

Impact and reactivity of Fe(III)-OM complexes and Fe(III) polymerization in SOM fractions under different land uses

Beatrice Giannetta (1), Matthew G. Siebecker (2), César Plaza (3), Claudio Zaccone (4), Pere Rovira (5), Costantino Vischetti (1), Donald L. Sparks (2,6)

Polytechnic University of Marche, Dept. of Agricultural, Food and Environmental Sciences, Ancona, Italy
(b.giannetta@pm.univpm.it), (2) University of Delaware, Delaware Environmental Institute, Newark, Delaware, United States,
(3) Institute of Agricultural Sciences Spanish National Research Council (CSIC), Madrid, Spain, (4) University of Foggia,
Dept. of the Sciences of Agriculture, Food and Environment, Foggia, Italy, (5) Forest Sciences Center of Catalonia, Solsona,
Spain, (6) University of Delaware, Dept. of Plant and Soil Sciences, Newark, Delaware, United States

Soil organic carbon dynamics are affected by climate change and are important for the buildup of soil organic matter (SOM) pools with long residence time in soils. Additionally, iron (Fe) (hydr)oxide minerals also influence SOM dynamics and have been suggested as an important phase for the stabilization of SOM.

Using state-of-the-art synchrotron-based techniques, numerous studies have focused on model metal (hydr)oxide system (e.g., pure Fe (hydr)oxides) complexation with different types of organic matter, including dissolved organic matter (DOM), peats, humic substances, and low molecular weight organic acids. However, Fe speciation in natural soils is highly dependent on environmental conditions, and it is less clear how Fe-stabilization of SOM in natural systems (rather than model systems) protects SOM from decomposition.

Here we studied the interactions between Fe(III) and SOM in several physically fractionated soils which are characterized by different land uses (e.g., coniferous and broadleaved forest soils, grassland soils, technosols and agricultural soils). We compared samples reacted and non-reacted with Fe(III). Specifically, we examined the combined fine silt and clay fraction (FSi+Cl), which was obtained by ultrasonic dispersion and wet sieving. In addition to batch experimental studies, we analyzed the speciation of Fe before and after reactions by Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). Different Fe species (i.e. chemical and mineral forms of Fe) have been also assessed by principle component analysis (PCA) and linear combination fitting (LCF) of EXAFS spectra.

Analysis of Fe EXAFS spectra suggested that Fe speciation can be dependent on land use and C concentration. Results indicate the formation of ferrihydrite-like, polymeric Fe(III) oxides in the reacted coniferous forest and grassland soil samples, which had higher C and Fe concentrations. Conversely, mononuclear Fe(III)-SOM complexes dominated Fe speciation in the technosols and agricultural soils, which were characterized by lower C and Fe concentrations, inhibiting the hydrolysis and polymerization of Fe (III). Consequently, this study provides useful insights into storage and sequestration of C in different real-world soil ecosystems and unique information relevant to regulation of global terrestrial SOM cycling. These are important steps to achieving sustainable soil management.