The Regulatory Role of CO₂ on Nutrient Releases from Rice-Straw Phytoliths

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Abstract

Phytolith has been widely known as a porous silica structure in numerous silicon (Si) accumulator plants, e.g., rice, that contain various nutrients and other beneficial elements too. When rice straw is returned to paddy fields, the silica structure of phytolith can be dissolved, thereby releasing its occluded nutrients. While the intrinsic characteristics and dissolution properties of phytoliths under the effect of solution chemistry have been intensively studied, the effect of gas phases, especially CO₂, on phytolith stability and the implications for nutrient release are not fully known. Here, dissolution properties of phytolith ashes obtained from dry ashing of rice straw at 400, 600 and 800°C were investigated by quantifying Si release together with other nutrients under two atmospheric conditions, i.e., without and with CO₂ support (aeration). In a time span of 6 days, the releases of nutrients (K, P, Ca, Mg) showed high dependence on the overall dissolution of the phytolith ashes. CO₂ significantly reduced the dissolution rate of the phytolith ashes but increased the release rates of cationic as well as anionic nutrients. The aeration of CO₂ shifted the carbonate equilibrium (H₂CO₃, HCO₃⁻ and CO₃²⁻) towards H₂CO₃, reducing solution pH, thereby decreasing the dissolution rate of phytoliths. Following this, intensification of H⁺ exchange promoted vast evacuation of cationic nutrients from the phytolith ashes. This indicates contrast responses of phytoliths and their occluded nutrients to CO₂, and provides a better insight on the fate of soil phytoliths and the tendency of nutrient budgets from rice straw phytoliths in soils.

Introduction

Phytolith is an amorphous silica structure that is commonly found in rice plants (*Oryza sativa* L.). Phytolith is formed due to the deposition of silicic acid in inter-and intracellular space throughout the rice plant body (Zhang et al. 2013; Nguyen et al. 2014). Recently, phytolith has received extensive attention in climate research and agro-environmental sciences because of its ability to store/encapsulate organic carbon (Li et al. 2013; Sun et al. 2017; Nguyen et al. 2019) and nutrients (Nguyen et al. 2015; Trinh et al. 2017) in its structure. However, it remains controversial regarding the fate of phytoliths, e.g., highly soluble or highly recalcitrant (Kögel-Knabner et al. 2010) and their role in sequestering organic matter (Song et al. 2016; Santos and Alexandre 2017). In straw, given amounts of nutrients might locate within phytolith and this nutrient budget has been suggested as a potential “biofertilizer” source (Nguyen et al. 2015; Trinh et al. 2017; Li and Delvaux 2019). Therefore, cycling of straw to soil is crucial to re-utilize straw phytolith and its occluded nutrients. When phytolith is dissolved, it can gradually serve as P, K, Si (Nguyen et al. 2015; Trinh et al. 2017) and other elements such as Ca, Mg, Mn for crops (Hodson and Sangster 1988). It means that the insights of dissolution properties of phytoliths are crucial for better management of the nutrient budgets from straw phytolith.

Although dissolution of phytoliths has been intensively studied for the past few decades, mechanistic understanding is still under debate (Kögel-Knabner et al. 2010; Hodson et al. 2020). Contrasting observations on dissolution properties have been reported in recent studies that examined ‘fresh’ (in straw), ‘ashed’ (in burned straw) and ‘aged’ phytoliths (in soils). It is likely that dissolution of phytoliths is

simultaneously controlled by various factors such as intrinsic characteristics (Haynes, 2017), pretreatment methods, solution chemistry (Frayse et al. 2009; Nguyen et al. 2014) and soil properties (Nguyen et al. 2019). However, there still might exist other unknown factors (e.g., microbial mining, gas exchange) that are likely involved in the dissolution of phytoliths. For example, soil gas flux and its effect on phytolith dissolution was obviously overlooked. In paddy soils, CO₂ and CH₄ are among the most common components derived from decomposition of soil organic matter and their formation/emission are tightly regulated by soil conditions such as water content, pore size distribution, temperature, pH, redox potential or microbial activity. Although the relative ratio of CO₂/CH₄ most likely depends upon the field conditions, i.e., aerobic or anaerobic environments (Yang et al. 2012; Khalid et al. 2019), the overwhelming emission of CO₂ has been commonly observed. Soil CO₂ fluxes under the aerobic condition of paddy soil can reach 8.62 μmol m⁻² s⁻¹ (Liu et al. 2013). A recent study revealed that the gas phase, e.g., CO₂, can also alter dissolution rate of phytoliths (Nguyen et al. 2021b). It was observed that increasing CO₂ can reduce solution pH, intensify surface protonation, thereby preserving the surface of phytoliths from nucleophilic attacks by water molecules and anions. A marked decrease in dissolution rate was observed in response to intensifying presence of CO₂ in phytolith suspensions (Nguyen et al. 2021b). This means that increasing CO₂ concentration can more or less inhibit dissolution of phytoliths. As a consequence, the soil phytoliths can likely exist over a longer period under the enriched CO₂ environment. Yet, to date there has been little information available to illustrate the possible governance of CO₂ gas on the fate of soil phytoliths and their occluded nutrient budgets.

Nutrients such as K and P are dominant in phytolith structure and their associations with the internal surfaces are regulated by both physical and chemical processes (Nguyen et al. 2020). The precipitation of Si to form phytolith structure throughout plant tissues was known to encapsulate/subcompartment organic matter (Song et al. 2016) and nutrients into the structure of phytoliths (Nguyen et al. 2015; Trinh et al. 2017). The association of phytolith and encapsulated/subcompartmented substances can be strengthened by various chemical processes. Although P and Si are chemical analog and theoretically making them closely occur in the phytolith structure by a mutual replacing mechanism, the resulting associations have not been proven so far. Chemically, P can connect with Si via P = Si bonds (Driess 1995). For alkaline cations such as Ca²⁺, Mg²⁺ and K⁺, they likely form new linkages with Si–O⁻ sites on phytolith surface (Nguyen et al., 2014; Nguyen et al., 2020). Their bonds (e.g., O–K) can be strengthened through agglomeration or slagging of phytolith upon burning or heating (Nguyen et al. 2020).

When straw is returned to paddy field, either by direct incorporation in the chopped form or as ashes after open burning, can lead to the release of phytoliths to soils (Nguyen et al. 2019). In contact with water, phytoliths can be dissolved, thereby releasing their occluded nutrients. As soil CO₂ flux occurs throughout the soil, it can be presumed that CO₂ and related carbonate forms contact directly with phytoliths or soil solution which is in contact with phytoliths. Although the regulatory effect of CO₂ on phytolith dissolution has been reported, with complex relevant mechanisms, it remains unclear whether or to what extent CO₂ can alter the release rate of nutrients from phytoliths.

In this study, releases of nutrients such as P, K, Ca, Mg in rice straw phytoliths under two atmospheric conditions, without or with CO₂ support (aeration), were examined. The aeration of CO₂ might not reflect the realistic soil condition and lead to overstatement of CO₂ effect. However, it can reveal the extent to which CO₂-induced changes of phytoliths can be. As CO₂ can alter solution pH and surface ionization, thereby changing the dissolution and release rates of nutrients, together with determining the releases rate of nutrients, pH and surface charge (SC) were also recorded simultaneously. Generally, the findings are expected to demonstrate the possible susceptibility of soil phytoliths and phytolith nutrient pools under the context of elevated soil CO₂, particularly when intermittent irrigation is promoted as a practice to mitigate CH₄ emission from paddy fields. The obtained results are potential to improve the prediction of the fate of millions of tons of straw phytoliths and their accompanied nutrients that are annually cycled in many paddy fields worldwide.

Materials And Methods

Sample preparation

Rice straw sample was collected from a rice field in the middle of the Red River delta at harvesting time in June 2019. The sample was washed, air-dried at room temperature, chopped into c.a. 5-cm segment, and then dried at 70°C in an oven for 48 h. Dry ashing technique was applied to separate phytoliths from the rice straw sample. Because temperature can induce various physico-chemical changes (Mai et al. 2019), the ashing procedure was conducted at low (400°C), medium (600°C) and high (800°C) temperatures. This ashing temperature was also expected to represent possible thermodynamic changes of rice straw under various thermal treatment conditions. An amount of 50 g rice straw was placed in a furnace and the pyrolysis was set up at a heating rate of 10°C min⁻¹ and then kept at target temperatures (i.e., 400, 600 and 800°C) for 1 h. The obtained phytolith ashes named as Phyt400, Phyt600 and Phyt800 (respectively) were gently grinded in an agate mortar, passed through 0.25 mm sieve. The fine phytolith ashes were washed three times with double-distilled water by centrifugation and decantation to remove free salts and were finally air-dried.

Sample characterization

A leaf from the rice straw was scanned by ZEISS Xradia 520 Versa 3D X-Ray microscope at the University of Kassel, from which phytolith structure and the principal arrangement of organic matter were visualized. The open-code YaDiV software (Friese et al. 2013) was used to assemble individual 2D image slices with 995 × 972 isotropic pixels with a pixel size of 1.14 µm and build up 3D images. The element densities were represented by the 256 greyscale values. Grey values of ca. 190–255 were assigned to the silica phytolith phase, whereas grey levels from 115–175 were attributed to the organic matter phase. The silica and organic matter phases were then visualized. For phytolith ashes, the samples were prepared on thin laminated glass slides for microscopic observation. Microstructural and morphological properties of the phytolith ashes were examined by scanning electron microscopy (SEM, FEI Quanta 600 FEG) and powder X-ray diffraction (Bruker AXS D5005). The surface functional groups and changes due

to different pretreatments were identified by using Fourier-transform infrared spectroscopy (Nicolet™ iSTM5 FT-IR, Thermo Scientific). The chemical composition of the phytolith ashes (listed in Table 1) was analyzed using an energy-dispersive X-ray spectrometer (EDS, Oxford ISIS 300) that was coupled with the SEM.

Table 1
Chemical composition of the phytolith ashes, derived from the pyrolysis at 400°C (Phyt400), 600 °C (Phyt600) and 800 °C (Phyt800). Values were obtained from EDS spectra of the bulk phytolith ash samples.

Sample	C	O	Si	K	Ca	Mg	P
	(%)						
Phyt400	17.9	36.56	24.54	6.73	3.9	0.33	<i>n.d.</i>
Phyt600	25.5	38.12	20.4	3.91	4.6	0.9	<i>n.d.</i>
Phyt800	11.65	35.56	27.37	7.7	5.46	0.81	<i>n.d.</i>
<i>n.d.: not detectable</i>							

(Table 1)

Kinetic batch experiments

The dissolution of phytoliths accompanying releases of nutrients was examined by performing batch experiments. Each 100 mg of the phytolith ashes was mixed with 100 mL double-distilled water and then transferred to a 150 mL polyethylene plastic tube. To identify the effect of CO₂, two parallel systems, i.e., without or with CO₂ support (aeration of CO₂), were installed. For examining the releases of Si and nutrients (K, Ca, Mg and P) under the support of CO₂, the plastic tubes were connected with a CO₂-gas tank, and the aeration was controlled at the supply rate of 0.1 L min⁻¹. CO₂ gas (99.99%) was provided by Ha Bac Nitrogenous Fertilizer and Chemical Ltd. Company. Meanwhile, the experiments without CO₂ support were not connected to CO₂ source and exposed to ambient air. All the experiments were lasted for 6 days in which pH and SC were recorded every 24 h by a pH meter using a gel filled electrode and a particle charge detector (PCD 05, Muetek). Additionally, subsamples were also collected every 24 h and the supernatants were passed through a 0.45 µm cellulose acetate filter. Soluble concentrations of P, K, Ca and Mg were determined using inductively coupled plasma-mass spectrometry (ICP-MS 7900, Agilent Technologies), while soluble Si (represents phytolith dissolution) was analyzed using the molybdate blue method with a Spectrophotometer UV – Vis (L-VIS-400, Labnics Company), the detection limit of the method was 0.1 mg L⁻¹. All experiments were conducted in triplicate.

Statistical analysis

Principal component analysis (PCA) was based on the correlation matrix between released elements from the kinetic batch experiments as variables to identify differences in the quantitative characteristics of

release between Si and other nutrients. PCA was illustrated graphically by plotting the eigenvector values and PC scores in the plane of the first two principal components (PC1 and PC2). The plots were created using the XLSTAT add-on installed in Microsoft Excel software. Additionally, Pearson's correlation analysis was performed using SPSS software to enable us to evaluate direct bivariate relations among released ions.

Results

Phytolith in rice plant and its derived ashes

Tomographic 3D image captured for a dry leaf fragment is shown in Fig. 1a. The silicified phytolith structure can be indicated by the two distinctive parts, the silica and organic matter phase. The deposition of Si likely occurred throughout the rice leaf, leading to the formation of silica layers that often cover the organic matter phase. The evolution of the silica layers formed a skeleton coating the organic matter to some part, hindering the exposure of the organic matter phase and limiting exchange of internal pore spaces with the surrounding pore solution. Such inter-connecting holes could trap a certain amount of organic matter. Meanwhile, phytolith ashes show various shapes (sticks or irregularly shaped plates) and sizes (up to 100 μm) as revealed in electron microscopic images in Fig. 1b. Black carbon was also observed in the bilobate cells of phytoliths.

(Fig. 1)

In the phytolith ashes from three different heat treatments from 400 to 800°C, morphological changes could not be detected by SEM indicating that the leaf structure is conserved by a thermally stable inorganic phase. (Fig. 2a-c). In contrast, the micromorphology element maps indicate large discrepancies in surface chemical composition between Phyt400, Phyt600 and Phyt800. For Phyt400 and Phyt600, Si, C, and O are major elements that build up the surface, while K, Ca, and Mg appear in minor amounts. For Phyt800, Si and O are the two most dominant elements on the surface. The signal of C was readily reduced, indicating the decomposition of C when the pyrolysis temperature changed from 600 to 800°C. Remarkably, C was not completely during oxidation at 800°C for 1 h indicating the recalcitrance of the organic phase. The FTIR spectra reflect the surface chemical associations of the phytolith ashes (Fig. 2d). The molecular vibrations at 3450–3400 cm^{-1} , 2950–2850 cm^{-1} , 1600–1560 cm^{-1} , 1430–1400 cm^{-1} , and 1100 and 810 cm^{-1} were respectively assigned to O–H stretching of hydroxyl groups, C–H stretching of aliphatic CH_x , C=O stretching of carboxyl groups, C–C stretching of aromatic groups, and stretching and the bending of the Si–O–Si internal tetrahedra bonds. The XRD patterns (Fig. 2e) indicated the presence of mineral phases in the phytolith ashes. Calcite was likely formed in all the phytolith ashes as the result of carbonatization of Ca during pyrolysis, while tridymite and cristobalite were observed for Phyt600 and Phyt800, respectively.

(Fig. 2)

Dissolution of phytolith ashes

The dissolution of phytolith ashes can be reflected through the amount of released Si. Remarkable turnover was indicated by the increasing concentrations of Si in the solutions over time (Fig. 3a). For all the phytolith ashes, large discrepancies in released Si concentrations under the atmospheric conditions with or without CO₂ support were observed, suggesting strong effects of CO₂. Without CO₂ support, the highest dissolution rate was revealed for Phyt400. In a time span of 6 days, soluble Si was substantially increased from 0 to ~ 53 mg g⁻¹. Phyt600 and Phyt800 showed similar dissolution rates which were remarkably significantly lower than that of Phyt400. After 6 days, the soluble Si of Phyt600 and Phyt800 reached ~ 33 mg g⁻¹. Under the support of CO₂, the dissolution rates of the phytolith ashes were reduced at least by half (for Phyt400) or even about one order of magnitude (for Phyt600 and Phyt800). After 6 days, the CO₂-mediated Si concentrations of Phyt400, Phyt600 and Phyt800 were 19.0, 3.7 and 5.6 mg g⁻¹, respectively. The plots of released Si concentrations of the phytolith ash suspensions under the atmospheric conditions with or without CO₂ support (Fig. 3b) indicated linear relationships (R² values were > 0.87). It means that CO₂ gas homogeneously affects the dissolution rates of the phytolith ashes.

(Fig. 3)

Releases of nutrients from phytoliths

Releases of the nutrients (K, Ca, Mg and P) from phytolith suspensions under the atmospheric conditions with or without CO₂ support are shown in Fig. 4. In general, gradual increases in nutrient concentrations were observed for all suspensions containing phytolith ashes in the time span of 6 days. The amounts of dissolved nutrients decreased in the following order: K > Ca > Mg > P. The released nutrients were generally higher under CO₂ support than under the atmospheric condition without CO₂ support. K was the most common element released from the phytolith ashes. The highest released amount for K was 52.8 mg g⁻¹ (in Phyt400), whereas the lowest released amount was 43.7 mg g⁻¹ (in Phyt600). The effect of CO₂ in accelerating K release was most obvious for Phyt600. Whereas the trends of released K in Phyt400 and Phyt800 did not clearly reflect the effect of CO₂. It was different for the case of the divalent cations, i.e., Ca²⁺ and Mg²⁺. They were the second and third abundant elements, releasing from the phytolith ashes. The effect of CO₂ clearly showed large differences between the course of Ca and Mg releases over time for atmospheric conditions with and without CO₂ support. For these two divalent cations, their binding in the siliceous structure can be assumed to be stronger than for monovalent cation (e.g., K⁺). CO₂ resulted in 2-fold increases in Ca and Mg releases in the Phyt400 and Phyt600 suspensions, while it is ca. 1.5-fold increase in the Phyt800 suspension. For Phyt800, the support of CO₂ resulted in a quick dissolution in which Ca and Mg were mostly released within 1 day. The amounts of the trivalent anion PO₄, which can substitute Si to some part in the siliceous structure, were relatively similar in the phytolith ashes. The release rates of P were lowest as compared to those of K, Ca and Mg. The support of CO₂ resulted in minor increases in the release of P, suggesting that releasing mechanisms differ between cations and anions.

(Fig. 4)

Dissolution of phytoliths in relation to nutrient releases

The PCA diagrams represent the possible relationships among releases of Si and other nutrients (K, Ca, Mg and P) that were co-released during the dissolution of phytolith ashes without CO₂ support (Fig. 5a) or with CO₂ support (Fig. 5b). According to the ordination of variables in the PCA diagrams, Si tends to associate with Ca, K and Mg rather than P. It suggests that Si, Ca, K and Mg might share the route to be released, while the release of P might be regulated by other factors, for example binding to Fe, Mn and Al oxides (in phytoliths). With CO₂ support, the eigenvector of Si shifts away from those of other elements. It was likely that the support of CO₂ altered the relation of Si and other elements towards less relevant. This means that CO₂ gas (through acidification) rather than the dissolution of phytolith regulated the releases of nutrients from phytolith ashes.

(Fig. 5)

Relations between released Si and other elements were described by scatter plots and bivariate correlations, as shown in Fig. 6. Without CO₂ support, co-increases of Si and all other elements studied were clearly observed. The positive correlations between Si and K, Mg, Ca and P demonstrate that the releases of these elements were either involved directly in the dissolution of the phytolith ashes or shared the same route/mechanism to be released. The correlations were also warranted by the Pearson coefficients (provided in Table S1). The bivariate correlations of Si and other elements showed the significances at least at $p < 0.05$. With CO₂ support, all the regression lines were shifted to lower Si concentrations and to higher concentrations of other elements. However, increases in Si concentration were still followed by those of all other elements except P. Overall, the support of CO₂ reduced the dissolution rate of the phytolith ashes, but strong correlations between Si and other elements were still observed. The release of P was more heterogeneous under the support of CO₂. The content of P in the phytolith ashes was significantly lower than that of Si. Therefore, the release of P was likely susceptible or easily interfered with other processes that differ from those relevant for K, Mg and Ca.

(Fig. 6)

Discussion

As revealed from the tomographic analysis (Fig. 1a), phytoliths appeared as a carrier for encapsulation of plant organic matter. The formation of phytolith was initiated with the deposition/polymerization of Si to evolve silica body from which other neighboring substances can be inadvertently encapsulated into phytolith structure as schematized in Fig. 7. The assimilation of Si from soil solution was governed by various transporters such as Lsi1 and Lsi2 (Ma et al. 2006; Ma et al. 2007). Together with other nutrients (e.g., P, K, Ca, Mg), Si was transferred to different organs. Where Si is enriched, polymerization of Si can be activated to form phytolith structure. The evolution of phytolith accompanying encapsulation of foreign substances (i.e., nutrients) can follow different stages (Fig. 7), such as: (1) co-transport of Si and

nutrients in vascular space, (2) deposition of Si forms phytolith wall, (3) evolution of phytolith structure creates isolated space and obstructs the transports of Si and nutrients in vascular system, (4) phytolith structure is condensed/solidified and nutrients are completely isolated. The encapsulation of nutrients was simply a physical process; however, the association of organic matter and silica wall might be strengthened by chemical bonds. The occurrences of Si–C and Si–O–K bonds have been reported in previous studies (Pan et al. 2017; Nguyen et al. 2020; Nguyen et al. 2021a). This means that both physical and chemical processes can simultaneously affect the encapsulation of organic matter and nutrients in plant transport sap into phytolith structure. As the resolution of the tomographic image is relatively low (i.e., 1.14 μm), the nano-to-micro pores of the phytolith silica body could not be visualized. As a result, the possible encapsulation of organic matter and nutrients in the nano-to-micro pores was also beyond the resolution provided here.

(Fig. 7)

Heat treatment results in significant changes in chemical composition of straw (Yang et al. 2021). While organic matter tends to be transformed into gases and also other elements such as Na and K get volatile, phytolith remained in the ash form. It is well known that changes in inorganic phases in straw occur under heat treatment, leading to the formation of new mineral phases (Nguyen et al. 2015). Under the pyrolysis at the temperature range from 400 to 800°C, organic matter in straw was reduced from ~ 40 to ~ 10% and it occurred as a fine-sized composite within phytoliths in the ashes (Fig. 2a-c). With the resolution provided by the element maps, the presence of K can be clearly observed, whereas Ca, Mg and P were not detectable. The predominance of C and Si was also confirmed by the FTIR spectra (Fig. 2d). These two elements together with O form various surface chemical linkages that can govern the dissolution of phytolith. However, the siloxanes, i.e., >Si-O-Si< , attributed to the IR peaks at 1100 and 810 cm^{-1} , were the major linkages at phytolith's surface and their susceptibility or stability will determine the dissolution or destruction of phytoliths. With increasing pyrolysis temperature, Si was enriched and transformed to more stable crystalline phases such as cristobalite and tridymite (Fig. 2e). This is a common fact when straw is pyrolyzed as observed in numerous previous studies (Xiao et al., 2014; Nguyen et al., 2015; Yang et al., 2021). As a result, the formation of crystalline SiO_2 phases reduced the Si release from the phytolith ashes (Fig. 3a). It was probable that the crystallization can encapsulate nutrients and more or less obstruct the diffusion of nutrients in phytolith structure.

The mechanistic progress of phytolith dissolution has intensively been studied in recent years. The nucleophilic attacks and resulting breaking of >Si-O-Si< chains are generally accepted as the main process that governs the dissolution rate of phytoliths. Polarized compounds such as water molecules, or anions can be adsorbed onto the >Si-O-Si< chain, leading to a transfer of electron density to Si–O bond, by which stretching the length of Si–O bond and eventually breaking it (Dove and Crerar, 1990). The soluble Si amounts (released) decreased following the order: Phyt400 > Phyt600 > Phyt800 (Fig. 3a). It was likely that increases in pyrolysis temperature resulted in slagging of silica or altered the silica into more stable silicates (Fig. 2e). As a consequence, the dissolution rate of the phytolith ashes (indicated through released Si amounts) was remarkably decreased. CO_2 was even more effective in

decelerating the dissolution of the phytolith ashes (Fig. 3a), and this fact was in agreement with a recent finding from (Nguyen et al. 2021b). The dissolution rates of the phytolith ashes declined at least by half (for Phyt400) or by about one order of magnitude (for Phyt600 and Phyt800) in presence CO₂ support. Here it is most likely that CO₂ affected phytolith dissolution through an indirect process by its effect on decreasing pH). In parallel systems enabling recording of SC and pH simultaneously, the SC of the phytolith ash suspensions increased substantially under the support of CO₂ (Fig. S1). It can be deduced that the presence of CO₂ in this system decreased pH, favoured protonation of phytolith surface, thereby mitigating nucleophilic attacks from anionic agents and eventually reducing the dissolution rate of phytoliths (Fraysse et al. 2009; Nguyen et al. 2014).

Strong correlations between Si and the elements K, Mg and Ca (Fig. 6 and Table S1) are clearly indicative for the possible dependence of these nutrients on phytolith dissolution. It was most probable that the dissolution of Si resulted in physical removal of phytolith compounds from the external surface and this process could lead to the release of the occluded nutrients into the solution. The support of CO₂ substantially decreased the dissolution of the phytolith ashes, thus it would have resulted in decrements of released nutrients. Nevertheless, a contrasting scenario, in which CO₂ increased release rates of the nutrients, was observed. This suggests that the releases of nutrients could involve in parallel processes. Here we suppose a hypothesis that: CO₂ on the one hand prohibits the dissolution rates of the phytolith ashes thereby decreasing releases of occluded nutrients; CO₂ on the other hand intensifies the substitution of absorbed cations by H⁺ and favors the release of cations (e.g., K⁺, Ca²⁺ and Mg²⁺). By this way, the total amounts of released cationic nutrients increased under the support of CO₂ gas. The mechanism is schematized as shown in Fig. 8. It means that CO₂ gas can intensify the evacuation of nutrients adsorbed on phytolith surface while it tends to protect the 'structural' nutrients encapsulated within phytoliths. Release of anionic nutrient, i.e., P, might relate to either the physical destruction of phytolith that release P from isolated space, or the dissociation of P bonds. However, these processes are beyond the detection capability as P content is low.

(Fig. 8)

Other mineral phases such as the carbonate calcite also occurred in the ashes (Fig. 2e). Their direct dissolution can be an additional process that serves for the release of free ions into the solution. Releases of alkaline nutrients (e.g., Ca, Mg and K) can alleviate the effects of CO₂ because they act against the reduction of pH, activate the conversion of CO₂ into anionic species, HCO₃⁻ and CO₃²⁻, favour the adsorption of the anionic species on phytolith surface at which the anionic species can stimulate the dissolution of the phytolith ashes (Nguyen et al. 2021a). However, in the sense of this study, CO₂ was continuously supported. The effects of the releases of the alkaline nutrients were, therefore, obscured. The chemodynamic state of CO₂ in soil is complex and depends on various factors under field conditions, such as diurnal and seasonal changes (Nishimura et al. 2015) and water regime or soil properties/processes (Yang et al., 2012; Khalid et al., 2019). As a consequence, the resulting changes in nutrient release from phytolith ashes will not be easily anticipated. However, intermittent irrigation, a

major strategy in response to the world call to mitigate CH₄ emission from wetlands (Earth Security Group 2019), will elevate CO₂ levels in wetlands. We presume that elevated CO₂ will accelerate nutrient releases from straw phytolith ashes but decelerate the cycle of straw phytoliths in paddy systems.

Conclusion

The phytolith ashes were demonstrated as a slow-release platform that can serve as a potential nutrient source for soil and crops. Phytolith ashes, containing nutrients (e.g., K, P, Ca, Mg) and beneficial elements (e.g., Si), can gradually be released when the phytolith ashes are dissolved. This study emphasizes CO₂ as a factor that can readily alter the dissolution rate of the phytolith ashes. Intensifying presence of CO₂ can lower pH, thereby modifying the dissolution rate of the phytolith ashes towards lower levels but favouring nutrient releases through co-dissolution and ion exchange processes. The findings are useful to better understand the contribution of the straw phytolith ashes to the soil nutrient pool and can be a premise for management of straw recycling practice under the context of climate change and circular economy. Creating added values from agricultural by-products provides an accelerating momentum towards achieving sustainable agriculture and other applications of straw phytoliths are, therefore, needed to be encouraged. We highlight phytoliths as a potential “biofertilizer” for soil, and its application in aquaponic agriculture, where CO₂ can be simply supplied/controlled, should also be considered.

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Figures

Figure 1

Silica intergrown with organic matter in: (a) dry leaf fragment presented in a tomographic 3D image, and (b) ash fractions obtained from pyrolysis at 400, 600 and 800°C viewed by electron microscopy.

Figure 2

SEM images and their corresponding element maps indicating surface chemical composition of the phytolith ashes obtained from the pyrolysis at: (a) 400°C (Phyt400), (b) 600°C (Phyt600), and (c) 800°C (Phyt800). Surface and structural properties revealed by (d) FTIR spectra and (e) XRD patterns.

Figure 3

Dissolution rates of the phytolith ashes obtained from 400, 600 and 800°C treatments (i.e., Phyt400, Phyt600 and Phyt800, respectively) under different atmospheric conditions with or without CO₂ support: (a) Released Si concentrations as a function of time; (b) Plots of released Si concentrations of the suspensions with or without CO₂ support.

Figure 4

Dissolution rates of phytolith occluded K, Ca, Mg and P under different atmospheric conditions, with and without CO₂ support.

Figure 5

Score plots of PC1 versus PC2 for released Si and other nutrients: (a) without CO₂ support, and (b) with CO₂ support.

Figure 6

Cross-correlation of the released Si with K, Ca, Mg and P. The data were derived from the kinetic batch experiments shown in Fig. 3 and 4.

Figure 7

Illustration of the mechanism for the evolution of phytolith structure during plant growth and accompanying encapsulation of nutrients: (a) transports of Si and nutrients in vascular space; (b) association of Si on cell wall followed by polymerization of silica to form silica layer; (c) evolution of silica layer to form silica structure and create partially or completely isolated space containing nutrients; (d) silica matrix is condensed, dehydrated and solidified.

Figure 8

Schematic description of the fate of phytolith ashes and their accompanying nutrients (i.e., K) under the atmospheric conditions with or without CO_2 support.

Supplementary Files

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