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Do oscillating redox conditions affect long-term Si release from phytoliths?

Nicolai Koebernick[1], Klaus Kaiser[1], Anika Klotzbücher[1], Robert Mikutta[1], Doris Vetterlein[1,2], and Thimo Klotzbücher[1]

[1]Martin Luther University Halle-Wittenberg, Institute for Agronomy and Nutritional Sciences, Soil Science and Soil Protection, Halle (Saale), Germany (nicolai.koebernick@landw.uni-halle.de)

[2]Helmholtz Centre for Environmental Research - UFZ, Department of Soil System Science, Halle (Saale), Germany

Phytoliths are a major source of plant-available Si in weathered soils, particularly for crops with high Si demand, such as rice. Yet, not much is known about the evolution of Si release from phytoliths under real soil conditions. The extraction of phytoliths from soil is difficult and usually leads to changes in phytolith surface chemistry. Paddy rice cultivation induces oscillations in redox potential by alternating submergence and drainage. These oscillations may have a major impact on the evolution of phytolith Si release. For instance, reduced Fe^{2+}, abundantly in solution under low redox potential may sorb onto negatively charged phytolith surfaces and form iron oxide coatings when redox potential rises after drainage. We thus hypothesise that phytolith Si release decreases with time in soil as phytolith surfaces are increasingly coated with oxides and organic matter. To test the effect of oscillating redox potential on phytolith surface chemistry and implicit changes in Si release we conduct experiments with phytoliths extracted from rice straw by dry ashing. Extracted phytoliths are sequentially exposed to soil solutions with contrasting redox potentials (anoxic vs. oxic), using either alternating anoxic-oxic solutions or exclusively oxic solutions. Anoxic exposure is conducted in Ar atmosphere (< 1% O_2 partial pressure). After each exposure events the filtrate is analysed for pH and redox potential, Fe^{2+} with the Ferrozine method, and total Fe, Al and Si with inductive-coupled plasma-optical emission spectrometry. Filter residues are sampled and analysed after 1, 2, 4, and 8 exposure steps (each lasting 2 hours), respectively. Surface chemical composition is analysed with X-ray photoelectron spectroscopy. Specific surface area is determined with N_2 gas adsorption at 77 K and surface charge is measured by determining electrophoretic mobility using dynamic light scattering. Batch dissolution experiments in mini-reactors are carried out for assessing the Si release of untreated and treated phytoliths. The experimental results will provide important information on the changes of phytolith surface chemistry and Si release from phytoliths in systems with alternating redox potentials such as rice paddies.