



## Phytolith carbon sequestration in China's croplands

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### ABSTRACT

A relatively recent found persistent component of the carbon (C) sink is C occluded within plant phytoliths. We constructed a silica–phytolith content transfer function and used crop production data to explore the phytolith C sink within China's croplands. The purposes of the study are to offer references for agricultural management and contribute to mitigating climate change. The Chinese cropland phytolith sink represented approximately 18% of world's croplands ( $24.39 \pm 8.67 \text{ Tg yr}^{-1}$ ) and sequestered  $4.39 \pm 1.56 \text{ Tg yr}^{-1}$  of carbon dioxide ( $\text{CO}_2$ ); more than the USA or India. The predominant crop species were rice (*Oryza sativa* L., 40%), wheat (*Triticum* sp., 18%) and corn (*Zea mays*, 30%), while the main contributing areas were the midsouthern (28%) and eastern (26%) Chinese regions. The sink has doubled since 1978 owing to fertilizer application and irrigation. Therefore, fertilizer application and irrigation in conjunction with other management practices (such as crop pattern optimization) may further enhance the cropland phytolith C sink and thereby mitigate climate change.

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## 1. Introduction

As a long-term carbon (C) sink, biogeochemical C sequestration in terrestrial ecosystems mediates long-term global C cycle (Lackner, 2003; Piao et al., 2009; Parr et al., 2010; Song et al., 2012a,b). Phytoliths, silica opals formed in plant tissues, usually occlude 1–6% of C (phytolith-occluded carbon, PhytOC) (Parr and Sullivan, 2005; Song et al., 2012a). Cereal crops (Parr et al., 2009; Parr and Sullivan, 2011; Zuo and Lü, 2011; Rajendiran et al., 2012; Li et al., 2013b), bamboo (Meunier et al., 1999; Parr et al., 2010), and grassland and wetland grasses (Song et al., 2012a; Li et al., 2013a) are found to be PhytOC accumulators. Protected by silica, the PhytOC is highly resistant to decomposition (Wilding, 1967; Wilding et al., 1967; Mulholland et al., 1992; Parr and Sullivan, 2005). For example, it has been reported that the age of phytoliths in soils and sediments can be older than 8000 aBP and phytoliths can

contribute 15–37% of long term biogeochemical C sequestration (Parr and Sullivan, 2005).

As one of the largest crop-producing countries of the world, China has approximately  $160 \times 10^6$  ha of croplands, of which  $91 \times 10^6$  ha are cereal croplands (Piao et al., 2009). Quantifying the PhytOC production in China's croplands is essential so that the magnitude of phytolith C sink may be established. In addition, quantifying PhytOC yields would guide the management of crop-land ecosystems and contribute to mitigating climate change. In this study, we constructed a silica–phytolith content transfer function and calculated the magnitude of the phytolith C sink within China's croplands. Calculations were performed using relevant crop data such as the land productivity, the Si-rich organ ratio, silica and PhytOC content, and the PhytOC stability factor.

## 2. Materials and methods

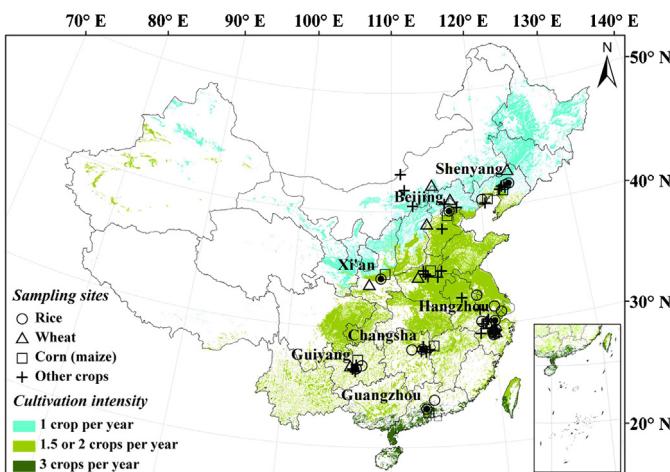
### 2.1. Construction of silica–phytolith content transfer function

We collected various mature crop samples (including 11 rice samples, 8 wheat samples, 10 corn samples and 20 other crop samples) from China to construct silica–phytolith content transfer function (Fig. 1). The sampling locations were selected randomly within each defined plot where representative and healthy crop plants were sampled. Each sample of rice, wheat and other small crops was made up of approximately 300 g of composite plant

**Abbreviations:** C, carbon; PhytOC, phytolith-occluded carbon; SOC, soil organic carbon; FAO, Food and Agriculture Organization of the United Nations; SRO, Si-rich organs.

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**Fig. 1.** Distribution of arable crops across China and sampling sites in this study.

materials including leaves, stems and sheath. Each sample of corn was made up of 300–600 g above-ground parts of a plant.

Crop samples were cleaned, oven-dried at 75 °C, and cut into small pieces (<5 mm). They were fused with Li-metaborate at 1000 °C and analyzed for silica content by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 7000 DV Series, Perkin Elmer) (Song et al., 2012a). Plant phytoliths were separated with a microwave digestion process followed by a Walkley–Black digest to remove extraneous organic materials (Parr et al., 2010). The isolated phytoliths were then dried in a fan-forced oven at 75 °C for 24 h and weighed to calculate plant phytolith content (Parr et al., 2010; Li et al., 2013b). Modified from methods of Kroger et al. (2002), the dried phytoliths samples were dissolved in 1 mol/L HF at 45 °C for 100 min to remove phytolith-Si. The exposed organic C from phytoliths after HF treatment was dried at 45 °C and analyzed for C content with classical potassium dichromate digestion method (Li et al., 2013b).

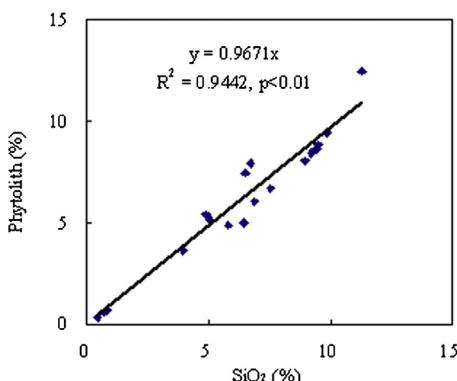
The silica–phytolith content transfer function was derived from Fig. 2:

$$\text{Phytolith content (wt\%)} = \text{silica content (wt\%)}$$

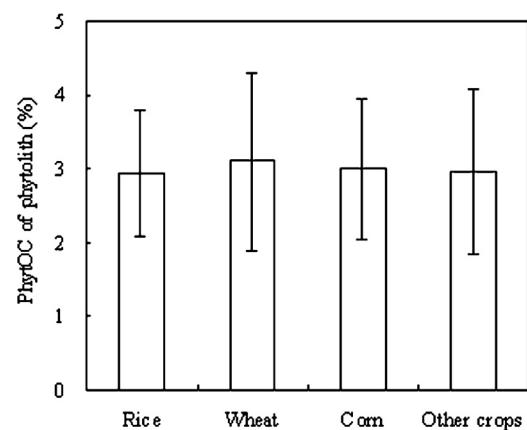
$$\times 0.9671 (R^2 = 0.9442, p < 0.01) \quad (1)$$

## 2.2. Data collection and estimation of phytolith and PhytOC content

Crop production data was obtained from China Statistical Yearbook (National Bureau of Statistics of China, 2012), FAO: Statistics



**Fig. 2.** The correlation of phytolith content to the SiO<sub>2</sub> content in different crop species ( $p < 0.01$ ).



**Fig. 3.** The average and variation of PhytOC content in phytolith of rice, wheat, corn and other arable crops. The sample numbers for rice, wheat, corn and other crops are 11, 8, 10 and 20, respectively.

(FAO, 2012) and China Agriculture Statistical Report (Ministry of Agriculture of PRC, 2011). Silica and phytolith data were from published monographs (Hou, 1982; Xu et al., 1998), papers (Ding et al., 2008; Parr and Sullivan, 2011; Zuo and Lü, 2011) and determined in this study. The phytolith content was estimated from silica content of a crop species using a transfer coefficient of 0.9671 (Eq. (1)). Phytolith content data was used to estimate the PhytOC content in plant organs using a PhytOC content in phytolith of  $3 \pm 1\%$  (Fig. 3).

## 2.3. Estimation of PhytOC production flux and rate

The PhytOC production flux was estimated as (Song et al., 2013):

$$\text{PhytOC production flux} = \text{PhytOC content}$$

$$\times \text{SRO Production flux} \times 44/12 \quad (2)$$

where PhytOC production flux is the annual PhytOC production by crop's Si-rich organs ( $\text{kg CO}_2 \text{ha}^{-1} \text{yr}^{-1}$ ) and PhytOC content is the PhytOC concentration in crop's Si-rich organs (SRO) (wt%). The SRO production flux is the above-ground production of Si-rich crop organs of unit area ( $\text{kg ha}^{-1} \text{yr}^{-1}$ ), which is estimated from the crop output of unit area and mass ratios of the Si-rich organ: crop output (Tables 1 and 2). 44/12 is the mass transfer coefficient of  $\text{CO}_2/\text{C}$ .

The PhytOC production rate was estimated from PhytOC production flux and crop area (Song et al., 2013):

$$\text{PhytOC production rate} = \text{PhytOC production flux} \times \frac{\text{area}}{1000} \quad (3)$$

where PhytOC production rate is the total PhytOC production of an area ( $\text{Tg CO}_2 \text{yr}^{-1}$ ), PhytOC production flux ( $\text{kg CO}_2 \text{ha}^{-1} \text{yr}^{-1}$ ) can be estimated from Eq. (2) and area is expressed as  $10^6 \text{ ha}$ .

## 2.4. Estimation of phytolith C sink flux and rate

The flux at which the PhytOC is conserved in croplands can be estimated from phytolith stability factor and the PhytOC production flux for a particular crop (Song et al., 2013):

$$\text{Phytolith C sink flux} = \text{phytolith stability factor}$$

$$\times \text{PhytOC production flux} \quad (4)$$

where phytolith C sink flux is the net phytolith C sink flux, the stability factor of phytoliths is assumed to be  $0.9 \pm 0.05$  as soils contain approximately 10,000 times more phytolith than the aboveground biomass (Blecker et al., 2006), and most phytoliths have been proved stable for hundreds to thousands of years though a few

**Table 1**

Phytolith content in mature Si-rich organs of dominant crop species in China.

Crop types	Species	Phytolith (%)		Data sources
		Mean	SE	
Cereal	<i>Oryza sativa</i> L.	8.38	1.80	This study; 1, 2
	<i>Triticum</i> sp.	5.50	1.83	This study; 4
	<i>Zea mays</i>	5.19	1.49	This study; 3
	<i>Setaria italica</i>	7.49	3.00	3, 5
	<i>Sorghum vulgare</i>	5.99	2.34	This study; 3
	<i>Hordeum sativum</i> Jess.	3.37	0.84	This study; 2
Soybeans	Average	5.99	2.61	
	<i>Glycine max</i>	0.71	0.25	This study
	<i>Solanum tuberosum</i> L.	0.73	0.25	This study
	<i>Ipomoea batatas</i> Lam.	0.56	0.18	This study
Oil-bearing crops	Average	0.65	0.25	
	<i>Arachis hypogaea</i>	0.96	0.42	This study; 3
	<i>Brassica</i> spp.	0.37	0.14	This study; 2
	<i>Sesamum orientale</i>	6.38	1.53	This study
Cotton	Average	2.57	2.20	
	<i>Gossypium</i> spp.	0.79	0.21	This study; 3
	<i>Saccharum officinarum</i>	8.23	1.65	This study

Data sources: 1 – Ding et al. (2008); 2 – Xu et al. (1998); 3 – Hou (1982); 4 – Parr and Sullivan (2011); 5 – Zuo and Lü (2011).

small phytolith particles may be preferentially dissolved depending on the phytolith composition and formation sites in plant organs, and phytolith sink environments after plant tissue decomposition (Meunier et al., 1999; Parr and Sullivan, 2005; Parr et al., 2010; Song et al., 2013). PhytOC production flux is estimated from Eq. (2).

Knowing the Phytolith C sink flux, one can use the cropland area to determine the phytolith C sink rate (Song et al., 2013):

$$\text{Phytolith C sink rate} = \text{Phytolith C sink flux} \times \frac{\text{area}}{1000} \quad (5)$$

where Phytolith C sink rate ( $\text{Tg CO}_2 \text{ yr}^{-1}$ ) is the total annual Phytolith C sink of an area, Phytolith C sink flux ( $\text{kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) can be estimated from Eq. (4) and the area is the cropland area expressed as  $10^6 \text{ ha}$ .

### 3. Results

#### 3.1. Phytolith and PhytOC content for different crops

The phytolith content in plant matter above the soil varied greatly among different crop types (0.37–8.38%, average 3.68%) and even among crop species of the same crop types (Table 1). The PhytOC content of the predominant arable crops in China displayed a similar variation (0.019–0.251%, average 0.111%) (Table 2). Generally, sugarcane and cereals such as rice, wheat and corn had a

higher contents of phytolith (3.37–8.38%, average 5.99%) and PhytOC (0.156–0.251%, average 0.168%) than other crops.

#### 3.2. The production of PhytOC in crops

With regard to PhytOC production flux, rice ( $68 \pm 19 \text{ kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) generated more per unit area annually than corn ( $44 \pm 17 \text{ kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ), wheat ( $38 \pm 17 \text{ kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$ ) or any other crop. The mean PhytOC production flux generated within China's croplands was estimated at  $36 \text{ kg CO}_2 \text{ ha}^{-1} \text{ yr}^{-1}$  (Table 3). The PhytOC production rate varied greatly among different crops (Table 3), with a rice:corn:wheat ratio of 2.2:1.6:1.0. The production rate of PhytOC by rice ( $2.04 \pm 0.58 \text{ Tg CO}_2 \text{ yr}^{-1}$ ) was greater than that of corn ( $1.49 \pm 0.57 \text{ Tg CO}_2 \text{ yr}^{-1}$ ), wheat ( $0.91 \pm 0.41 \text{ Tg CO}_2 \text{ yr}^{-1}$ ) or other crops in China. The total annual PhytOC production within China's croplands was  $4.88 \pm 1.73 \text{ Tg CO}_2 \text{ yr}^{-1}$ .

#### 3.3. The phytolith C sink in croplands

The phytolith C sink rate and flux of different crops depended on PhytOC production rate as well as the flux of different crop types and species (Table 3). The total phytolith C sink rate generated within China's croplands was  $4.39 \pm 1.56 \text{ Tg CO}_2$  during 2011 (Figs. 4 and 5). This quantity represented approximately 5.3% of the

**Table 2**

General information and PhytOC content of the predominant arable crops in China.

Crops	Area ( $10^6 \text{ hm}^2$ ) <sup>a</sup>	Si-rich organs	PhytOC (%) <sup>b</sup>	
			Mean	SE
Rice	30.1	Stem, sheath and leaf	0.25	0.07
Wheat	24.3	Stem, sheath and leaf	0.16	0.07
Corn	33.5	Stem, sheath and leaf	0.16	0.06
Other cereal	6.2	Stem, sheath and leaf	0.17	0.09
Soybeans	10.7	Stem and leaf	0.02	0.01
Tubers	8.9	Stem and leaf	0.02	0.01
Oil-bearing crops	13.9	Stem and leaf	0.08	0.07
Cotton	5.0	Stem and leaf	0.02	0.01
Sugarcane	1.9	Sheath and leaf	0.25	0.07
Total	134.5		0.16	0.06

<sup>a</sup> Values are from National Bureau of Statistics of China (2012).

<sup>b</sup> Estimated from Table 1 using an PhytOC content in phytolith of 3 ± 1% (Fig. 3).

**Table 3**

Estimated PhytOC production by Chinese crops.

Farm crops	Crop output (kg ha <sup>-1</sup> yr <sup>-1</sup> ) <sup>a</sup>	SRO factor <sup>b</sup>	SRO production flux (kg ha <sup>-1</sup> yr <sup>-1</sup> ) <sup>c</sup>	PhytOC production flux (kg CO <sub>2</sub> ha <sup>-1</sup> yr <sup>-1</sup> ) <sup>d</sup>		PhytOC production rate (Tg CO <sub>2</sub> yr <sup>-1</sup> ) <sup>e</sup>	
				Mean	SE	Mean	SE
Rice	6687	1.10	7356	68	19	2.04	0.58
Wheat	4837	1.29	6225	38	17	0.91	0.41
Corn	5748	1.35	7771	44	17	1.49	0.57
Other cereal	1323	1.76	2329	14	8	0.09	0.05
Soybeans	1792	1.50	2688	2	1	0.02	0.01
Tubers	3675	0.58	2132	2	1	0.01	0.01
Oil-bearing crops	476	2.20	1046	3	2	0.04	0.03
Cotton	6564	2.91	19,101	17	6	0.08	0.03
Sugarcane	58,751	0.18	10,575	96	26	0.19	0.05
Total			6144	36	13	4.88	1.73

<sup>a</sup> Values from the Ministry of Agriculture, PRC (2011).<sup>b</sup> Mass ratios of the Si-rich organ: crop output from Huang et al. (2007) and Zhu et al. (2012).<sup>c</sup> SRO production flux is the above-ground production of Si-rich crop organs of unit area (kg ha<sup>-1</sup> yr<sup>-1</sup>).<sup>d,e</sup> Estimated from PhytOC content (Table 2) and SRO production flux data (Table 3) using Eqs. (1)–(3).

net soil C sink generated from croplands between 1980 and 1999 (Lal, 2004a; Huang et al., 2007; Piao et al., 2009).

## 4. Discussion

### 4.1. Evolution and spatial distribution of phytolith C sink

The PhytOC released from litters of terrestrial plants can be accumulated in soil profiles along with other inert organic C forms (Wilding et al., 1967; Mulholland et al., 1992; Parr and Sullivan, 2005). This acts as a stable C sink in terrestrial ecosystems (Parr and Sullivan, 2005; Song et al., 2012a).

The relatively low contribution of phytoliths to the net C sink during 1980 and 1999 was enhanced due to the rapid increase in manure supplementation and a greater production of root matter and crop residues (Huang et al., 2007). The improved SOC content resulting from manure addition, increased root matter and crop residues was estimated to range from 311 to 401 Tg between 1980 and 1999 (Li et al., 2003; Huang and Sun, 2006).

The total phytolith C sink rate of China's croplands had doubled since 1978 and could be divided into three stages (Fig. 4). The total phytolith C sink increased rapidly from 2.08 Tg CO<sub>2</sub> yr<sup>-1</sup> to 3.89 Tg CO<sub>2</sub> yr<sup>-1</sup> (or 14 to 25 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) from 1978 to 1998 due to a rapid increase in the cereal yield per unit area. From 1999 to 2003, the total phytolith C sink decreased to 3.25 Tg CO<sub>2</sub> yr<sup>-1</sup> (or 21 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) due to a decrease in cereal-producing area. The total phytolith C sink increased rapidly to 4.39 Tg CO<sub>2</sub> yr<sup>-1</sup> (or

27 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) from 2004 to 2011 due to an increase in cereal (especially corn) production area and yield.

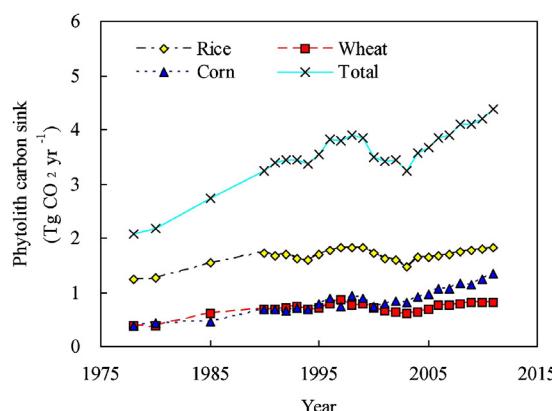
The largest phytolith C sinks in China occurred in the midsouthern (1.23 Tg CO<sub>2</sub> yr<sup>-1</sup>, or 29 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>), eastern (1.14 Tg CO<sub>2</sub> yr<sup>-1</sup>, or 30 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) and northeastern regions (0.77 Tg CO<sub>2</sub> yr<sup>-1</sup>, or 36 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>); these accounted for 28, 26 and 18% of the total national arable crop land area, respectively (Fig. 5). Regional analysis of the cropping patterns and land productivity (National Bureau of Statistics of China, 2012) suggests that the high phytolith sinks in these three regions could be attributed to the relatively high production of rice, frequent fertilizer application and irrigation.

### 4.2. The role of cereals in cropland phytolith C sink enhancement: national and global perspectives

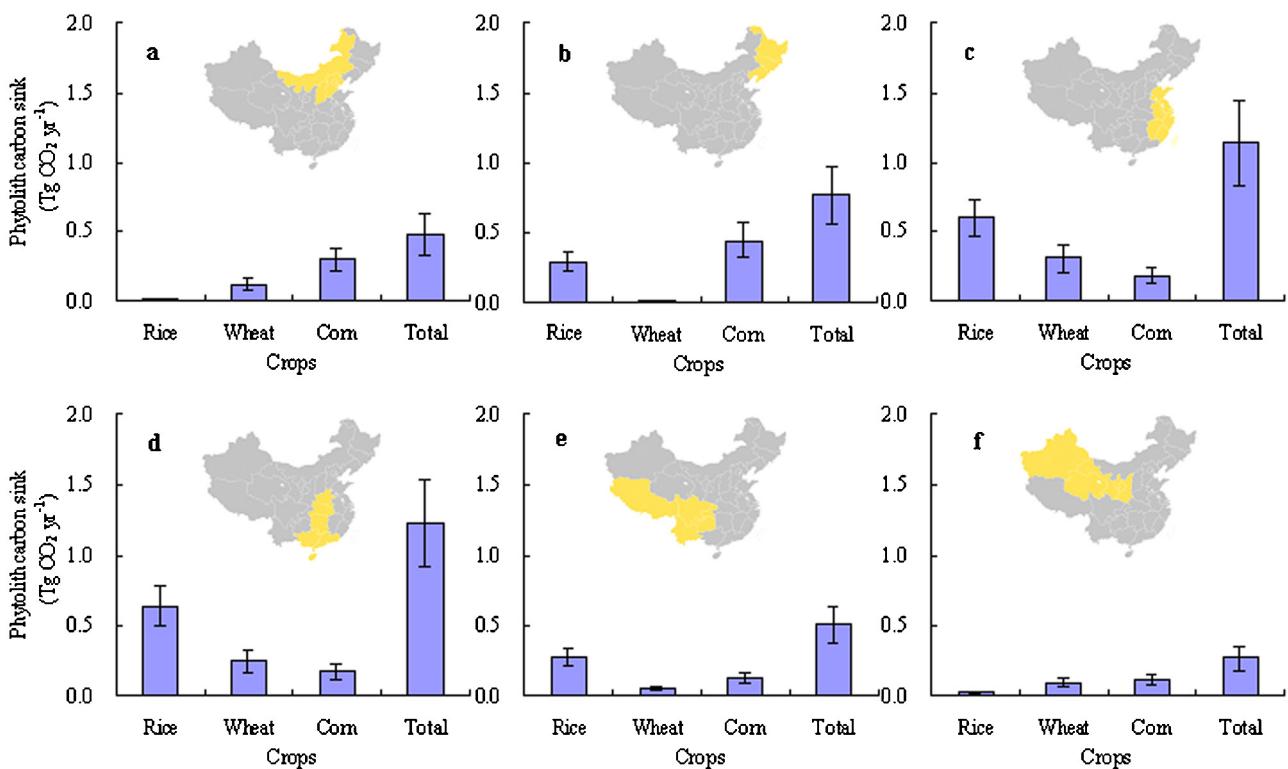
Assuming a similar phytolith C sink flux for each crop, approximately 24.39 ± 8.67 Tg yr<sup>-1</sup> of CO<sub>2</sub> could be sequestered globally. The Chinese cropland phytolith sink would sequester approximately 4.39 ± 1.56 Tg yr<sup>-1</sup> of CO<sub>2</sub> and represented approximately 18% of world's croplands (Fig. 6a). As can be seen in Fig. 6a, the total cropland phytolith C sink of China was higher than that of the USA (3.16 ± 1.12 Tg CO<sub>2</sub> yr<sup>-1</sup>) or India (2.62 ± 0.93 Tg CO<sub>2</sub> yr<sup>-1</sup>). The magnitude of the phytolith C sequestration per unit area in China (33 ± 13 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) was not significantly different to that of the USA (34 ± 14 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>), but it was higher than the annual sequestration per unit area in India (19 ± 7 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) and the world average (29 ± 12 kg CO<sub>2</sub> ha<sup>-1</sup> yr<sup>-1</sup>) (Fig. 6b). The greater cropland phytolith C sink flux in China and the USA is due to the relatively higher percentage of cereal crops such as rice and corn, frequent applications of fertilizers and the use of irrigation in these two countries, demonstrating that the national and global cropland phytolith carbon sink could be further enhanced through cropping system optimization, and rational fertilization and irrigation.

### 4.3. Contribution of phytolith C sink to C balance in croplands

Agricultural production in China and throughout the world is essential to feed the large population. Although agricultural systems were traditionally considered as one of the largest C source of atmosphere (Houghton, 1999; Houghton et al., 1999; Schimel, 1995; IPCC, 2001; Smith, 2004), they may also become important C sinks under rational management (Lal, 2001, 2004a,b,c; Six et al., 2004; Piao et al., 2009). For example, agricultural soils in China have lost 30–50% or more of the original soil organic carbon (SOC) pool (Lal, 2004a). Lal (2004a) estimated that soil C



**Fig. 4.** Phytolith C sink rate produced by arable crops in China from 1978 to 2011. Total represents the sum of all arable crops from China. The estimation is based on productivity of arable crops from 1978 to 2011 (National Bureau of Statistics of China, 2012) and Tables 2 and 3 using Eqs. (1)–(4).



**Fig. 5.** Phytolith C sink rate of arable crops in different regions of China in 2011: (a) northern China; (b) northeastern China; (c) eastern China; (d) midsouthern China; (e) southwestern China; (f) northwestern China. *Total* represents the sum of all arable crops in the same region. The estimation is based on productivity of arable crops in each region (National Bureau of Statistics of China, 2012) and Tables 2 and 3 using Eqs. (1)–(4).

sequestration potential in China is 119–226 Tg C y<sup>-1</sup> of SOC up to 50 years through adoption of recommended management practices such as integrated nutrient management (INM) and conservation tillage. This means that the total greenhouse gas production

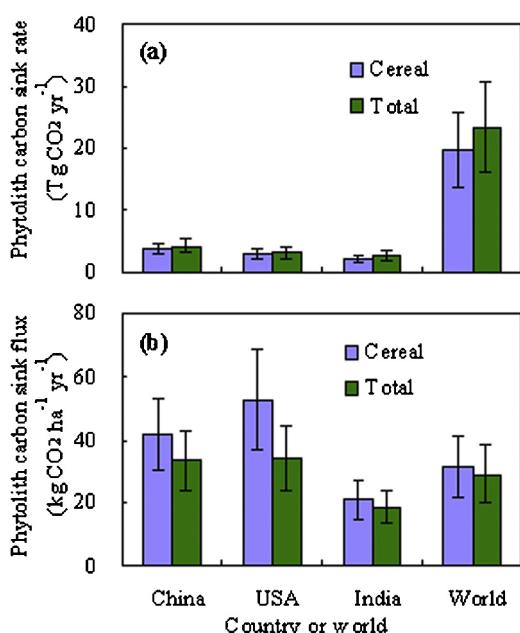
associated with fertilizer application, irrigation and other on-farm and off-farm practices can be offset by soil C sequestration in agricultural systems.

We estimated that the phytolith sink in Chinese croplands would sequester  $4.39 \pm 1.56$  Tg yr<sup>-1</sup> of CO<sub>2</sub>. Relative to other biomass carbon sequestration in agricultural systems, the carbon sequestered by phytoliths is relatively small but very stable. For example, substantial amount of straw is burned or fed to the cattle in China every year. This will cause the loss of traditional “biomass carbon” from the system. However, little PhytOC will be lost from the system because the PhytOC, protected by silica, is resistant to burning and animal digestion (Song et al., 2012b), and ash derived from straw combustion and cattle manure are usually applied back to croplands as organic fertilizers to maintain soil fertility.

Although the estimated phytolith carbon sink may not represent the net carbon balance in agricultural systems, phytolith C sequestration may contribute to the mitigation of net greenhouse gas emission in agricultural production.

## 5. Conclusions

In this paper we have estimated the phytolith C sink in China's croplands and demonstrated the role of cereals in enhancing the national and global cropland phytolith C sink. The phytoliths of croplands in China sequestered  $4.39 \pm 1.56$  Tg yr<sup>-1</sup> of CO<sub>2</sub> and represent approximately 18% of world's croplands. The cropland phytolith C sink generally increases with an increase in crop production or an increase in the relative amount of cereal crops in the croplands. Our data indicate that beneficial cropland management practices such as rational irrigation and fertilizer application, and crop pattern optimization may be taken to further enhance the phytolith C sink in croplands. Global climate change could be partially



**Fig. 6.** Phytolith C sink rate (a) and flux (b) produced by arable crops in China, USA, India and the world in 2011. *Cereal* includes rice, wheat, corn and other cereal crops, while *Total* includes all arable crops. The estimation is based on productivity of arable crops in China, USA, India and the world (FAO, 2012) and Tables 2 and 3 using Eqs. (1)–(5).

offset by increasing cropland phytolith C sequestration at both a national and global scale.

## Conflict of interest

The authors have declared no conflict of interest.

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