10.1080/24749508.2018.1522838.

Song, Z. *et al.* (2017) "Phytolith carbon sequestration in global terrestrial biomes," *Science of The Total Environment*, 603, pp. 502–509. Available at: https://doi.org/10.1016/j.scitotenv.2017.06.107.

Song, Z. *et al.* (2022) "High potential of stable carbon sequestration in phytoliths of China's grasslands," *Global Change Biology*, 28(8), pp. 2736–2750. Available at: https://doi.org/10.1111/gcb.16092.

Song, Z.L., McGrouther, K. and Wang, H.L. (2016) "Occurrence, turnover and carbon sequestration potential of phytoliths in terrestrial ecosystems," *Earth-Science Reviews*, 158, pp. 19–30. Available at: https://doi.org/10.1016/j.earscirev.2016.04.007.

Trading Economics (no date) *Estonia – Barley: Area (cultivation/harvested/production)*. Available at: https://tradingeconomics.com/estonia/barley-area-cultivation-harvested-production-eurostat-data.html (Accessed: August 18, 2023).

Wang, L. and Sheng, M. (2022) "Phytolith occluded organic carbon in *Fagopyrum* (Polygonaceae) plants: Insights on the carbon sink potential of cultivated buckwheat planting," *Frontiers in Plant Science*, 13, 1014980. Available at: https://doi.org/10.3389/fpls.2022.1014980.

Wenjuan, L. *et al.* (2022) "The spatial distribution of phytoliths and phytolith-occluded carbon in wheat (*Triticum aestivum* L.) ecosystem in China," *Science of The Total Environment*, 850, 158005. Available at: https://doi.org/10.1016/j.scitotenv.2022.158005.