



# The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide



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## ARTICLE INFO

### Article history:

Received 31 May 2012

Received in revised form 23 May 2013

Accepted 28 May 2013

Available online xxxx

### Keywords:

Soil carbon stabilisation

Surface areas

Clay mineralogy

Binding mechanisms

Electrostatic interaction

## ABSTRACT

Sorption of organic carbon onto phyllosilicate clays and hydrous iron oxides influences the accumulation and stabilisation of organic carbon in soils. However, the effects of interactions between hydrous iron oxides and phyllosilicate clays on the sorption of dissolved organic carbon (DOC) are poorly understood. We carried out a batch experiment to examine the effects of goethite coatings on kaolinite, illite, and smectite on DOC sorption. The effect of coating illitic clay with different hydrous iron oxides (haematite, goethite, ferrihydrite) on DOC sorption was studied in another experiment. Organic matter extracted from dried medic (*Medicago truncatula* cv. Praggio) shoot residue was reacted with minerals at DOC concentrations ranging from 0 to 200 mg C L<sup>-1</sup> at pH 6.0. The maximum adsorption capacity ( $Q_{max}$ ) of phyllosilicate clays, as determined from fits to the Langmuir equation, increased in the order kaolinite < illite < smectite on a mass basis and illite < smectite < kaolinite on a surface area basis. The sorption capacity of kaolinitic clay increased significantly with goethite coating, whereas the sorption capacity of illitic and smectitic clays was not affected by goethite coating. Ferrihydrite coating increased the sorption capacity of the illitic clays, while haematite coating decreased the sorption capacity; goethite-coated illitic clays had a sorption capacity similar to pure illitic clays. Desorption experiments resulted in the removal of 6–14% of the sorbed DOC. The presence of goethite reduced desorption from kaolinitic clays but did not influence desorption from illitic and smectitic clays. The results suggest that interactions of hydrous iron oxides and phyllosilicate clays can modify DOC sorption and desorption, probably by affecting the surface charges. Therefore, sorption and desorption of organic matter from soils may vary with mineral assemblage, with increasing suppression of the contribution of hydrous oxides at circumneutral to slightly alkaline soil reaction.

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## 1. Introduction

Sorption of organic matter (OM) onto mineral surfaces is important in a variety of natural environments. The sorption of OM can alter the physicochemical properties of minerals (Angove et al., 2002; Wang and Xing, 2005) and influence the transport and availability of nutrients and contaminants in soils and waters (Xing, 2001). Generally, most OM sorbed to mineral surfaces is hard to remove (Butman et al., 2007; Kahle et al., 2004; Kaiser and Guggenberger, 2007), indicating a high stability of OM–mineral associations. In addition, OM sorbed to clay minerals and oxides decomposes more slowly and to lesser extent than OM either dissolved or not attached to minerals (Kalbitz et al., 2005; Mikutta et al., 2007; Schneider et al., 2010). This suggests that sorption processes influence the accumulation and stabilisation of organic carbon in soils.

Clay minerals and oxides play an important role in the sorption of OM in soils. Hydrous iron oxides have been found to be particularly effective in sorbing and stabilising OM in soils (Kaiser and Guggenberger, 2000, 2003; Kaiser et al., 2007). Phyllosilicates or clay minerals have also been shown to be involved in preservation of OM (Balcke et al., 2002; Feng et al., 2005; Kahle et al., 2004). However, the capability of clay minerals to sorb OM is generally less than that of oxides (Chorover and Amistadi, 2001; Kaiser and Guggenberger, 2003). Tombácz et al. (2004), for example, observed that iron oxides (haematite and magnetite) adsorbed more humic acids than clay minerals (kaolinite and montmorillonite). In addition, Meier et al. (1999) found that the maximum amount of sorption of dissolved organic carbon (DOC) to goethite at pH 4.0 was 0.25–0.3 mg C m<sup>-2</sup>, whereas kaolinite was only able to sorb 0.08–0.10 mg C m<sup>-2</sup> under the same conditions. Acidic conditions favour the sorption of DOC to hydrous oxides; their sorption capacity drops with increasing pH (e.g., Gu et al., 1994). Therefore, in agricultural soils, typically being not strongly acidic, the contribution of hydrous oxides to OM binding might be less dominant than in strongly acidic forest soils.

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The effect of interactions between clay minerals and hydrous oxides on the preservation of organic carbon has received little attention. Hydrous oxides may attach to both clay minerals and organic compounds (Ohtsubo, 1989; Tombácz et al., 2004) to form clay–oxide–organic associations, which may significantly influence the capacity of soils to adsorb DOC. In some studies, sorption of DOC has been found to increase with increasing contents of dithionite-extractable Fe ( $\text{Fe}_d$ ) in soil (Kahle et al., 2004; Kaiser and Guggenberger, 2000). In a recent study, we reported that at pH 6, the presence of goethite coatings on illitic and smectitic clays did not influence the stabilisation of plant residue-derived OC as compared to those clays without goethite addition (Saily et al., 2012). Hence, the relative contribution of hydrous oxides and phyllosilicate clays on OC sorption remains uncertain. One possible reason could be partial or even complete compensation of the hydrous oxides' positive charge upon their association with negatively charged phyllosilicate clays.

Most studies on the sorption of OM on iron oxides have been carried out using soil samples containing different amounts of oxalate or dithionite-extractable Fe (e.g., Benke et al., 1999; Kahle et al., 2004; Kothawala et al., 2009) or in experiments where sorption was measured separately on phyllosilicate clays and oxides (e.g., Feng et al., 2005; Meier et al., 1999; Mikutta et al., 2007). These approaches do not allow for comprehensive testing of different types of phyllosilicate clays and hydrous oxides on the sorption of OM. There are few studies in which sorption has been measured in systems consisting of dissolved OM added to mixtures of clay minerals and hydrous oxides (Fusi et al., 1989; Kaiser and Zech, 1998). This approach enables the interactive effect of hydrous oxides and phyllosilicate clays on OC sorption to be tested directly.

The goal of this study was to examine the effect of interactions between clay minerals and hydrous iron oxides on the sorption of plant-derived soluble OM. The objectives were to: (i) determine the sorption–desorption characteristics of OC to different clays, (ii) examine the effect of the addition of iron oxide (goethite) on the sorption–desorption of OC to clays differing in mineralogy, and (iii) examine the effect of adding different hydrous iron oxides on the capability of illitic clay to sorb and desorb OC.

## 2. Materials and methods

### 2.1. Clay minerals, hydrous iron oxides and chemical characterisation

Kaolinite, illite and smectite clays were obtained from the collection of clay minerals at CSIRO Land and Water, Adelaide, Australia. The clays were prepared by the flocculation of the  $<2 \mu\text{m}$  fraction with  $\text{CaCl}_2$  and removing the excess salt by dialysis until the electrical conductivity (EC) was  $<10 \text{ mS cm}^{-1}$  and freeze-drying.

Goethite ( $\alpha\text{-FeOOH}$ ) was produced as described by Atkinson et al. (1967), by slowly neutralising a  $\text{FeCl}_3$  solution with NaOH and aging the precipitate at  $55 \text{ }^\circ\text{C}$  for 3 days. Two-line ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) was prepared by neutralising a  $0.1 \text{ M FeCl}_3$  solution with NaOH (Schwertmann and Cornell, 1991). Haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) was produced by aging a suspension of fresh ferrihydrite at pH 7 and a temperature of  $90 \text{ }^\circ\text{C}$  (Schwertmann and Cornell, 1991). The nature of the three mineral phases has been confirmed by X-ray diffraction (D5005, Siemens AG/Bruker AXS, Karlsruhe, Germany), and tests for solubility in dithionite–bicarbonate–citrate reagent (Mehra and Jackson, 1958) as well as in acid oxalate solution (Schwertmann, 1964). The specific surface areas (as determined by  $\text{N}_2$  adsorption–desorption (Nova 4200 analyser, Quantachrome Corp., Boynton Beach, USA)) were  $36 \text{ m}^2 \text{ g}^{-1}$  (haematite),  $73 \text{ m}^2 \text{ g}^{-1}$  (goethite), and  $212 \text{ m}^2 \text{ g}^{-1}$  (ferrihydrite).

Hydrous iron oxide coated clays (kaolinite, illite and smectite with goethite; illite with goethite, haematite and ferrihydrite) were prepared through the precipitation of clay (30 g) with hydrous oxide (3 g) in  $0.01 \text{ M CaCl}_2$ . Separate suspensions of clay (kaolinite, illite or smectite) and hydrous oxides (goethite, haematite or ferrihydrite) were prepared

in  $0.01 \text{ M CaCl}_2$  (1:10 = w:v) and their pH was adjusted to 6.0 with HCl or NaOH. The suspensions were combined, stirred, centrifuged at  $5500 \text{ g}$  for 10 min, and decanted carefully. The coated clays were then re-suspended in demineralised water and centrifuged at  $5500 \text{ g}$  for 10 min. This procedure was repeated until the EC of the supernatant was  $<100 \mu\text{S cm}^{-1}$ . The coated clays were freeze-dried and then sieved to  $<200 \mu\text{m}$ . The coated clays had between 8 and 9 g of hydrous oxide per kg clay. The clays without coating received similar treatments to clays with hydrous iron oxide coating.

Clay mineralogy was determined by X-ray diffraction (Siemens AG/Bruker AXS D5000). The specific surface area (SSA) of clay minerals and coated clay minerals was determined by nitrogen adsorption at  $77 \text{ K}$  and subsequent desorption of nitrogen with a Tristar 5-point BET-instrument on freeze-dried samples. Nitrogen cannot access interlayer spaces of phyllosilicate clays, thus, the SSA is an estimate of external surfaces. Interlayer surfaces do not contribute to the DOC sorption of phyllosilicate clays (Baham and Sposito, 1994), hence external surfaces represent the interfaces where DOC sorption takes place. The cation exchangeable capacity (CEC) of clays and coated clays was determined using the ammonium acetate (pH 7) method (Rhoades, 1982). Exchangeable bases (Na, K, Ca and Mg) were analysed by atomic absorption spectroscopy (AAS) after extraction with ammonium acetate. The contents of dithionite-extractable iron ( $\text{Fe}_d$ ) were measured using the method of Blakemore et al. (1987). Briefly,  $0.5 \text{ g}$  aliquots of freeze-dried clays and coated clays were shaken with  $1 \text{ g}$  sodium dithionite and  $50 \text{ mL}$  sodium citrate for 16 h. Then  $0.05 \text{ M MgSO}_4$  was added as a flocculant, the samples were centrifuged and the supernatant decanted. The supernatant was made up to  $100 \text{ mL}$  with deionized water, and the concentration of Fe was determined by inductively coupled plasma spectroscopy.

### 2.2. Preparation of dissolved organic carbon (DOC) solutions

Dissolved organic carbon (DOC) was extracted from an oven-dried medic (*Medicago truncatula* cv. Praggio) shoot residue by adding  $2 \text{ L}$  deionized water to  $200 \text{ g}$  of ground medic ( $<2 \text{ mm}$ ). After 10 min of gentle stirring, the suspension was allowed to settle for 40 h at  $22 \text{ }^\circ\text{C}$  and then filtered through a  $0.45\text{-}\mu\text{m}$  membrane filter (Millipore Corporation, USA). The filtrate contained  $14.7 \text{ g C L}^{-1}$  and  $1.44 \text{ g N L}^{-1}$  (determined by Thermalox total organic C – total N analyser; Analytical Sciences Limited, Cambridge). The pH of the DOC solution was adjusted to 6.0 by addition of HCl or NaOH. Ten DOC solutions ranging in concentration from 0 to  $200 \text{ mg C L}^{-1}$  were prepared for sorption experiments by diluting with a solution containing  $10 \text{ mg NaCl L}^{-1}$ ,  $20 \text{ mg CaCl}_2 \cdot 2\text{H}_2\text{O L}^{-1}$  and  $24 \text{ mg K}_2\text{SO}_4 \text{ L}^{-1}$ . The pH of the diluted DOC solutions was adjusted to 6.0 by addition of HCl or NaOH.

### 2.3. Sorption experiments

Two sets of experiments were carried out: *experiment 1* to assess the effect of goethite coatings on DOC sorption onto different phyllosilicate clays, and *experiment 2* to examine the effect of the coating of three different hydrous iron oxides (haematite, goethite and ferrihydrite) on DOC sorption onto illitic clay. Sorption experiments were carried out using the batch equilibrium method in triplicate at pH 6.0 by adding  $30 \text{ mL}$  of DOC solution to  $0.03 \text{ mg}$  clay or clay-oxide in  $50\text{-mL}$  centrifuge tubes. The ratio of 1:1000 (g clay dry weight:mL DOC solution) was chosen to achieve maximum sorption and ensure reliable analysis of the mineralisation of sorbed DOC. The suspensions were shaken at  $22 \text{ }^\circ\text{C}$  for 12 h in the dark. Preliminary tests showed this time to be sufficient to reach equilibrium. Blanks without clay minerals were included to measure the initial DOC concentration. The suspensions were then centrifuged for 30 min at  $2000 \text{ g}$ , and the supernatants were filtered through  $0.45\text{-}\mu\text{m}$  syringe filters (Millex-HV, Millipore Ireland Ltd, Tullagreen, and Carrigtwohill). The concentration of DOC in the filtrate was measured using a Thermalox TOC-TN analyser. The replicate variability in DOC concentration was  $<3\%$ . The amount of OC sorbed was

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