



Naturally occurring clay nanoparticles in Latosols of Brazil central region: detection and characterization

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Stability and reactivity of minerals change as a particle size function, which makes mineral nanoparticles (defined here as <100 nm) fundamentally distinct from the larger size materials. Naturally occurring mineral nanoparticles contribute to many biogeochemical processes, however much remains to be learnt about these materials, their size dependent behavior and environmental significance. Advances in analytical, imaging and spectroscopic techniques made it now possible to study such particles; however we still have limited knowledge of their chemical, structural and morphological identity and reactivity, in particular in soils. The aim of this research was to characterize the naturally occurring nanoparticles in three soils from Brazil central region. The samples were collected in the A horizon, treated with H_2O_2 to remove organic material, dispersed in ultrasonic bath and wet sieved (53 μm) to remove the sand fraction. The clay fraction was collected by siphoning the supernatant, conditioned in 1000 ml cylinder, according to the Stock's law. This fraction was further processed by re-suspension in water, sonication and repeated centrifugation, to separate the fraction smaller than 100nm. This material, called here the soil "nanofraction", was analyzed using a range of techniques: 1) nanoparticle size/morphology and crystallinity with Transmission Electron Microscopy (TEM operating in scanning (HAADF-STEM) and High Resolution (HRTEM) mode), 2) size distribution in water with Dynamic Light Scattering (DLS) and surface charge estimated from electrophoretic mobility measurements 3) crystal phase and crystallite size with X-ray Diffraction (XRD) 4) Chemical composition by quantitative analysis of elements (e.g., Si, Fe, Al, Ti) and their spatial distribution with HRTEM/EDS elemental mappings.

The nanofraction had an average hydrodynamic particle diameter ranging from 83 to 92nm with a low polydispersity index of 0.13-0.17 and was found highly stable in aqueous suspension (no change in average particle size up to several months of storage). Particle surface charge (in water) ranged from -31mV to -34.5mV (pH = 5.7 - 6.2), this reflects the predominantly negative surface charge of kaolinites in soil environment effectively screening the positive charge of Fe oxides. Kaolinites appeared as single crystals (pseudo hexagonal platelets) while Fe oxides occurred mostly as micro-aggregates, with individual particles often not morphologically distinct with particle size <10nm. In addition, several anatase (TiO_2) nanoparticles were also found. Both kaolinites and Fe oxides nanoparticles were crystalline, as evidenced from XRD measurements and HRTEM imaging. Distinction between different crystalline forms of Fe oxides (mainly hematite and goethite) was only possible with XRD, which revealed also subtle differences in mineralogical composition of the clay fraction (<2 μm) and nanofraction (<100nm). The kaolinite's crystallite size (calculated from XRD data) was found to range 14-17nm in the nanofraction and 26-50nm in the clay fraction. For hematite, it was 13nm in the nanofraction and ranged from 21-30nm in the clay fraction. Such small particles can be expected to play an important role in soil sorption processes with implications on nutrient and contaminant cycling. Identification and understanding of the properties of naturally occurring nanoparticles in soils can therefore help soil scientists to better understand retention/mobilization of nutrients and pollutants in soils.