Potential of Global Cropland Phytolith Carbon Sink from Optimization of Cropping System and Fertilization

Zhao Liang Song1,2,3,*, Jeffrey F. Parr4, Fengshan Guo2
1 Zhejiang Provincial Key Laboratory of C Cycling in Forest Ecosystems and C Sequestration, Zhejiang Agricultural and Forestry University, Lin’an, Zhejiang, China, 2 School of Environment and Resources, Zhejiang Agricultural and Forestry University, Lin’an, Zhejiang, China, 3 State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, China, 4 Southern Cross GeoScience, Southern Cross University, Lismore, New South Wales, Australia

Abstract

The occlusion of carbon (C) by phytoliths, the recalcitrant silicified structures deposited within plant tissues, is an important persistent C sink mechanism for croplands and other grass-dominated ecosystems. By constructing a silica content-phytolith content transfer function and calculating the magnitude of phytolith C sink in global croplands with relevant crop production data, this study investigated the present and potential of phytolith C sinks in global croplands and its contribution to the cropland C balance to understand the cropland C cycle and enhance long-term C sequestration in croplands. Our results indicate that the phytolith sink annually sequesters 26.35 ± 10.22 Tg of carbon dioxide (CO2) and may contribute 40 ± 18% of the global net cropland soil C sink for 1961–2100. Rice (25%), wheat (19%) and maize (23%) are the dominant contributing crop species to this phytolith C sink. Continentally, the main contributors are Asia (49%), North America (17%) and Europe (16%). The sink has tripled since 1961, mainly due to fertilizer application and irrigation. Cropland phytolith C sinks may be further enhanced by adopting cropland management practices such as optimization of cropping system and fertilization.

Introduction

Present understanding of the global carbon (C) cycle and climate feedbacks is limited by uncertainty over terrestrial C balance [1–5]. As one of the largest terrestrial ecosystems deeply influenced by human activities, the croplands cover an area of 15.33×106 hm² globally and may play a significant role in terrestrial C balance [3,6]. Although croplands were traditionally considered to be the largest biospheric source of C lost to the atmosphere in most areas of the world [7–12], they may also be significant C sinks under proper management [3,6,13–15].

Phytolith-occluded C (PhytOC), where C is entrapped within recalcitrant silicified structures when they are deposited within plant tissues [16–18], is particularly prolific in many crops such as rice [19], wheat [20], millet [21] and sugarcane [22]. PhytOC is highly resistant against decomposition [18,23–25] and may accumulate in soil for several thousands of years after plant decomposition [18], demonstrating the potential of phytoliths in the long-term biogeochemical sequestration of atmospheric carbon dioxide (CO2) [5,26]. Soil PhytOC accumulation is an important persistent C sink mechanism for croplands [18–22] and other grass-dominated ecosystems [26,27]. Moreover, Jansson et. al. [28] suggest that the production of PhytOC in croplands could be greatly enhanced through crop breeding. However, the present and potential of global cropland phytolith C sink have not been revealed.

In the present study, we quantified the present and potential of phytolith carbon sink and its contribution to the global cropland C balance by constructing a silica content-phytolith content transfer function and calculating the magnitude of the phytolith C sink in global croplands with relevant crop data including the PhytOC and silica content, farm crop output, the Si-rich organ ratio (mass ratios of the Si-rich organ: crop output) and the PhytOC stability factor. The purposes of the study are to guide the management of cropland ecosystems to maximize phytolith C sequestration and mitigate climate change.

Materials and Methods

Ethics Statements

No specific permits were required for the described field studies, because the experimental field is owned by Zhejiang Agricultural and Forestry University, and the School of Environment and Resources performs the management. No specific permits were required for these locations/activities, because the location is not privately-owned or protected in any way, the field studies did not involve endangered or protected species, and each sample consisted of no more than 500 grams (fresh weight).
Constructing the Transfer Function for the Phytolith:Silica Content

Plant phytolith content may be estimated from plant silica content data using the transfer function for the phytolith:silica content [26]. To construct the silica content–phytolith content transfer function, mature crop organ samples were collected—each sample consisted of approximately 500 g of composite plant material.

Plant samples were oven-dried at 65°C to a constant mass and cut into small pieces (<5 mm). They were ashed at 500°C to remove organic matter, fused with lithium metaborate, dissolved in dilute nitric acid and analyzed for silica content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Optima 7000 DV, Perkin Elmer, Massachusetts, USA). Plant phytoliths were isolated using a microwave digestion process followed by a Walkley–Black type digestion to ensure the removal of extraneous organic material [19,27]. The isolated phytoliths were dried to a constant mass at 75°C for 24 h in a fan-forced oven and weighed to determine the plant phytolith content. The occluded-C content within phytoliths was also determined [19,27]. The error was <5% in phytolith and silica measurements and <10% in PhytOC measurements using plant standards (GSV-1) and triplicate analyses.

The plant silica content–phytolith content transfer function was constructed using regression analysis based on the phytolith and silica contents determined for the samples (Figure 1). Silica content was converted to phytolith content using the following equation \( R^2 = 0.806 \), \( p<0.01 \):

\[
\text{Phytolith content (wt %)} = 0.9664 \times \text{silica content (wt %)} \quad (1)
\]

Data Collection, Phytolith and PhytOC Content Estimation

Farm productivity data was obtained from Food and Agriculture Organization of the United Nations (FAO) Statistics [29]. Silica content data was obtained from published monographs [30,31], papers [19–21,32,33] and also determined in the present study. Silica content of crop species was used to estimate phytolith content using a conversion factor of 0.9664; see equation (1). The PhytOC content in plant organs was estimated from phytolith content data using an occluded-C content in phytolith of 2–4% (average 3%) according to the present study and references [19–21,27].

Estimating PhytOC Production and the Phytolith C Sink

The production of PhytOC is primarily affected by plant PhytOC concentration and aboveground net primary productivity (ANPP) of Si-rich organs [34], where plant PhytOC is mainly determined by PhytOC content in phytoliths [26] and plant Si content [30,33]. This allowed the crop PhytOC production rate to be estimated from the PhytOC content and total ANPP of the Si-rich organs of an area as:

\[
\text{PhytOC production rate} = \text{PhytOC content} \times \text{ANPP of Si-rich organs} \times 44/12 \quad (2)
\]

where PhytOC production rate is the PhytOC production by a particular crop’s Si-rich organs per year (Tg CO₂ yr⁻¹). PhytOC content is the concentration of PhytOC in a crop’s Si-rich organs (wt %) and ANPP is the total aboveground net primary productivity of Si-rich crop organs (Tg yr⁻¹) of an area estimated from Si-rich organ factor [35,36] and crop output [29].

As the PhytOC sequestration rate is controlled by the PhytOC production rate in plants and the stability of phytolith in environments, the phytolith C sink rate can be estimated from data of PhytOC production rate and phytolith stability factor as:

\[
\text{Phytolith C sink rate} = \text{PhytOC production rate} \times \text{phytolith stability factor} \quad (3)
\]

where PhytOC production rate may be estimated from equation (2) and the phytolith stability factor is assumed to be 0.9±0.05 as most phytoliths have been proved stable for thousands of years though some small phytolith particles containing little carbon may be partly dissolved depending on formation sites and chemical
composition of phytoliths in plant organs, and deposition environments of phytoliths after plant decay [18,25].

**Results**

**Distribution of PhytOC in Dominant Arable Crops**

The global area of croplands is $1552.6 \times 10^6$ ha, about half of which is covered by cereals (Table 1). The PhytOC content varies greatly among different crops (0.02–0.25%, with an average of 0.13%) (Table 1). Generally, sugar cane and cereals have higher PhytOC contents in dry biomass (0.16–0.25%) than other crops (0.02–0.08%). Within cereals, rice has higher PhytOC content in dry biomass (0.25±0.07%) than other cereal crops such as wheat (0.16±0.08%) and maize (0.16±0.05%).

| Farm crops          | Crop output (Tg yr$^{-1}$)$^a$ | Si-rich organ factor$^b$ | ANPP$^c$ of Si-rich organs (Tg yr$^{-1}$)$^c$ | Phytolith C sink (Tg CO$_2$ yr$^{-1}$)$^d$ |
|---------------------|---------------------------------|--------------------------|-----------------------------------------------|----------------------------------------|
|                     |                                 |                          |                                               | Mean                                   |
| Crops (total)        | 1.43                            | 8091                     | 26.35                                         |
| Cereals (total)      | 2587                            | 1.37                     | 3557                                          |
| Rice                 | 723                             | 1.1                      | 795                                           |
| Wheat                | 704                             | 1.29                     | 906                                           |
| Maize                | 883                             | 1.35                     | 1194                                          |
| Soybeans             | 261                             | 1.5                      | 391                                           |
| Roots and Tubers     | 807                             | 0.58                     | 468                                           |
| Oil-bearing crops    | 105                             | 2.2                      | 231                                           |
| Seed cotton          | 77                              | 2.91                     | 225                                           |
| Sugar cane$^e$       | 1794                            | 0.18                     | 323                                           |

$^a$Values from FAO [29];
$^b$mass ratios of the Si-rich organ: crop output from Huang et al. [35] and Zhu et al. [36];
$^c$ANPP: above-ground net primary productivity;
$^d$Estimated from the crop output and Si-rich organ factor and PhytOC content in Table 1 using equations (2, 3);
$^e$The crop output of sugar cane is fresh cane weight.

doi:10.1371/journal.pone.0073747.t002

Figure 2. Phytolith carbon sink production by farm crops from different continents in 2011. Where A: Asia, B: Europe, C: Africa, D: North America, E: South America, F: Oceania. ‘Crops’ represents the sum of all farm crops and “Cereals” represents the sum of all cereal crops including rice, wheat, maize etc.

doi:10.1371/journal.pone.0073747.g002
Phytolith Carbon Sink of Global Croplands

The phytolith C sink varies greatly among different crops (Table 2). The phytolith C sinks generated by rice, wheat and maize (6.60±1.99, 4.93±2.30 and 6.14±2.46 Tg CO2 yr⁻¹, respectively) are much higher than other crops. The total phytolith C sink produced by global farm crops is around 26.35±10.22 Tg CO2 yr⁻¹, 85% of which is contributed from cereals, including rice (25%), wheat (19%) and maize (23%).

Figure 2 displays the relative land area of the major continents and the phytolith C sink produced by farm crops in each in 2011. The largest phytolith C sinks occur in Asia (12.80±4.90 Tg CO2 yr⁻¹), North America (4.50±1.74 Tg CO2 yr⁻¹) and Europe (4.21±1.66 Tg CO2 yr⁻¹), which account for 49, 17 and 16% of the total global croplands, respectively.

The total phytolith C sink of global croplands has tripled since 1961 (Figure 3). In general, the evolution of the phytolith C sink since 1961 may be divided into three stages:

1) 1961–1982: the total phytolith C sink increased steadily from 8.61 to 16.57 Tg CO2 yr⁻¹.
2) 1983–2002: the total phytolith C sink fluctuated, with a slow increase from 15.99 to 20.51 Tg CO2 yr⁻¹.
3) 2003–2011: the total phytolith C sink increased, with some fluctuation, from 21.14 to 26.35 Tg CO2 yr⁻¹.

| Period | Phytolith C | Soil C | Phytolith C contribution (%) |
|--------|------------|--------|-----------------------------|
|        | 1961–2100  | 1961–2015       | 2016–2100              |
| Sink rate (Pg CO₂ yr⁻¹) | 0.03±0.01 | -2.93 | 2.02 | 0.08 | 40±18 |
| Total sink (Pg CO₂) | 4.2±1.9 | -161.2 | 171.7 | 10.6 | 40±18 |

Table 3. Contribution of the phytolith C sink to the global cropland C balance for 1961–2100.

Sinks are positive values and sources are negative values.

**Note:** The average soil C sink rate data of 1961–2015 are after Ruddiman [37]. The average soil C sink rate data of 2016–2100 are after Lal [6,14] assuming judicious land use and recommended management practices (RMPs) are applied worldwide during 2016–2100.

doi:10.1371/journal.pone.0073747.t003
cropping index may significantly increase the total cropland phytolith C sink by enhancing crop output with low costs.

Fertilization measures include silicon fertilizer application, rock powder amendment, organic mulching, and traditional fertilization (Table 4). Silicon fertilizer application, rock powder amendment and organic mulching will increase soil bioavailable silicon input, plant silicon uptake and phytolith content for cereals and sugarcane [5,19]. Traditional fertilization (N, P, K fertilizer application) may also increase total phytolith C sink in croplands by enhancing crop output.

Although the potential measures proposed for promoting cropland phytolith C sink based on the study are verifiable, more data is required. The exact efficiency and costs of the proposed measures need further assessment before practical measures may be implemented to sequester globally-significant amounts of atmospheric CO2.

Conclusions

Relative to the liable biomass C sink, the phytolith C sink in croplands is certain and stable, and can be sustained for several hundreds or thousands of years in most regions of the world. The phytolith sink of global croplands is a stable net sink of 6.26.35±10.22 Tg CO2 yr⁻¹, and may play a significant role in global cropland C balance for 1961–2100. The high phytolith sinks in Asia, North America and Europe can be attributed to the relatively high production of rice, maize, and wheat, respectively. The total phytolith C sink of global croplands has tripled since 1961 mainly due to fertilization, irrigation and cropland expansion. Taking an average phytolith C sink rate of 0.03 Pg CO2 yr⁻¹, the total phytolith C sink of global croplands during 1961 and 2100 is 4.2±1.9 Pg CO2 yr⁻¹, 40±18% of the total net soil C sink. Our data suggest that the cropland phytolith C sinks may be further enhanced by adopting cropland management practices such as optimization of cropping system and fertilization.

Acknowledgments

We thank Mr. David Cushley of ISE for language editing.

Author Contributions

Conceived and designed the experiments: ZLS JFP. Performed the experiments: ZLS FSG. Analyzed the data: ZLS. Contributed reagents/materials/analysis tools: ZLS. Wrote the paper: ZLS JFP FSG.

References

1. Cao M, Woodward FI (1998) Dynamic responses of terrestrial ecosystem carbon cycling to global climate change. Nature 393: 249–252.
2. Heimann M, Reichstein M (2008) Terrestrial ecosystem carbon dynamics and climate feedbacks. Nature 451: 289–292.
3. Piao S, Fang J, Ciais P, Pei L, Huang Y, et al. (2009) The carbon balance of terrestrial ecosystems in China. Nature 458: 1008–1013.
4. Pan Y, Birdsey RA, Fang J, Houghton R, Kauppi PE, et al. (2011) A large and persistent carbon sink in the world’s forests. Science 333: 988–993.
5. Song ZL, Wang HL, Strong P, Li ZM, Jiang FK (2012a) Plant impact on the coupled terrestrial biogeochemical cycles of silicon and carbon: Implications for biogeochemical carbon sequestration. Earth-Sci Rev 155, 319–331.
6. Lal R (2004a) Soil carbon sequestration impacts on global climate change and food security. Science 304: 1623–1627.
7. Houghton RA (1992) Changes in the storage of terrestrial carbon since 1850 In: Lal R, Kimble JM, Levine E, Stewart BA (Eds.), Soils and Global Change, CRC/Lewis, Boca Raton, FL, pp. 45–65.
8. Houghton RA (1999) The annual net flux of carbon to the atmosphere from changes in land use 1850 to 1990. Tellus 50B: 298–313.
9. Houghton RA, Hackett JL, Lawrence KT (1999) The U.S. carbon budget: contributions from land-use change. Science 285: 574–578.
10. Schimel DS (1995) Terrestrial ecosystems and the carbon cycle. Global Change Biol 1: 77–91.
11. Intergovernmental Panel on Climate Change (IPCC) (2001) Climate Change: The Scientific Basis. Cambridge Univ Press, Cambridge, UK.
12. Smith PC (2004) Carbon sequestration in croplands: the potential in Europe and the global context. Eur J Agron 20: 229–236.
13. Lal R (2001) Managing world soils for food security and environmental quality. Adv Agron 71: 155–192.
14. Lal R (2004b) Soil carbon sequestration to mitigate climate change. Geoderma 123: 1–22.
15. Six J, Ogle SM, Jay breith F, Courant KT, Mosier AR, et al. (2004) The potential to mitigate global warming with no-tillage management is only realized when practiced in the long term. Global Change Biol 10: 155–160.
16. Siever R, Scott RA (1963) Organic geochemistry of silica, in: Berger IA (Ed.), Organic Geochemistry. Pergammon Press, Elmsford, NY, pp. 579–595.
17. Piperme DR (1980) Phytolith Analysis: An Archaeological and Geological Perspective. Academic Press, London.
18. Parr JF, Sullivan LA (2005) Soil carbon sequestration in phytoliths. Soil Biol Biochem 37: 117–124.
19. Li ZM, Song ZL, Parr JF, Wang HL (2013) Occluded C in rice phytoliths: implications to biogeochemical carbon sequestration. Plant Soil. Published online first. DOI: 10.1007/s11104-013-1661-9.
20. Parr JF, Sullivan LA (2013) Phytoliths occluded carbon and silica variability in wheat culinaria. Plant Soil 362: 165–171.
21. Zuo X, Lu H (2011) Carbon sequestration within millet phytoliths from dry-farming of crops in China. Chinese Sci Bull 56: 3451–3456.
22. Parr JF, Sullivan LA, Quirk R (2009) Sugarcane phytoliths: Encapsulation and sequestration of a long-lived carbon fraction. Sugar Tech 11: 17–21.
23. Wilding LP (1967) Radiocarbon dating of biogenic opal. Science 156: 66–67.
24. Mulholland SG, Prior C (1993) Processing of phytoliths for radiocarbon dating by AMS. Phytolithenarian Newsletter 7: 7–9.

Table 4. Potential measures to enhance global cropland phytolith carbon sink.

| Types | Measures | Mechanisms | Comments |
|-------|----------|------------|----------|
| Optimization of cropping system | Enhancement of cereal percentage in croplands | Enhancing crop output and phytolith content | High efficiency in all croplands with low costs |
| | Enhancement of multi- cropping index | Enhancing crop output | High efficiency in all croplands with low costs |
| Fertilization | Silicon fertilizer application | Enhancing crop phytolith content | High efficiency in cereal croplands and sugarcane with high costs |
| | Rock powder amendment | Enhancing crop phytolith content | High efficiency in cereal croplands and sugarcane with low costs |
| | Organic mulching | Enhancing crop output and phytolith content | High efficiency in cereal croplands and sugarcane with low costs |
| | Traditional fertilization | Enhancing crop output | High efficiency with high costs |
25. Meunier JD, Colin F, Alarcon C (1999) Biogenic silica storage in soils. Geology 27: 835–838.

26. Song ZL, Liu HY, Si Y, Yin Y (2012b) The production of phytoliths in the grasslands of China: implications to biogeochemical sequestration of atmospheric CO2. Global Change Biol 18: 3647–3653.

27. Parr JF, Sullivan LA, Chen B, Ye G, Zheng W (2010) Carbon bio-sequestration within the phytoliths of economic bamboo species. Global Change Biol 16: 2661–2667.

28. Jansson C, Wallischleger SD, Kalluri UC, Tuskan GA (2010) Phytosequestration: Carbon biosequestration by plants and the prospects of genetic engineering. BioScience 60: 685–696.

29. Food and Agriculture Organization of the United Nations. FAO (2012): Statistics. Available: http://faostat.fao.org/site/567/default.aspx, from 1961 to 2011.

30. Hou X (1982) Vegetation Geography of China and Chemical Composition of its Dominant Plants, Science Press, Beijing, pp, 188–243.

31. Xu X, Yang L, Dong Y (1998) Rice field ecosystem in China. China Agriculture Press.

32. Zhou Q, Li Y, Liu J, Ye Y, Yang L (2005) Effects of irrigation on the vascular bundle structures and contents of silicon, magnesium and zinc in leaves of two sugarcane varieties. Sugar Crops of China (in Chinese with English abstract) 2: 1–4.

33. Ding TP, Tian SH, Sun L, Wu LH, Zhou JX et al. (2008) Silicon isotope fractionation between rice plants and nutrient solution and its significance to the study of the silicon cycle. Geochim Cosmochim Ac 72: 5600–5615.

34. Blecker SW, McCulley RL, Chadwick OA, Kelly EF (2006) Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochem Cy 20: 1–11.

35. Huang Y, Zhang W, Sun WJ, Zheng XH (2007) Net primary production of Chinese croplands from 1950 to 1999. Ecol Appl 17: 692–701.

36. Zhu J, Li R, Yang X (2012) Spatial and temporal distribution of crop straw resources in 30 years in China. Journal of Northwest A & F University (in Chinese with English abstract) 40: 139–145.

37. Ruddiman WF (2003) The anthropogenic greenhouse era began thousands of years ago. Climate Change 61: 261–293.

38. Fang J, Chen A, Peng G, Zhao S, G Li (2001) Changes in forest biomass carbon storage in China between 1949 and 1998. Science 292: 2320–2323.