Geoderma 261 (2016) 169–177

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Sorption of paddy soil-derived dissolved organic matter on hydrous iron oxide–vermiculite mineral phases

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ARTICLE INFO

Article history:
Received 28 May 2015
Received in revised form 20 July 2015
Accepted 21 July 2015
Available online 5 August 2015

Keywords:
Organic matter retention
Clay mineralogy
Surface properties
Binding mechanisms
Sorption isotherms

ABSTRACT

Sorption of organic matter (OM) onto soil minerals affects OM dynamics, and is strongly controlled by mineral surface properties. Moreover, the degree and mechanism of interaction between different minerals may influence their surface reactivity. We therefore aimed to understand mineral surface modifications brought about by different Fe (hydr)oxide–vermiculite associations, and their influence on OM sorption. This could have important implications on OM dynamics in young hydromorphic soils where seasonal variations in redox conditions may affect mineral surfaces. Paddy soil-derived dissolved OM was used in sorption isotherms on mixed mineral phases obtained by precipitating different amounts of Fe (hydr)oxides on vermiculite. Results evidenced that the surface properties of vermiculite strongly drove Fe (hydr)oxide precipitation, and consequently OM sorption mechanisms. The change in surface charge with increasing Fe loading resulted in a higher retention of dissolved organic carbon. However, dissolved organic nitrogen adsorption isotherms and FTIR carboxyl vibrational shifts revealed the occurrence of two binding mechanisms, one driven by electrostatic attraction of N-containing compounds by the negatively charged vermiculite surface, and another involving ligand exchange of carboxylic compounds with the positive oxides, precipitated in localized nucleation sites. Moreover, the modification of both solution and solid properties during sorption, promoted the selective adsorption of aromatic molecules with increasing Fe coverage.

1. Introduction

The interaction of soil organic matter (OM) with the mineral phase is known to affect a variety of biogeochemical and environmental processes including the retention, preservation and accumulation of OM on one hand (Eusterhues et al., 2005; Kalbitz and Kaiser, 2008; Mikutta et al., 2007; Schneider et al., 2010; von Lützow et al., 2006), but also the rate of growth, degree of crystallization and consequently the surface reactivity of mineral phases on the other (Bachmann et al., 2008; Kaiser et al., 2007).

Organic matter sorption is primarily controlled by variable charge minerals, mainly iron (Fe) and aluminium (Al) (hydr)oxides (Feng et al., 2005; Kaiser et al., 1996; Wattel-Koekkoek et al., 2001). In particular, poorly crystalline (hydr)oxides can show a high retention capacity due to their large reactive surface area and positive charge at pH < 8–9. However, in soil these oxides are often present, not as separated phases, but associated with or precipitated on other mineral particles, such as phyllosilicates. Association with metal (hydr)oxides modifies the properties of phyllosilicates, in particular electrical charge, specific surface area and porosity (Celi et al., 2003; Dimirkou et al., 1996). This results in complex mineral systems showing a different reactivity for OM which depends on the kind of phyllosilicate involved (Celis et al., 1998; Saidy et al., 2013), the percentage of Fe coverage (Celi et al., 2003), degree and mechanism of interaction (physical or chemical association) between the two minerals (Saidy et al., 2012; Sakurai et al., 1990), and chemical composition of the soil solution (Karim, 1984; Schwertmann and Thalmann, 1976).

Many studies have evaluated the effects of 1:1 phyllosilicate–Fe oxide associations (Arias et al., 1995; Celi et al., 2003; Celis et al., 1998; Dimirkou et al., 1996; Ioannou and Dimirkou, 1997; Jones and Saleh, 1986, 1987; Sakurai et al., 1990; Yong and Ohtsubo, 1987), while less attention has been paid to 2:1 phyllosilicates. Saidy et al. (2012, 2013) showed that the capacity of illitic and smectitic clays to sorb dissolved organic matter (DOM) was slightly affected by physical coating with different Fe oxides as a result of small variations in surface properties. This was in contrast with the findings of Celis et al. (1998) who reported that the surface area of montmorillonite–Fe oxide systems was much higher than that of the clay alone, and the pore

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http://dx.doi.org/10.1016/j.geoderma.2015.07.014

structure depended on the amount of Fe in the system. To the best of our knowledge, no studies after Carstea et al. (1970) investigated vermiculite–Fe oxide systems. These phyllosilicates are particularly abundant in young hydromorphic soils (Cucu et al., 2014) where seasonal variations in redox conditions may induce the reductive dissolution and subsequent reprecipitation of Fe (hydr)oxides on 2:1 clays. In these soils, the frequent alternations in redox conditions may result in significant modification of mineral surfaces with important implications on the sorption and desorption of DOM. In fact, OM stabilization in hydromorphic soils, such as rice paddies, may be strongly controlled by sorption on Fe (hydr)oxide–vermiculite systems, particularly in temperate regions. We therefore hypothesized that (i) the precipitation of Fe (hydr)oxides on vermiculite may bring about important mineral surface modifications which depend on the amount of Fe loading, (ii) these changes may strongly influence the extent and mechanisms of OM sorption, and (iii) interaction between OM and mineral surfaces may modify the reaction environment, which, in turn, affects OM retention. To test these hypotheses we synthesized and characterized different hydrous Fe oxide–vermiculite mineral phases with increasing Fe loading, and evaluated their interaction with a paddy soil-derived DOM through sorption isotherms.

2. Materials and methods

2.1. Preparation and characterization of mineral phases

Vermiculite (VM), supplied by Palabora Mining Company (South Africa), was first milled and then purified. Briefly, carbonate salts were removed by treatment with sodium acetate buffered at pH 4.8, Fe oxides by dithionite–citrate–bicarbonate, and OM by sodium hypochlorite oxidation at pH 8. The <1 μm fraction of purified VM was then separated by sedimentation, K-saturated with 1 M KCl, washed with deionized water until salt-free, and freeze-dried. Small aliquots were was also Mg-saturated with 1 M $MgCl_2$, and treated with ethylene glycol for spectroscopic analysis.

Four Fe (hydr)oxide–vermiculite systems (Fe–VM) with increasing proportions of Fe (1.3, 2.8, 4.7, and 5.6 mol Fe kg^{-1}, hereafter named 1Fe–VM, 2Fe–VM, 3Fe–VM and 4Fe–VM, respectively) were prepared by neutralizing different amounts of $Fe(NO_3)_3$ in a suspension of VM. For each system, 4 g of VM were dispersed in 800 mL of deionized water and left to equilibrate for 24 h under stirring. A known volume of 0.025 M $Fe(NO_3)_3$ at pH 2.0 was added dropwise to the VM suspension over 40 min under vigorous stirring. The pH of each suspension was then increased to 7.5 ± 0.3 with 1 M KOH, and subsequently centrifuged, washed with deionized water until the electrical conductivity was <10 μS cm^{-1}, and freeze-dried.

The VM and the four *x*Fe–VM mixed systems were characterized for their mineralogical and surface properties. X-ray diffraction (XRD) spectra were acquired on air-dried oriented slides of the Mg- and K-saturated VM and mixed systems at 25 °C, and after thermal treatments at 105 and 300 °C (40 kV and 20 mA, Fe filtered Co–Kα radiation; Philips PW 1710, Almelo, The Netherlands). Scans were made from 3 to 80° 2θ at a speed of 0.01° 2θ min^{-1}. The total content of precipitated Fe in the systems was determined by sodium dithionite–citrate–bicarbonate extraction (Fe_{DCB}; Mehra and Jackson, 1960), while the presence of poorly ordered Fe (hydr)oxides was estimated from the extraction of Fe with an ammonium oxalate solution buffered at pH 3.0 (Fe_O; Schwertmann, 1964). The specific surface area (SSA) and porosity of freeze-dried minerals were determined by adsorption–desorption of N_2 at 77 K after 24 h of out-gassing at 313 K under vacuum ($<10^{-4}$ kPa) with a surface area analyzer (Sorptomatic 1900, CarloErba, Rodano, Italy). The SSA was estimated by applying the Brunnauer–Emmet–Teller (BET) equation to the N_2 sorption data obtained in the relative pressure (p/p_0) range of 0.05 to 0.30 (Gregg and Singh, 1982). The SSA due to mesopores (2–50 nm) was derived from the adsorption branch of the isotherms using the Barrett–Joyner–Halenda model (Barrett et al., 1951), while the micropore surface (<2 nm) was calculated as the difference between the total SSA and the mesopore surface. The cation exchange capacity (CEC) was determined using the ammonium acetate method (Wilson, 1987), while the permanent negative charge (σ_0) was calculated as the ratio between the CEC and the SSA of each mineral. The zeta potential (ζ) was calculated from the electrophoretic mobility determined on a suspension adjusted to pH 5.5 and equilibrated for 24 h in 5 mM KCl, by Laser Doppler Velocimetry coupled with Photon Correlation Spectroscopy (LDV-PCS) using a spectrometer (DELSA 400, Beckman Coulter Inc., Hialeah, FL) equipped with a 5 mW He–Ne laser (632.8 nm).

2.2. Organic matter extraction and characterization

Water extractable organic matter (WEOM) and an alkali-extractable, acid-soluble OM fraction (AF) were obtained from a field fresh soil sampled from the Ap horizon (0–15 cm) of a rice paddy (Haplic Gleysol, NW Italy). These two OM pools were chosen to represent organic compounds stabilized on Fe (hydr)oxides under oxic conditions but potentially released into solution under anoxic conditions. Chemical and physical properties of the soil used were reported in Said-Pullicino et al. (2014). Briefly, WEOM was extracted from soil (<2 mm) with deionized water at a soil:solution ratio of 1:3 (w/v). After 2 h of shaking the suspension was centrifuged at 3500 rpm for 15 min, and the supernatant filtered through a 0.7-μm pore-sized glass fibre filter (GF/F, Whatman International Ltd., Maidstone, UK) and freeze-dried. The soil residue was subsequently extracted with 0.1 M NaOH using the same soil:solution ratio for 16 h. The alkaline extract was then acidified to pH 1.0 allowing for the acid-insoluble fraction to precipitate, and subsequently the supernatant was filtered through 0.7-μm pore-sized glass fibre filter, purified on Amberlite XAD-8, protonated by passing through an Amberlite IR-120 strongly acidic cation exchange resin, and finally freeze-dried. Filtration of WEOM and AF extracts at 0.7 μm instead of the conventional 0.45 μm was adopted because OM released into solution under anoxic conditions could have a high charge to mass ratio and dimensions >0.45 μm. Different proportions of WEOM and AF fractions were mixed to obtain a single OM fraction having a C_{AF}/C_{WEOM} ratio of 2.22, similar to that determined in the bulk soil. Since this mixture was assumed to represent organic compounds potentially released into solution under reducing conditions, it will be hereafter called *r*DOM.

The *r*DOM was characterized by chemical and spectroscopic analyses. Total C and N contents were determined by dry combustion (NA2500, Carlo Erba Instruments, Milano, Italy). Total acidity and carboxyl content were determined by potentiometric titration with $Ba(OH)_2$ and Ca acetate, respectively (Schnitzer and Gupta, 1965). Determination of the concentration of anions (Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}) was carried out by ion chromatography (AS50, Dionex, California; USA) while cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{3+}) were quantified by atomic absorption spectrometry (PerkinElmer AAnalyst 1400, USA). NH_4^+ concentration was determined spectrophotometrically by a modified Berthelot method involving reaction with salicylate in the presence of alkaline sodium dichloroisocyanurate (Crooke and Simpson, 1971). FTIR spectra of *r*DOM at pH 5.5 and 2.0 were acquired between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} (PerkinElmer Spectrum 100, USA) on pellets obtained by pressing 1.0 mg of *r*DOM with 200 mg of KBr. Liquid-state ^{13}C NMR spectra were acquired with a 400 MHz spectrophotometer (Jeol EX-400, USA). An aliquot of 200 mg of freeze-dried material was dissolved in 1 mL of 0.5 M NaOD/D_2O. The spectra were recorded at a ^{13}C resonance frequency of 100.53 MHz with inverse-gated decoupling, 0.2 s acquisition time, a 45° pulse, and 2 s relaxation delay for a total acquisition time of 24 h. The free induction decays were processed by applying 50 Hz line broadening and baseline correction.