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Changes in minerals and organic-mineral associations in soils under redox fluctuation

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Submerged rice cultivation is characterized by redox fluctuations and results in the formation of paddy soils, often accompanied by organic carbon (OC) accumulation. It is unknown how the soil's mineral composition and particularly the redistribution of Fe oxides affect OC storage. Non-paddy and neighboring paddy profiles of three different parent soils with contrasting mineral composition (Alisol, Andosol and Vertisol) were sampled and analyzed by horizon for pedogenic Fe oxides and OC contents and stocks. X-ray photoelectron spectroscopy (XPS) was used for carbon speciation of mineral-bound organic matter (OM). Topsoil samples of Alisol and Andosol were selected for Mössbauer analyses of Fe oxides as well as for an incubation experiment with eight redox cycles, mimicking paddy soil development. Incubated soils received rice straw labelled with 13C (228 ‰ at the beginning of each cycle. As control we used a second set of samples without straw addition as well as samples under static oxic conditions with and without straw. At the end of the experiment, mineral-associated OM was isolated by density fractionation and characterized for δ13C and biomarkers.

The original Vertisol and Alisol revealed no measurable changes in phyllosilicates and gibbsite during paddy management, while the Andosol rich in short-range-ordered minerals showed loss of allophane and imogolite-type phases and increase in halloysite. All soils but the Vertisol lost Fe oxides from the topsoil, with the remaining Fe oxides exhibiting lower crystallinity in the Alisol and higher crystallinity in the Andosol. Despite distinct Fe oxide losses upon paddy management, topsoil OC stocks remained similar or even increased in the Alisol and Andosol, respectively. XPS analyses revealed that the initially different composition of the mineral-associated OM in the Alisol and Andosol was more similar in the respective field paddy soils. These results from the field-derived samples were confirmed by the incubation experiment. In both soil types, a larger proportion of the added straw was converted to mineral-associated OM under fluctuating redox conditions than under static oxic conditions. Also, added OM being bound to minerals during incubation was less microbially processed than the initial OM, irrespective the soil type.

Overall, rates of redox-mediated mineral transformations increase with increasing content of short range-ordered minerals and pedogenic Fe oxides and are slow when phyllosilicates dominate the mineral assemblage. Quantitative and structural changes in minerals as well as changes in (mineral-associated) OC contents during redox fluctuations depend on the mineral composition of the original soil type. Changes in the composition of mineral-associated OM, however, seem to be independent of soil type. A direct influence of Fe oxide redistribution on OC stabilization was not observed.