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Adsorption-desorption behavior of dissolved organic carbon by soil clay fractions of varying mineralogy

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ABSTRACT

Soil clay minerals significantly influence the accumulation and stabilization of organic carbon (OC). However, the effect of interactions among phyllosilicate clay minerals, native OC and sesquioxides (Fe/Al oxides) on the adsorption-desorption of dissolved organic carbon (DOC) under different background electrolyte types and concentration is poorly understood. A set of batch adsorption-desorption experiments were conducted using pedogenic clays extracted from soils dominated by kaolinite-illite (Kaol-Ill), smectite (Smec) and allophane (Allo). The clay samples were sequentially treated to remove native OC and sesquioxides, and tested for adsorption-desorption of DOC under various solution conditions. All the experiments were conducted at pH 7 using water extractable fraction of OC from wheat residues. DOC adsorption increased with increasing background electrolyte concentration, and the presence of Ca^{2+} significantly enhanced the uptake in comparison to Na^+ due to a possible cationic bridging effect. Under all electrolyte conditions, the maximum DOC adsorption capacity (Q_{max}) (mg g^{-1}) of the soil clay fractions (SCF) maintained the order: Allo > Smec > Kaol-Ill. A similar order was also observed when the adsorption capacities were normalized to the specific surface area (SSA) of the SCFs (mg m^{-2}). DOC adsorption showed a positive relationship with SSA, and sesquioxides and allophanic minerals provided the largest contributions to the SSA in the SCF. Removal of sesquioxides from the SCF resulted in a decrease in SSA and thus DOC adsorption, whereas removal of native OC increased the SSA and subsequent DOC adsorption. Because this study used pedogenic SCFs which represented soils formed in different environments instead of processed clays from geological deposits, it provided realistic information about the interaction of DOC with SCF in relation to their native OC and sesquioxide contents. It also revealed the importance of Ca^{2+} in enhancing the carbon adsorption capacities of these SCFs.

1. Introduction

In the global carbon (C) cycle, adsorption of organic carbon (OC) on clay mineral surfaces is an important process for stabilizing soil OC under the natural environment (Feng et al., 2005). Adsorption of dissolved organic carbon (DOC) by phyllosilicate clays and Fe/Al oxides controls its mobility, retention and degradation through mineralization, thus leading to stabilization of OC in soils (Mikutta et al., 2007; Kothawala et al., 2008; Bolan et al., 2011; Saidy et al., 2015). DOC, along with other plant nutrients can also be leached into the groundwater or lost from the soil surface through runoff (Baldock and Skjemstad, 2000), which ultimately degrades the drinking water quality (EPA-South-Australia, 1998). Also, leaching of DOC from the soil surface can impact the nutrient availability to plants and degradation of soil structure (Kalbitz et al., 2000; Mavi et al., 2012). The free movement of DOC is mainly controlled by its adsorption to soil clay surfaces (Ussiri and Johnson, 2004).

The ability of a soil to sequester C may depend on the nature of dominant clay minerals and also the clay content (Shen, 1999; Kahle et al., 2003). In general, soil clays with higher specific surface area (SSA), cation exchange capacity (CEC) and Fe/Al oxides lose less C through mineralization (Ransom et al., 1998; Kahle et al., 2003). Despite having similar clay contents (texture), allophanic and smectitic soils retained more C than kaolinitic or vermiculitic soils (Saggar et al., 1996, 1999). Kaolinitic clay minerals (low activity clays) have a 1:1 layer structure, a low CEC, low SSA and some pH-variable charge. Smectitic clay minerals have a 2:1 structure, a higher CEC and SSA, and predominantly permanent negative charge. Illitic clay minerals, which are non-expanding, have a SSA and CEC that are higher than kaolinitic clay minerals but lower than smectitic types. Allophanes are poorly crystalline, have a very high SSA, but a pH-variable charge that only gives a moderate CEC

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(Churchman and Lowe, 2012). The presence of sesquioxides in the soil clay fractions (SCF) greatly influences the DOC adsorption capacity due to their higher SSA (Wiseman and Püttmann, 2006; Spielvogel et al., 2008; Saidy et al., 2013) and specific chemical interactions (Kleber et al., 2015).

A number of mechanisms for the adsorption of DOC on clay mineral surfaces have been proposed including inner sphere complexation (e.g., ligand exchange and cationic bridging) or outer sphere complexation also known as physical adsorption (e.g., hydrogen bonding), van der Waals forces and pi–donor–acceptor interactions (Gu et al., 1994; Guggenberger and Kaiser, 2003; Mikutta et al., 2007; Rashad et al., 2010; Keiluweit and Kleber, 2009).

Earlier studies also showed strong effects of background electrolyte, ionic strength, pH, native OC, sesquioxides and soil mineral contents on adsorption-desorption of DOC (Kahle et al., 2004; Lützow et al., 2006; Kothawala et al., 2009; Rashad et al., 2010). An increased DOC adsorption to clay surfaces could be attributed to a higher background electrolyte concentration in the soil solution (Mavi et al., 2012). Divalent cations (e.g., Ca^{2+}) would form stronger bonds between negatively charged clay minerals and DOC through cation bridging than monovalent cations (e.g., Na^{+}) (Marchuk and Rengasamy, 2011; Roychand and Marschner, 2014; Setia et al., 2013). The ratio between Ca^{2+} to Na^{+} in soil- solution would also affect the DOC adsorption-desorption behavior on clay mineral surfaces (Chorom and Rengasamy, 1995).

Despite many studies reporting on the adsorption of DOC by clay minerals under various conditions, a lack of understanding of adsorption mechanisms remains. Most of the previous studies were conducted using refined aluminosilicate minerals obtained from geological clay-deposits (Guggenberger and Kaiser, 2003; Feng et al., 2005; Rashad et al., 2010; Saidy et al., 2013) while pedogenic soil clays with or without native OC or sesquioxides could behave differently than clay minerals from deposits (Churchman and Lowe, 2012). Soil clay minerals are very different from processed clay minerals from clay-deposits because of their formation in highly heterogeneous and dynamic soil environments (Churchman, 2010; Churchman et al., 2012; Churchman and Lowe, 2012). Coating with OM or sesquioxides, or both, on their reactive surfaces typify many soil clays, and the properties of the clays may reflect the characteristics of the coated material rather than the aluminosilicate component of clay itself (Kahle et al., 2004; Churchman and Lowe, 2012). Soil clay minerals might undergo a greater degree of weathering, represent a smaller particle size, contain a greater proportion of amorphous materials and have different SSA and charge characteristics in comparison to processed clay minerals (Wilson, 1999; Churchman, 2010; Churchman and Lowe, 2012). Also, the dominant exchangeable cations in soil clay minerals could be completely different from that of a processed clay mineral (Churchman and Lowe, 2012). As a result, the interactions of DOC with soil clays could be different from that of clay minerals from deposits. The interactions could also vary for soil clays originating in different environments (Churchman, 2010; Churchman and Lowe, 2012). Therefore, batch DOC adsorption-desorption experiments were conducted in this study with three pedogenic SCFs (kaolinitic-illitic, smectitic and allophanic) with and without native OC and sesquioxides under different solution conditions. Instead of using aluminosilicates from deposits, soil-isolated clays were used in order to get a better understanding of the behavior of the C sequestration capacity of clay minerals in soils. It was hypothesized that: (1) high electrolyte concentration would favor DOC uptake in contrast to low electrolyte concentration; (2) higher adsorption would occur in the presence of a divalent cation (Ca^{2+}) than a monovalent cation (Na^{+}) on the exchange complex; and (3) DOC uptake would vary with varying SSA of the SCF as influenced by their native OC and sesquioxide contents.

2. Materials and methods

2.1. Clay isolation, removal of OC and physico-chemical characterization

This study included clays which were extracted from clay-rich (5–20 cm depth) soils, collected from 3 different sites in South Australia - Hoyleton, Waite campus and Mt. Schank. The Hoyleton soil (from the location of the virgin soil studied by Churchman et al. (2010)) was rich in kaolinite and illite with small amounts of inter-stratified illite-smectite, smectite, quartz, feldspar and iron oxide (goethite). Smectite was the dominant clay mineral in the Waite campus soil (from the same location as soil A1024 in Stace et al. (1968)) but with a small amount of inter-stratified illite-smectite, smectite, illite, quartz, feldspar and iron oxides (goethite and hematite). Mt. Schank soil (from the Laslett Road location in Lowe and Palmer (2005)) was dominant in allophane with small amounts of inter-stratified kaolinite- smectite, quartz, feldspar and Fe oxides (ferrihydrite and goethite). The mineralogical composition and pH of the experimental soils and the CEC values of the isolated SCF are summarized in Table 1.

The soils were passed through a 2 mm sieve and stored air-dry prior to clay extraction. Clay extraction was carried out using a prolonged shaking method for the disintegration of soil particles (Churchman and Tate, 1986; Roychand and Marschner, 2013). The prolonged shaking method was employed in order to retain the natural physico-chemical properties of the isolated clays. The air-dried soil (50 g) was placed in a 2 L Schott bottle with 500 mL Milli-Q water (18.2 Ω) (1 soil: 10 water ratio). After end-over-end shaking (40 rev min^{-1}) for 24 h, the suspension was transferred to a 1 L measuring cylinder. The 30 cm height of the soil-water solution in the measuring cylinder was achieved by topping up with Milli-Q water, stirring, and then left to settle for 16 h at 22 °C. According to Stoke's Law, the <2 μm clay fraction was collected by siphoning off the top 22 cm of the soil suspension using a pump to avoid disturbance in the suspension. The clay suspension was centrifuged for 30 min at 3500 rpm, and the clear supernatant was discarded. The precipitated clay was collected, freeze dried, and stored in a desiccator for further analysis.

Total OC concentration in the SCF was analyzed by combustion using a Leco C/N analyzer (Leco TruMac® CNS/NS, USA) following complete elimination of inorganic carbon using HCl. The combustion temperature and oxygen flow time were 1300 °C and 5 s, respectively. The CEC of SCF was measured using a method described by Rayment (2011). In brief, a 0.5 g sample was mixed with 30 mL solution of 1 M sodium acetate (pH 7) and shaken for 15 min using an end-over-end shaker. This process was repeated 4 times. After complete saturation with sodium acetate, the sediment was washed with ethanol (>99% purity) to achieve

Table 1
Properties of experimental soils and clay fractions.

Soil types	Clay % in soil	Clay fractions present	pH	CEC of SCF (cmol (P^{+}) kg^{-1})
Kaolinitic-illitic	18	Co-dominant: kaolinite, illite sub-dominant:illite- smectite, smectite, quartz	7.83	9.4
Smectitic	44	Co-dominant: smectite, kaolinite sub-dominant: illite-smectite, kaolinite, quartz, feldspar	8.25	70
Allophanic	28	Dominant: allophane sub-dominant: kaolinite-smectite, quartz, feldspar	7.7	48