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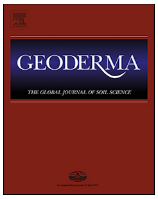

Phytolith content in Vietnamese paddy soils in relation to soil properties

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ABSTRACT

Understanding of the fate of phytolith in soils is important because of its role as an agronomical nutrient resource and for carbon sequestration. Accumulation of phytolith derived silica occurs in paddy soils when phytolith input, here through straw incorporation, is higher than silica removal through crop offtake, dissolution and leaching. Phytolith dissolution is thought to be the main reason for diminishing of phytolith derived silica in soil, with this dissolution being highly dependent on soil chemical properties. In this study, phytolith content from 78 paddy soils sampled in the Red River (RRD) and Mekong River (MRD) Deltas, Vietnam, were quantified and related to pH, electrical conductivity (EC), oxalate-extractable Al and Fe (Al_{ox} and Fe_{ox}), organic carbon (OC) and clay content. Average phytolith contents within the topsoil (0–20 cm) were 4.8 ± 1.98 and 7.74 ± 2.97 $mg\,g^{-1}$ for the RRD and MRD, respectively. Positive correlation coefficients obtained for Al_{ox}, OC, clay content and EC, implying that these parameters might enhance phytolith resistance to dissolution. Soil pH had a negative correlation coefficient with phytolith content. Lower pH and higher Al_{ox} content explained the predominance of the phytolith in the MRD compared to the RRD. Soil pH adjustment can be proposed as an active management strategy to maintain phytolith added Si, source for crops and for carbon sequestration.

1. Introduction

Rice (*Oryza sativa L.*) is a silicon (Si) accumulator, with a Si-content of 5–10% of plant dry matter (Marschner, 1995). Rice Si content is greater than that of essential nutrients such as nitrogen (N), phosphorus (P) and potassium (K). By deposition in inter- and intracellular spaces throughout leaves and stems, silicified structures are formed representing biogenic silica, phytoliths (Parr and Sullivan, 2005). Phytoliths can increase mechanical strength, resistance to fungal stress, reduce transpiration rates, and enhance light interception also promotes photosynthesis (Liang et al., 2015). Overall, sufficient Si supply in paddy soils is an important measure to ensure optimal yield. After harvesting, phytoliths contained in straw and husks can be cycled back into the soil through direct incorporation of these residues, or by burning and returning ash to soils (Klotzbücher et al., 2016; Nguyen et al., 2016). The role of phytoliths recycling to soil through incorporation of harvest residues to soil is increasingly considered important, not only for Si nutrition (Conley, 2002; Street-Perrott and Barker, 2008; Struyf et al., 2009), but also for K cycling (Keller et al., 2012; Nguyen et al., 2015; Seyfferth et al., 2013), and for carbon sequestration (Li et al., 2013; Parr and Sullivan, 2005; Song et al., 2016; Song et al., 2014).

Generally, accumulation of phytolith occurs in soils when its turnover rate is greater than losses by Si dissolution (Meunier, 1999). Phytoliths in the soil can be preserved with increasing ionic strength and presence of cations, especially Al^{3+}, in solution (Nguyen et al., 2014; Wilding et al., 1979). Soil pH is well understood as a crucial factor driving phytolith-dissolution kinetics via protonation or deprotonation reactions. In addition, other factors such as ambient temperature or redox conditions can also affect phytolith dissolution (Drees et al., 1989). However, no systematic study has been conducted to confirm the effects of soil chemical properties on the conservation of phytoliths in the field.

It is known that the dissolution of phytolith in aqueous solutions occurs via hydrolysis of $\equiv$Si-O-Si$\equiv$ bonds (Dove and Crerar, 1990; Rimstidt and Barnes, 1980) and this process is highly affected by pH (Fraysse et al., 2006; Loucaide et al., 2008; Nguyen et al., 2014). In particular, the acceleration of the dissolution rate with increasing pH is

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explained by the increase in number of deprotonated ≡Si-O⁻ sites at the solid's surface (Brady and Walther, 1990). The negatively charged sites promote dissolution kinetics, either by enhancing the nucleophilic properties of water (Dove, 1994) or polarizing, and thus weakening, surface ≡Si-O-Si≡ bonds (Brady and Walther, 1990). Adsorption of cations (especially Al^{3+}) from aqueous solution onto deprotonated ≡Si-O⁻ sites might accelerate polymerization (Weres et al., 1981), and the surface of phytolith might, therefore, be strengthened to resist dissolution (Fraysse et al., 2009; Nguyen et al., 2014). Phytolith occluded organic matter (OM) is known as another factor to strengthen the phytolith surface against dissolution because organic matrix may act as a protective shield against hydrolysis of the silica (Parr and Sullivan, 2005; Van Cappellen et al., 2002). When rice straw is burnt (a common practice in paddy farming in Vietnam) at low temperature (i.e. < 600 °C), OM might be more recalcitrant and remained in ashes (Lai et al., 2009; Nguyen et al., 2014). The effect of OM originated by pyrolysis of biomass, i.e. black carbon (biochar), on dissolution of phytoliths is not yet fully known.

Leaching of dissolved Si under water high percolation rates results in diminution of soil phytolith pools (Fishkis et al., 2010; Fishkis et al., 2009; Nguyen et al., 2016). Transport with surface runoff might also lead to a translocation of phytoliths to aquifers, rivers and oceans (Conley, 2002; Farmer et al., 2005; Frings et al., 2014a; Frings et al., 2014b). From investigation of distribution of soil phytolith-occluded carbon, Zuo et al. (2014) found that large amounts of phytolith from Chinese Loess Plateau can be eroded and exported to rivers. Contrasting observations on leaching of soil phytolith within their soil profiles have been reported. Fisher et al. (1995) found soil phytolith did not readily move downward, while Alexandre et al. (1997b) and (Fishkis et al., 2010) have shown evidence for vertical transport of phytolith derived Si.

In this study, we examined soil phytolith contents for 78 soil samples collected from paddy fields in the Red River Delta (RRD) and Mekong River Delta (MRD), Vietnam by using alkaline Na_2CO_3-extraction (DeMaster, 1981). Other soil physio-chemical properties, pH, electro-conductivity (EC), organic carbon (OC), non-crystalline Al and Fe, and particle size, were determined to relate to soil phytolith content. Statistical analysis using *t*-test (Student's *t*-test, $p < 0.05$) and principal component analysis (PCA) enabled us to identify differences of quantitative characteristics and correlations between the soil phytolith and each selected soil properties. Multiple regression analysis was also executed to identify dependencies between phytolith content and soil properties. This work, based on statistical analysis of relation between the soil phytolith and the soil properties for two largest deltas in Vietnam, is an attempt to clarify the dynamics of soil phytolith and suggest possible management options on the one hand for adjustment of specific parameters in the soil (e.g. optimum pH and EC in the soil) and on the other hand fertilizer Si applications.

2. Materials and methods

2.1. Study area

Sampling strategy was designed to cover almost all rice cultivation areas (approx. 4.8 million hectares) in the RRD and MRD, two largest deltas in Vietnam (Fig. 1). The RRD, northern Vietnam, is formed from fluvial deposits of the Red river. The MRD is third largest delta in the world which covers nearly 10 million hectares (Coleman, 2003). We only considered the lower MRD that is within Vietnam territory. Rice has been continuously cultivated for hundreds of years in the RRD and MRD. The RRD has a dike system constructed in the 1990s to prevent river water from intrusion into the paddies. Eutric- and dytric Fluvisols are major soil types in the RRD, whereas the more acidic Salic- and Thionic Fluvisols dominate the MRD (classified by the FAO-Unesco system). Illite and kaolinite are two most dominant clay minerals found in soils in both the RRD and MRD (Hoang et al., 2016; Kirov and Truc, 2012; Nguyen et al., 2009b). While the RRD has four typical distinguished seasons (tropical wet, hot, and with an average annual rainfall of > 1600 mm), the MRD has only two seasons (dry- and rainy) with lower annual rainfall (~1100 mm).

2.2. Crops and water regime

RRD rice cultivation has two-annual cropping cycles with a yield of ca. 12 tons ha^{-1} $year^{-1}$, while some parts in the MRD have three-annual rice cropping cycles, resulting in ~18 tons ha^{-1} $year^{-1}$. The spring season usually begins near the middle of January and ends toward the close of April, and the summer season lasts from the beginning of June to the middle of September. An extra season can also occur after the end of the summer season in some parts of the MRD. In this study, we only collected soil samples from double cropped per annum fields. At cropping time the water level is lowered, but typical for cultivation in deltas, the fields are kept flooded in most of the time. Following the spring harvest, the field is usually kept flooded and almost all rice straw is directly incorporated into the soils. At the end of the summer season, when the paddy fields become dry (and soils are unsaturated). The rice straw from the second harvest is usually burnt on site and the resultant ashes are spread on the fields.

2.3. Soil sampling and analysis

2.3.1. Soil properties

Soil samples were taken from 78 different sites (39 samples from each the RRD and MRD) in a campaign starting at the beginning of the winter season of 2015 when paddy fields were fallow. In each field a soil sample was taken by collecting top soil (0–20 cm) from at least 3 sampling sites and followed by thorough homogenization. The samples were air-dried and passed through a 1-mm sieve. Soil pH value was determined using 1 M KCl (w/v = 1:2.5). The organic carbon content was quantified using the Walkley and Black wet-oxidation method (Nelson and Sommers, 1996). Oxalate treatments were used to extract non-crystalline forms of Al and Fe oxides (Jackson et al., 1986; Pizarro et al., 2008). Oxalate-extractable Fe (Fe_{ox}) was determined by AAS (6800, Shimazu) and oxalate-extractable Al (Al_{ox}) by ICP-OES (PE 7300 V- ICP, PerkinElmer). Content of clay, silt and sand were quantified by sedimentation after removing organic matter with 30% H_2O_2 treatment. EC was measured in DI water (w/v = 1:10) using an electrical conductivity meter (AD3000, ADWA). Chemical composition was examined by PIXE (Particle Induced X-Ray Emission) method, using proton beam of Tandem accelerator (5SDH-2 Pelletron accelerator system, manufactured by National Electrostatics Corporation, USA).

2.3.2. Extraction of biogenic silicon

A 100 mg sample of < 2 mm sieved soil was pretreated with H_2O_2 at 80 °C in a water bath to remove organic matter, following centrifugation and decantation. The sediment in the centrifuge tube was transferred with 100 mL of 1% Na_2CO_3 solution to plastic flasks in a water bath at 85 °C for 7 h. Aliquots were taken from the sample flasks after 1, 2, 3, 4, 5, 6, and 7 h. Extraction was conducted in triplicate for each soil sample. The supernatant was separated by centrifugation and decantation and Si in the solutions was analyzed by the molybdate blue method (Mortlock and Froelich, 1989) using a spectrophotometer (L-