



## Characterization and dissolution properties of phytolith occluded phosphorus in rice straw



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### ABSTRACT

Silicon (Si) is assimilated from soil by rice and is deposited in shoots in inter- and intracellularly, resulting in the formation of siliceous structures, namely phytoliths. During the precipitation of Si, elements present in xylem/phloem sap, including phosphorus (P), can also be occluded in the phytolith. We examined the release of Si and P from the rice straw derived phytolith to elaborate the desilification mechanism, and the potential effects of phytolith as a nutrient amendment. Data from batch heating experiments revealed that P trapped in the phytolith structure could be released accompanying with the dissolution of the phytolith. The highest values of soluble Si and P were found in the range of 500–700 °C. The chemical composition, X-ray diffraction, infrared spectra and specific surface area (SSA) data suggested that the presence of occluded organic carbon at < 500 °C and crystallization of silica at > 700 °C were the main reasons for lower dissolution rates of phytolith and decreasing P release. With respect to practices of burning rice straw, it can be recommended that treatment temperature needs to be taken into account to maximize P release for crops.

### 1. Introduction

Rice straw derived phytolith, a siliceous structure formed through Si precipitation in rice plant tissues (Parr and Sullivan, 2005), has been widely known as a potential source to sustain soil Si nutrient pools when it is cycled to soils (Dobermann and Fairhurst, 2000; Nguyen et al., 2014, 2015; Seyfferth et al., 2013). However, there has been a lack of systematic information on the fate of rice straw derived phytolith in soils, and to what extent this nutrient pool can benefit crops. Phosphorus (P) is among the most important nutrient elements in rice. P is taken up from the soil solution by root absorption, transport across cell membranes and compartmentation, and redistribute within different parts of rice plant (Agarie et al., 1996; Schachtman et al., 1998; Yamaji et al., 2008). During rice growth, P can be re-translocated through rice's xylem/phloem system (Schachtman et al., 1998), and some parts might be trapped within phytolith structure (so-called phytOP) when Si precipitates. This means that even if rice straw is cycled to soil, this P pool might still exist inside phytolith and unavailable for plant uptakes. There has been a knowledge gap and

lack of experimental evidence for the fate of phytOP and its capacity to serve as an additional P source for crops.

Generally, dissolution of phytolith is regulated by the desilification in aqueous solution. This process occurs via hydrolysis of  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  bonds of the silica surface in which water molecules orient their electronegative pole towards the Si atoms in silica structure, resulting in a transfer of electron density to the  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  bonds, thereby raising their length and consequently breaking them (Dove and Crerar, 1990). pH is well understood as a crucial factor driving phytolith dissolution kinetics via protonation or deprotonation reactions (Frayse et al., 2009; Nguyen et al., 2014) which can either increase resistance of the surface or make the surface more vulnerable from nucleophilic attacks (Dove and Crerar, 1990). On the other hand, occluded organic matter can be another factor in preserving phytolith since it may act as a protective shield against hydrolysis of the silica (Nguyen et al., 2014; Parr and Sullivan, 2005). In this study, the release of P was inspected in considering the dissolution rate of phytolith's silica body and influence of occluded organic matter content.

Open-field burning of rice straw after harvesting is a conventional

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method of disposal of straw to return nutrients to the soils in many rice-based countries. Although this method causes significant emission of greenhouse gases (e.g. CO<sub>2</sub>, CO, NO<sub>x</sub>), losses of nutrients (e.g. N, K, P,) and contributes to air pollution (Andreae and Merlet, 2001; Bijay et al., 2008; Dobermann and Fairhurst, 2000), it is the easiest way of returning most nutrients to the soils, and at present rice growers have little incentive to change this method. As burning of rice straw at different temperatures might result in various degrees of dehydroxylation of biogenic silica and organic matter contents, rice straw phytolith ash samples which were obtained from 300 to 1000 °C ashing temperatures were used to examine the release of P in batch experiments. X-ray tomographic microscopy (Marone et al., 2010), provided a visualization for siliceous structure of phytolith. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), specific surface area (SSA) and chemical composition analysis were carried out to evaluate transformation of phytolith and its effect on P release. Statistical analysis using Pearson's test can help to provide an additional information of correlation between the released Si and P. Based on the identification of relation between the release of P and dissolution of rice-straw phytolith, this study clarifies the dynamics of the phytOP and suggest possible management options on one hand to maximize the use of this phytOP pool, and on the other hand to adjust fertilization strategy.

## 2. Materials and methods

### 2.1. Study site and sample production

Rice-straw was collected from a paddy field (105°44' E long, 20°59' N lat) in the Red River Delta (RRD), a second largest delta in Vietnam. In the RRD, approx. 12 tons ha<sup>-1</sup> of the rice straw can be annually burnt and returned to the fields which serves as large amount of phytolith for paddy soils. The rice-straw was air-dried, milled and passed through a 1.0-mm sieve. Ashing was conducted by heating the rice straw sample in an furnace at a target temperature range between 300 and 1000 °C for 2 h. The derived phytolith containing ash was washed with DI water, followed by centrifugation and decantation, and finally were dried at 60 °C in an oven for 24 h. The samples from pretreatments at 300, 400, 500, 600, 700, 800, 900 and 1000 °C were used for chemical analysis, mineralogical characterizations, SSA analysis and batch dissolution experiments. For kinetic experiments, the samples treated at 400, 700 and 1000 °C were selected.

### 2.2. Sample characterization

#### 2.2.1. Tomographic and morphological analysis

A 3D image of the siliceous structures of a rice plant was built by using YaDiV software (Friese et al., 2013), and input data from X-ray tomographic microscopy by TOMCAT (TOMographic Microscopy and Coherent rAdiology experimenTs) beamline at the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland. Dry rice leaf was scanned under monochromatic beam from a 2.9 T superbending magnet at an energy of 11.1 keV. Micromorphology of the sample was inspected by using SEM (FEI Quanta 600 FEG, USA).

#### 2.2.2. Chemical composition

To examine chemical composition, the samples derived from pretreatments at 300 to 1000 °C were examined using the Particle Induced X-Ray Emission (5SDH-2 Pelletron accelerator system, USA). Total organic carbon (TOC) in the samples was measured by wet digestion with concentrated H<sub>2</sub>SO<sub>4</sub> and 0.5 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 170–180 °C.

#### 2.2.3. X-ray diffraction, FTIR and surface area analysis

Silica phases of the ash samples were examined by powder X-ray diffraction (Bruker AXS D5005, Germany). The surface groups of the ash samples were identified by using FTIR measurements (Nicolet™

iS™5 FT-IR, Thermo Scientific, USA). The SSA of the samples was measured with a Gemini VII 2390p surface area analyzer.

### 2.3. Kinetic batch experiments

To examine P and Si solubility, 300 mg of sample was mixed with 300 mL of DI water in 500-mL plastic tubes. Suspensions were gently shaken and allowed to stand for 24 h at room temperature. For the samples pre-treated at 400, 700 and 1000 °C, the batch experiments were in triplicates and extended up to 6 d with sampling at 24 h intervals. The suspensions were passed through a 0.45 μm filter paper. Soluble P was determined using ion chromatography (DX-600, Dionex-Thermo, USA) while soluble Si was examined by molybdate blue method with a Spectrophotometer UV-vis (L-VIS-400, Labnics, USA). Since the ash samples still contain certain amounts of OC, dissolution of the OC might affect releases of Si and P by changing phytolith exposure to solution. In all kinetic experiments, DOC was also analysed using a TOC Analyzer (VCPH, Shimadzu), to identify whether the released P was related to dissolution of occluded organic matter. Correlations between the released Si and P derived from all dissolution kinetic experiments were also evaluated by Pearson's test using SPSS 20.0 software program. The strength of correlation can be evaluated by using two levels of significance 0.01 and 0.05, representing relations between the released Si and P occurring by chance are 1 and 5%, respectively.

## 3. Results

### 3.1. Sample characterization

The arrangement of phytolith's siliceous structure in the rice leaf was visualized in Fig. 1. A high-porosity system with various size holes which might represent longitudinal vascular bundles, veins or fibers of the rice plant (Botha, 2013). Si covers, throughout, internal- and external surfaces of the vascular system to form a coating layer, coloured yellow, as shown in Fig. 1a. This layer is known as silica-rich epidermis which is developed to become the main strengthening tissue in the stem and leaf (Islam et al., 2009; Yamanaka et al., 2009). The holes can be fulfilled by organic matter which appears in violet (Fig. 1b). Excessive precipitation of Si can likely to form "closed holes" within the vascular bundles, capturing embedded organic matter, as well other occluded substances including P.

Heat treatments of the rice straw resulted in significant changes in chemical composition and SSA as shown in Table 1. The organic carbon was almost completely removed by heating at > 800 °C, whereas, only less than 30% of TOC was removed at 300 °C. In rice straw the total P and Si contents were 1.02 and 73.6 g kg<sup>-1</sup>, respectively. However, the contents of P changed from 1.21 to 2.55 g kg<sup>-1</sup> and those of Si varied from 87.6 to 184.2 g kg<sup>-1</sup>, when the heating temperatures of rice straw increased from 300 to 1000 °C. A severe decrease of the SSA was obtained with increasing heating temperature. The SSA decreased from 36.2 to 0.22 m<sup>2</sup> g<sup>-1</sup> with an increase of heating temperature from 300 to 1000 °C, indicating an enhanced condensation of silica structures at higher temperatures as shown in Fig. 2.

The XRD for phytolith derived from different treatment temperatures is shown in Fig. 3a. At temperatures < 700 °C, no specific reflection was observed, suggesting that silica occurs in amorphous form. Temperatures > 800 °C can favor crystallization and cause the formation of more stable silica crystalline structures, i.e., cristobalite and tridymite (Kordatos et al., 2008). Functional groups of the samples were revealed through FTIR spectra as described in Fig. 3b. The bands at ~1100 cm<sup>-1</sup> and 800 cm<sup>-1</sup>, representing for the stretching vibration of the SiO<sub>4</sub> tetrahedron and the bending vibration of inter-tetrahedral ≡Si–O–Si≡ bonds, were apparent for almost all pretreatments.

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