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Biogeochemical sequestration of carbon within phytoliths of wetland plants: A case study of Xixi wetland, China

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As an important long-term terrestrial carbon sequestration mechanism, biogeochemical sequestration of carbon within phytoliths may play a significant role in the global carbon cycle and climate change. The aim of this study is to explore the potential of carbon bio-sequestration within phytoliths produced by wetland plants. The results show that the occluded carbon content of phytoliths in wetland plants ranges from 0.49% to 3.97%, with a CV (coefficient of variation) value of 810%. The data also indicate that the phytolith-occluded carbon (PhytOC) content of biomass for wetland plants depends not only on the phytolith content of biomass, but also the efficiency of carbon occlusion within phytoliths during plant growth in herb-dominated fens. The fluxes of carbon bio-sequestration within phytoliths of herb-dominated fen plants range from 0.003 to 0.077 t CO_2 equivalents t-e-CO_2 ha^{-1} a^{-1}. In China, 0.04×10^6 to 1.05×10^6 t CO_2 equivalents per year may be sequestrated in phytoliths of herbaceous-dominated fen plants. Globally, taking a fen area of 1.48×10^8 ha and the largest phytolith carbon biosequestration flux (0.077 t-e-CO_2 ha^{-1} a^{-1}) for herb-dominated fen plants, about 1.14×10^7 t CO_2 equivalents per year would have been sequestrated in phytoliths of fen plants. If other wetland plants have similar PhytOC production flux with herb-dominated fen plants (0.077 t-e-CO_2 ha^{-1} a^{-1}), about 4.39×10^7 t-e-CO_2 a^{-1} may be sequestrated in the phytoliths of world wetland plants. The data indicate that the management of wetland ecosystems (e.g. selection of plant species) to maximize the production of PhytOC have the potential to bio-sequestrate considerable quantities of atmospheric CO_2.

carbon sequestration, fen plants, wetland, phytolith occluded carbon (PhytOC), China

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The global concentration of atmospheric CO_2 has increased significantly from ~280 to 391 ppmv since 1750 as a result of human activities such as fossil fuel combustion, deforestation, biomass burning and land use change [1]. As global increase of atmospheric CO_2 concentration may cause dangerous climate change [2], various approaches that can securely reduce and sequestrate carbon emissions are being pursued, and among the most promising is the terrestrial biogeochemical carbon sequestration [2,3].

One relatively stable form of organic carbon that is biogeochemically sequestrated within the silica biomineralisation features of terrestrial plants and that can accumulate in soil after the decomposition of that vegetation is the phytolith occluded carbon (PhytOC) fraction [4]. The PhytOC is more stable and can sustain much longer than other organic carbon fractions in the soil because of its strong ability to resist decomposition [4–9]. For example, it has been reported that PhytOC in soil and sediments ranges in age from 0 to 8000 a BP [4]. One previous work found that PhytOC remained in soil for 13300 ± 450 a BP [10]. As an important part of terrestrial carbon, it can reach 82% of total carbon in some soil and sediments after 2000 years of litter leaf de-

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*Corresponding author (email: songzhaoliang78@163.com) composition [4].

Phytoliths have great potential to sequestrate atmospheric CO_2 through the formation of PhytOC [11–15], and play a crucial function in the long-term terrestrial carbon cycle [3, 4] and climate change [16–18]. The fluxes of millet, wheat and sugarcane for phytolith carbon bio-sequestration range up to 0.038 [14], 0.246 [13] and 0.36 t-e-CO_2 ha^{-1} a^{-1} [11], respectively. In particular, the flux of carbon occluded within phytoliths of bamboo ranges up to 0.709 t-e-CO_2 ha^{-1} a^{-1}, and current global bamboo forests (22 million ha) can securely sequestrate 1.56×10^7 t of atmospheric CO_2 per year. Researchers have suggested that if all potentially arable land (4.1 billion ha) is exploited to grow bamboo or other similar grass crops, the global potential of phytolith carbon bio-sequestration would approximately be 1.5 billion t-e-CO_2 a^{-1} equivalent to 11% of the current increase in atmospheric CO_2 [12]. The data indicate that the management of plants with high PhytOC content to maximize biomass production could adequately improve the secure terrestrial carbon sequestration [12,13]. However, current estimation of global phytolith carbon bio-sequestration potential by Parr et al. [12] is based on a very small dataset. Under realistic conditions, much more work should be done before the strategy of PhytOC enhancement can be applied to sequestrate globally significant amounts of CO_2.

The widespread wetland ecosystem with fast plant growth and high biomass is an important terrestrial carbon sink, and plays an important role in global carbon cycle [19–21] and global climate change [22–24]. As one of the important constituents of terrestrial ecosystems, wetlands store 15% of the total terrestrial carbon though it occupies only about 1% of the terrestrial surface [25]. Furthermore, the wetlands are mainly dominated by Poaceae, which are known to be proficient silica accumulators [26–29]. However, to our best knowledge, the potential of wetland phytoliths in the long-term biogeochemical sequestration of atmospheric CO_2 has not been quantified globally and even regionally. The main purpose of this study is to examine the rates of silica accumulation and carbon bio-sequestration within the phytoliths of wetland plants.

1 Materials and methods

1.1 Collection of wetland plant materials

The Xixi wetland (30°3′35″–30°21′28″N, 120°0′26″–120°9′27″E), a rare urban natural wetland with an area of 10.64 square kilometers, is located in the west part of Hangzhou, Zhejiang Province, China (Figure 1) [30,31]. It has rich ecological resources and simple natural landscapes densely crisscrossed with scattered ponds, lakes and swamps [32]. The site has a subtropical humid monsoon climate with an average annual precipitation of 1400 mm, an annual mean temperature of 16.2°C. The site is composed of paddy soil, boggy soil, and deposited soil [33].

The entire Xixi wetland is mainly dominated by herbaceous plants (*Triarrhena sacchariflora*, *Phragmites australis*, *Cortaderia selloana*, *Arundo donax*, *Phyllostachys propinqua*, *Cyperus alternifolius*, *Arthraxon hispidus*, etc.). Some trees (*Salix spp*, *Melia azedarach*, *Broussonetia papyrifera*, *Morus,* etc.) and shrubs (*Clerodendrum trichotomum*, *Lonicera japonica*, *Rosa multiflora*, etc.) are growing around the edges of the river base [34]. According to the classification system of Scott and Jones [35], the Xixi wetland is classified as fen [36–38].

In this study, three replicates of the 18 plant species belonging to different growth types (riparian plants, shallow water emergent plants and floating-leaf aquatics) (Figure 1 and Table 1) were randomly sampled at different sites of Xixi wetland to determine the variations of phytolith accumulation and to examine the global phytolith carbon bio-sequestration potential in wetland ecosystem. All collected plants were the herbaceous species that have large aboveground net primary productivity (ANPP) in Xixi wetland. They were collected at maturity in October, 2011, to ensure valid comparison and to obtain maximum flux of phytolith

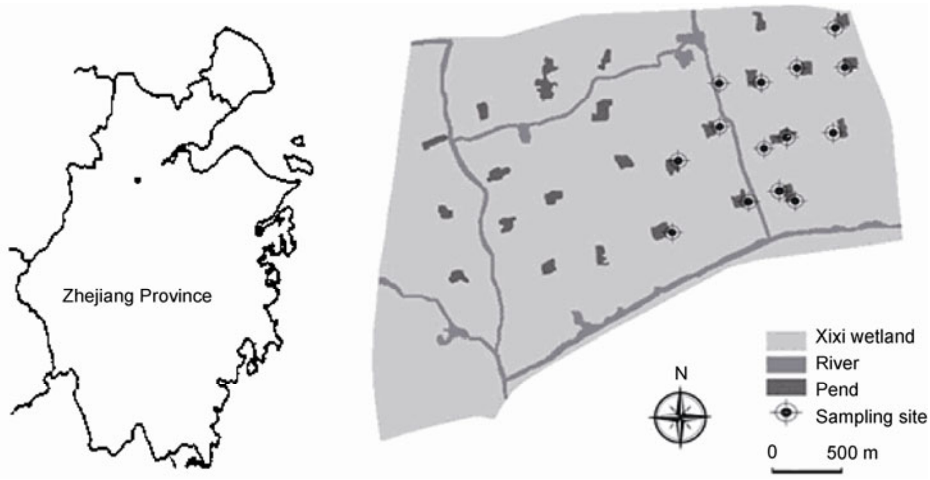

Figure 1 The location of Xixi wetland and sampling site.

accumulation [39–41].

1.2 Determination of Phytolith and PhytOC contents

The root of the collected plants was discarded and the rest of the samples such as the stem, leaf, and spike were placed in an ultrasonic bath for 15 min, rinsed three times with ultrapure water, dried at 75°C for 48 h, and then cut into small pieces (<5 mm). The phytolith samples were extracted by microwave digestion procedures [42]. This process was followed by a Walkley-Black type digest to thoroughly remove extraneous organic materials in the samples [12,43]. The possible extraneous organic materials outside of the phytolith cells were examined with 0.8 mol/L potassium dichromate. If the color of solution did not change within 5 min, it showed that the extraneous organic materials outside of the phytoliths were thoroughly removed. The phytoliths extracted were oven-dried at 75°C for 24 h in a centrifuge tube of known weight. The samples were allowed to cool and then weighed to obtain the phytolith quantities. The extracted phytolith samples were checked with an optical microscope (Olympus CX31, Japan) to ensure that all extraneous organic materials were thoroughly removed [12–15,44,45]. Based on the methods of Kroger et al. [46], the dried phytolith samples were treated with 1 mol/L HF at 55°C for 60 min to dissolve phytolith-Si. The organic carbon released from phytoliths after HF treatment was dried at 45°C and determined for carbon content using the classical potassium dichromate method [47]. The organic carbon data was monitored with standard soil samples of GBW07405. The precision is better than 7%.

2 Results

As Table 1 shows, the phytolith content of biomass has a significant variation (1.01%–7.69%) among the 18 plant species. The phytolith contents of biomass for riparian plants (2.32%–7.56%, average 4.88%) and shallow-water emergent plants (1.01%–7.69%, average 4.14%) are higher than that (1.88%–2.11%, average 2.00%) for floating-leaf aquatics. The occluded carbon contents of phytoliths from riparian plants (0.49%–3.94%, average 1.59%) and shallow-water emergent plants (1.10%–2.33%, average 1.56%) are also higher than that (0.91%–1.94%, average 1.42%) from floating-leaf aquatics (Table 1). There are substantial

Table 1 The content and production of phytoliths and PhytOC together with biomass in 18 plants

Growth types	Plants species	The phytolith content mean (s. d) (%)	The occluded carbon content of phytoliths mean (s. d) (%)	PhytOC content of biomass (dry weight) mean (s. d) (%)	Estimated PhytOC fluxes (kg-e-CO$_2$ ha^{-1} a^{-1})	Biomass (t-ha^{-1} a^{-1}) (Max)
Riparian plants	*Leersia sayanuka Ohwi*	5.29 (1.64)	2.66 (1.75)	0.14 (0.114)	0.076–0.745	0.080 [48]
	Setaria viridis	7.56 (0.23)	0.87 (0.50)	0.07 (0.040)	0.012–0.043	0.011 [49]
	Eleusine indica	4.11 (0.07)	1.50 (0.11)	0.06 (0.005)	0.365–0.432	1.181 [50]
	Digitaria ternata	6.88 (0.17)	1.06 (0.08)	0.07 (0.007)	0.462–0.565	0.200 [51]
	Arthraxon lanceolatus	5.51 (0.27)	2.91 (0.77)	0.16 (0.050)	12.342–23.562	3.060 [52]
	Arthraxon hispidus	3.40 (0.52)	3.97 (0.11)	0.13(0.024)	11.893–17.279	3.060 [52]
	Cynodon dactylon	6.35 (0.27)	0.64 (0.03)	0.04 (0.003)	15.602–18.132	11.500 [53]
	Trifolium incarnatum	2.32 (0.70)	0.49 (0.11)	0.01 (0.006)	1.321–5.286	9.010 [54]
	Echinochloa crusgalli	2.59 (0.69)	1.20 (0.11)	0.03 (0.011)	0.058–0.125	0.083 [55]
	Paspalum paspaloides	4.78 (0.22)	0.60 (0.30)	0.03 (0.013)	0.052–0.131	0.083 [55]
	Mean (s.d)	4.88 (1.78)	1.59 (1.18)	0.07 (0.052)		
	Total				42.183–66.298	28.268
Shallow-water emergent plants	*Canna indica*	1.01 (0.31)	1.10 (0.11)	0.01 (0.005)	3.775–11.325	20.590 [56]
	Cyperus alternifolius	1.51 (0.59)	1.70 (0.19)	0.03 (0.013)	21.213–53.701	34.060 [57]
	Arundo donax	4.22 (0.27)	1.31 (0.62)	0.06 (0.030)	19.558–58.674	17.780 [58]
	Cortaderia selloana	7.69 (0.03)	1.50 (0.24)	0.12 (0.019)	59.253–81.547	16.000 [59]
	Phragmites australis	6.60 (0.54)	2.33 (0.30)	0.15(0.032)	103.321–159.359	23.880 [60]
	Triarrhena sacchariflora	3.84 (0.18)	1.42 (0.34)	0.05 (0.016)	37.400–72.600	30.000 [61]
	Mean (s. d)	4.14 (2.66)	1.56 (0.43)	0.07 (0.055)		
	Total				241.083–426.91	142.310
Floating-leaf aquatics	*Halerpestes cymbalaria*	2.11 (0.26)	0.91 (0.07)	0.02(0.004)	58.186–87.278	99.180 [62]
	Salvinia natans	1.88 (0.36)	1.94 (0.77)	0.04(0.021)	0.320–1.029	0.460 [63]
	Mean (s. d)	2.00 (0.17)	1.42 (0.73)	0.03(0.012)		
	Total				58.506–88.307	99.640

variations (0.01%–0.16%) of PhytOC contents of biomass (dry weight) for the 18 plant species (Table 1). The PhytOC contents of biomass for riparian plants (0.01%–0.16%, average 0.07%) and shallow-water emergent plants (0.01%–0.16%, average 0.07%) are much higher than that (0.02%–0.04%, average 0.03%) of floating-leaf aquatics (Table 1).

As Figure 2 shows, no obvious correlation (R^2=0.0005, P>0.05) exists between the phytolith content of biomass and the occluded carbon content of phytoliths in the 18 plant species. There is a weak positive correlation (R^2=0.3477, P<0.05) between the phytolith content of biomass and the PhytOC content of biomass among the 18 plant species (Figure 3). A strong positive correlation (R^2=0.6066, P<0.01) exists between the occluded carbon content of phytoliths and the PhytOC content of biomass among the 18 plant species (Figure 4).

3 Discussion

3.1 Mechanisms of carbon occlusion within phytoliths of wetland plants and its application

Although the PhytOC content of biomass for different plants varies greatly, the factors controlling it remain to be found. Recent studies [11–14] indicate that the PhytOC contents of biomass for sugarcane, bamboo, wheat, and millet have no direct relationship with the actual content of silica (phytoliths) taken up by the plant, and mainly depend on the efficiency of the carbon occlusion within phytoliths during plant growth. However, the positive correlations between the phytolith content of biomass and PhytOC content of biomass (R^2=0.3477, P<0.05) (Figure 3), and between the occluded carbon content of phytoliths and the PhytOC content of biomass (R^2=0.6066, P<0.01) among the 18 wetland plants (Figure 4) indicate that the PhytOC content in wetland plants might depend on both the content of phytoliths and the nature of silica occluding carbon within cells of the phytoliths during plant growth. Thus, all factors that influence the phytolith content of biomass and the efficiency of carbon sequestration within phytoliths may influence the PhytOC content of biomass for plants [15]. For example, factors including species, location, disease resistance, and nutrient requirements may play a crucial role in the accumulation of phytoliths during plant growth [15, 64,65]. The different shapes of phytoliths between different plants (e.g. between Poaceae and Leguminosae) may also cause differences in the occluded carbon content of phytoliths because of differences in specific surface area (Table 1) [15, 66,67]. However, these indirect factors remain to be examined in further studies.

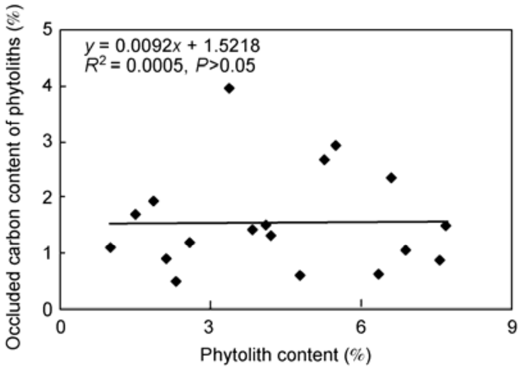

Figure 2 Correlation of the phytolith content of biomass for plants and occluded carbon content of phytoliths in the 18 plant species.

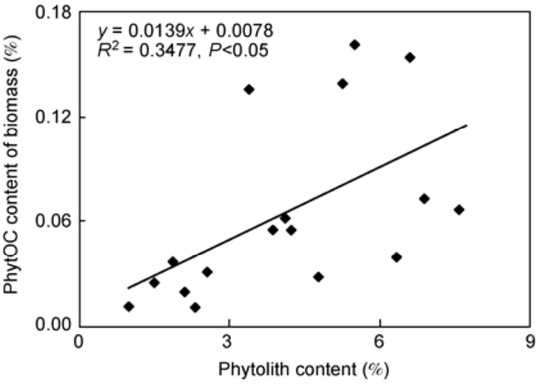

Figure 3 Correlation of the phytolith content of biomass and the PhytOC content of biomass for plants.

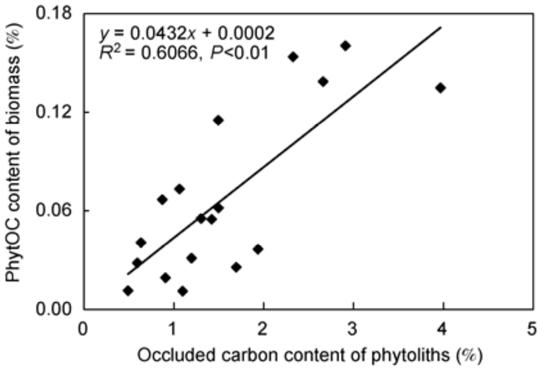

Figure 4 Correlation of occluded carbon content of phytoliths and the PhytOC content of biomass for plants.

It is possible to enhance the PhytOC content of biomass for plants by selecting plant species of high-phytolith content and high-phytolith carbon occlusion efficiency [12,13] and by regulating silicon nutrient supply. Although some plants have low phytolith carbon occlusion efficiency, it is still possible to improve the PhytOC content of biomass for plants by regulating silicon supply during plant growth. Some studies also demonstrate that the silica (phytoliths) content of biomass for plants can be effectively improved by adding silicon fertilizers [68–72], calcium-magnesium phosphate fertilizer [73], straws [74], and slag mucks [75]. Thus, it is possible to enhance the PhytOC content of biomass for plants by regulating silicon nutrient supply for some plants in artificial management ecosystems [15]. However, compared with regulation of silicon nutrient supply, the selection of plant species with high phytolith content and high phytolith carbon occlusion efficiency has a better opportunity to improve the amount of bio-sequestrated carbon during land use and land-use change [12,13,76]. As Table 1 shows, the occluded carbon content of phytoliths among 18 plants species ranges from 0.49% to 3.97%, a relative variation of 810%. Therefore, these results show that the selection of species with high-phytolith content and high-occluded carbon content of phytoliths would lead to substantial enhancement of PhytOC content of biomass for plants [11–13]. This is also applicable for other plant species with significant variation of phytolith content and the occluded carbon content of phytoliths, such as sugarcane [11], bamboo [12] and wheat [13].

3.2 Carbon sequestration potential within phytoliths of wetland plants

The annual biomass production for each of the 18 plant species was not available for the study site in Xixi wetland. However, our estimated above-ground net primary productivity (ANPP) of some wetland communities is within the range of the published data of biomass (Table 1). Thus, the published ANPP of similar wetland communities was used in conjunction with the PhytOC content of biomass to estimate the potential of each plant PhytOC fluxes (Table 1). Because of the difference of the PhytOC content of biomass and ANPP among different plants, the potential plant PhytOC fluxes range from 0.012 to 159.359 kg-e-CO_2-ha^{-1} a^{-1} (Table 1). The mean contents of phytoliths and phytolith occluded carbon for floating-leaf aquatics are much less than that of shallow-water emergent plants. The total flux (241.083–426.91 kg-e-CO_2-ha^{-1} a^{-1}) of PhytOC in shallow water emergent plants with the high-phytolith content, high-carbon occluded within phytoliths and high-biomass are significantly greater than that of riparian plants and floating-leaf aquatics. The flux (103.321–159.359 kg-e-CO_2-ha^{-1} a^{-1}) of PhytOC in *Phragmites australis* with higher content of phytolith and occluded carbon within phytoliths is much larger than that of other plants. So, it is significantly important to select a plant (e.g. *Phragmites australis*) with the high-phytolith content, high-carbon occluded within phytoliths and high-biomass grow to improve the total flux of PhytOC for plants in wetland ecosystems.

PhytOC sequestration flux of fen plant show that of herb-dominated fen ecosystem. According to the PhytOC sequestration flux of millet [14] and the global millet planting-area, the potential global total PhytOC sequestration rate of millet is estimated.

The published ANPP data of herb-dominated fen plants may be highly variable for different geographical locations and species [77–79]. For example, the estimated ANPP in mature herb-rich fen stands range from 1 to 29 t ha^{-1} a^{-1} by Wheeler and Shaw [36]. Using the published ANPP data (1–29 t ha^{-1} a^{-1}) of herb-dominated fen [36] and the mean PhytOC content of biomass for plants dry weight, the potential of PhytOC sequestration flux (0.003–0.077 t-e-CO_2 ha^{-1} a^{-1}) is quantified in herb-dominated fen ecosystem (Table 2). Compared with other studies (Table 2), the potential flux (0.003–0.077 t-e-CO_2 ha^{-1} a^{-1}) of the phytolith carbon sequestration in this study is likely to be smaller than that of bamboo, wheat, sugarcane and rice [11–13,15]. The main causes are likely that the herb-dominated fen plant's ANPP or the occluded carbon content within phytoliths is less than that of bamboo, wheat, sugarcane and rice.

According to the published fen area (1.37x10^7 ha) by NBSC [80] and our studied PhytOC sequestration flux (0.003–0.077 t-e-CO_2 ha^{-1} a^{-1}) from herb-dominated fen plants (Table 2), it is estimated that the potential rates of CO_2 occluded within phytoliths of herb-dominated fen plants vary from 0.04x10^6 to 1.05x10^6 t CO_2 equivalents per year in China. Taking the world fen area (1.48x10^8 ha) [81] and the largest phytolith carbon bio-sequestration flux (0.077 t-e-CO_2 ha^{-1} a^{-1}) of CO_2 occlusion within phytoliths from herb-dominated fen plants, about 1.14x10^7 t CO_2 equivalents per year would have been sequestrated in phytoliths of fen plants globally. As for the 5.7x10^8 ha of the world's wetlands [81], assuming a similar phytolith carbon bio-sequestration flux of 0.077 t-e-CO_2 ha^{-1} a^{-1}, the global potential rate for phytoliths carbon sequestration is estimated to be 4.39x10^7 t-e -CO_2 a^{-1}.

Although this study only chooses some Poaceae and other vegetation types to determine the variation of the PhytOC fluxes in herb-dominated fen ecosystems, the estimation of global potential CO_2 sequestration rate (4.39x10^7 t) of phytoliths in wetland plants is much higher than that of bamboo

Table 2 Comparison of estimated PhytOC fluxes and global total PhytOC rate in different ecosystems

World ecosystems	PhytOC content of biomass (dry weight) (%)	PhytOC sequestration fluxes (t-e-CO_2 ha^{-1} a^{-1})	Potential global total PhytOC sequestration rates (t-e-CO_2 a^{-1})	References
Fen	0.01–0.25	0.003–0.077	1.14x10^7	this study
Rice	0.04–0.28	0.026–0.125	1.94x10^7	[15]
Bamboo	0.24–0.52	0.008–0.709	1.56x10^7	[12]
Sugarcane	0.31–1.54	0.12–0.36	0.72x10^7	[11]
Wheat	0.06–0.60	0.006–0.246	5.3x10^7	[13]
Millet	0.04–0.27	0.008–0.038	0.27x10^7	[14]

[12], sugarcane [11], millet [14] and rice [15] (Table 2). In fact, the PhytOC as a relatively stable organic carbon formed within many plants has considerable potential for the bio-sequestration of atmospheric CO_2 [11–15]. As phytoliths can be conserved in significant quantities for thousands of years in some soils [82–84], the PhytOC may be considered as an important part of soil stable organic carbon and plays an important role in long-term carbon sequestration [4] and mitigation of global climate change [10–14]. However, this study is based on one particular type of herb-dominated fen but there are other types of wetlands with different vegetation compositions under different soil and climate conditions, and more studies need to be done to determine whether our conclusions can be extrapolated to other types of wetland ecosystems.

4 Conclusions

In this study, our results reveal that the occluded carbon content within phytoliths has substantial variation (0.49%–3.97%) in the 18 wetland plants. The data also show that the PhytOC content of biomass for plants mainly depends on the efficiency of the carbon occluded within phytoliths during plant growth, and secondarily on the phytolith content. The potential PhytOC flux for fen plants ranges from 0.012 to 159.359 kg-e-CO_2 ha^{-1} a^{-1}. The selection of species with high-phytolith content and high-occluded carbon content of phytoliths for plants would lead to substantial enhancement of the PhytOC content of biomass for plants.

The potential PhytOC sequestration fluxes vary from 0.003 to 0.077 t-e-CO_2 ha^{-1} a^{-1} in herb-dominated fen ecosystems. In China, herb-dominated fen plants may sequestrate 0.04×10^6 to 1.05×10^6 t CO_2 equivalents per year. Given the global fen area of 1.48×10^8 ha and the largest flux (0.077 t-e-CO_2 ha^{-1} a^{-1}) of the CO_2 occlusion within phytoliths of herb-dominated fen plants, we estimate that about 1.14×10^7 t CO_2 equivalents per year would have been sequestrated in phytoliths of fen plants. Our study results reveal that the 5.7×10^8 ha of the world's wetlands, assuming a similar phytoliths carbon bio-sequestration flux (0.077 t-e-CO_2 ha^{-1} a^{-1}) of herb-dominated fen plants, about 4.39×10^7 t-e -CO_2 a^{-1} may be sequestrated in phytoliths of wetland plants. However, more studies on the capacity of the PhytOC accumulation in other wetland plants are needed to quantify the global phytolith carbon bio-sequestration potential.

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