

Fe(III) fate after complexation with SOM pools under different land uses

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Adsorption to mineral surface may affect soil organic matter (SOM) protection and long-term accumulation in different ways depending on its molecular structure and pedo-climatic conditions. Iron (Fe) oxides have been suggested as a key regulator in the soil C cycle, and Fe speciation in soils is highly dependent on environmental conditions and chemical interactions with SOM. However, the molecular structure and hydrolysis of the Fe species formed in association with SOM is still poorly described. We hypothesize the existence of two pools of Fe: mononuclear Fe(III)-SOM complexes and precipitated Fe(III) hydroxides.

To verify our hypotheses, we studied the interactions between Fe(III) and several physically fractionated SOM fractions, i.e., fine silt plus clay (FSi+C) and fine sand (FSa), obtained by ultrasonic dispersion and wet sieving, and mineral-associated (Min) and free (FR) using a densimetric physical fractionation. Moreover, several land uses, including coniferous forest soil (FS C), grassland soil (GS), technosol (TS) and agricultural soil (AS), have been also taken into account.

Batch experiments were conducted at pH 7 to investigate the formation and stability of Fe(III)-SOM complexes; each SOM fraction was reacted with acidified Fe(III) nitrate solution, reaching a 200 mg Fe g⁻¹ OC loading. Synthesized complexes and supernatants were analyzed for C and Fe content. X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) were also performed. Attenuated total reflectance (ATR) infrared spectroscopy allowed assessing main functional groups involved in complexation and desorption experiments.

Spectra of the unreacted versus reacted SOM fraction revealed a shift of asymmetric carboxylic groups (1643 cm⁻¹) probably due to monomolecular Fe(III)-OM complexation, only in GS. The presence of a small peak at 1160 cm⁻¹, characteristic only of Min and FSi+C fractions in all land uses and associated to small changes in carboxylate groups, and in the carbohydrates region, mainly in all GS and TS fractions, could be indicative of hydrolysis products formation, maybe encapsulated by polysaccharides. Some Fe K edge extended X-ray absorption fine structure (EXAFS) spectra suggested an increase of ferrihydrite from 49% in unreacted to 66% Fe(III) reacted samples. Further EXAFS analyses will be conducted, allowing the determination of Fe(III) coordination chemistry.

This approach will help unveiling the mechanisms by which SOM pools can control Fe(III) speciation, and will elucidate how both Fe(III)-OM complexes and Fe(III) polymerization can affect SOM reactivity and, consequently, its mean residence time in different ecosystems.

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