



# Effects of natural organic matter on the binding of arsenate and copper onto goethite



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## ABSTRACT

Goethite is a common iron oxide present in the environment. It is used as a model system to represent the mineral fraction of the soil, whereas humic acid is used as a model system to represent natural organic matter (NOM). In this study, we tried to understand the behaviour of anionic and cationic pollutants in a model system, which could easily represent the organic-mineral interaction in the environment. Specifically, the retention of arsenate and copper over different organo-mineral systems was studied. The obtained results show an increase in the adsorption of copper as the pH and the C content in the organo-mineral composites was raised, whereas in the case of the arsenate, the opposite behaviour was observed. The adsorption behaviour was compared with that of the end-members goethite and humic acid. Furthermore, the NOM-CD model (natural organic matter-charge distribution model) was used to describe the reactivity of the pollutants in the solid/solution interphase and to predict the surface and aqueous speciation. To simulate the behaviour of the organo-mineral composites, a surface component was included to describe the chemical and electrostatic interactions of the NOM with the goethite in the modelling of the solid/solution interphase. This approximation allows the quantification of the effective organic matter, which can be used to describe the copper and arsenate reactivity in organo-mineral systems.

## 1. Introduction

In the last decades, anthropogenic activities have provoked great concern due to their relationship with environmental and health problems. These activities have produced an increase in the concentration of trace metals in soil and aquatic systems, exceeding common background levels. Trace elements, such as arsenic and copper are common contaminants released into the environment as a result of mining, industrial, and agricultural activities.

Arsenic is a very toxic element commonly present in the environment as As(III) and As(V), being the latter predominant in oxic systems. Due to its carcinogenicity, phytotoxicity and biotoxicity, arsenic pollution is of great concern. Its concentration in natural waters should be below 10 µg/L, which is the limit concentration proposed by the World Health Organization (WHO) for drinking water (WHO, 2011). Nevertheless, concentrations above this value are commonly found in systems affected by anthropogenic activities (Smedley and Kinniburgh, 2002). Copper, although considered essential for living organisms, also has the potential to be toxic or poisonous. The amount of copper required to produce toxic effects is not yet well established neither for

animals nor for plants (Hooda, 2010). The typical concentrations of copper found in aquatic systems vary from 0.0005 to 4.8 mg/L and depend on the pH and oxidation state. The limit concentration for drinking water proposed by the WHO (2011) is 2 mg/L.

Natural organic matter (NOM) and iron (hydr)oxides (FeOx) are nanosize colloidal particles present in soils, sediments, and aquatic systems. NOM is mainly constituted by small well-defined molecules and by large organic macromolecules, i.e. humic acid (HA), fulvic acid (FA) or humin. The interaction of NOM with mineral oxides and hydroxides often affect the fate and transport of ions in both aquatic and terrestrial environments (Mikutta et al., 2006; Mikutta et al., 2014). The acidic groups, mainly carboxylic and phenolic, present in the NOM are able to bind with the hydroxyl groups present at the mineral surfaces leading to the formation of organo-mineral composites. These organo-mineral composites can inhibit or enhance sorption of ionic compounds, enhance sorption of non-ionic compounds, enhance or inhibit mineral dissolution, and critically alter charge characteristics of soil surfaces. The presence of NOM can significantly reduce the number of oxyanions adsorbed onto mineral surfaces (Antelo et al., 2007; Gustafsson, 2006; Wang et al., 2015; Weng et al., 2009). However, the

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presence of NOM is known to enhance the sorption of cations due to changes in the electrostatic interaction and also the formation of ternary complexes (Moon and Peacock, 2013; Weng et al., 2008). Nevertheless, the way in which NOM mechanistically affects the adsorption of different ions on these organo-mineral composites has not been totally elucidated and few attempts to obtain a mechanism via spectroscopic methods have been made (Moon and Peacock, 2012).

Modelling trace metal sorption onto iron (hydr)oxide phases in the presence of NOM has also received much attention (Borggaard et al., 2005; Gustafsson, 2006; Moon and Peacock, 2013; Weng et al., 2008). Thus, different model approaches are often used to explain trace metal behaviour in these binary systems. It is common to use the NICA-Donnan model (Non-Ideal Competitive Adsorption-Donnan model) (Kinniburgh et al., 1996) to describe the interaction between the organic matter and metals and the CD-MUSIC (Charge Distribution MultiSite Complexation) model (Hiemstra and van Riemsdijk, 1996) to calculate ion adsorption over metal (hydr)oxides, considering that mineral surfaces have different types of surface groups with specific binding affinities. To explain ion adsorption in ternary systems, the linear additivity model has been used often, assuming that the ion adsorption properties of the organic matter (OM) or FeOx in the ternary systems are the same as in the binary systems (Moon and Peacock, 2013; Weng et al., 2008; Xiong et al., 2015). The calculation is done in two steps calculating the amount of metal adsorbed to the OM and FeOx with the NICA-Donnan and CD-MUSIC model, respectively. Then, the amount of metal adsorbed to the organo-mineral surface is calculated as the total amount of metal bound to FeOx and to the fraction of OM adsorbed. Several studies have evaluated metal ion binding in ternary systems (Christl and Kretzschmar, 2001; Moon and Peacock, 2012; Saito et al., 2005; Weng et al., 2008). A different approach in order to calculate the metal adsorption in ternary systems involves the more advanced LCD (Ligand and Charge Distribution) model (Filius et al., 2003; Weng et al., 2007), which integrates both NICA and CD-MUSIC models.

The purpose of this work is to understand the behaviour of anionic and cationic pollutants on a model system that could easily represent the mineral-organic matter interactions in the environment. In the present study, arsenate and copper binding onto several OM-mineral composites were studied. The binding behaviour was compared with that of single adsorbents, goethite and humic acid. Goethite is a common iron oxide in the environment and it is usually used as a model system for iron mineral surfaces, whereas HA is used for NOM. The charge distribution (CD) model has been used to model the ion binding and to predict surface and aqueous speciation. To simulate the behaviour of the organo-mineral systems a surface component has been included to describe the electrostatic and chemical interaction of NOM at the mineral-water interface (Hiemstra et al., 2010; Hiemstra et al., 2013). This approach allows the quantification of the effective OM loading, which may affect the ion binding in the organo-mineral associations.

## 2. Materials and methods

### 2.1. Reagents and materials

Arsenate was purchased as potassium monobasic salt from Sigma and copper as nitrate trihydrate salt from Merck. All other chemicals were of Merck p.a. quality. The experiments were carried out using double-distilled and CO<sub>2</sub> free water. A-grade glassware and polycarbo-

nate material were used in the preparation of stock solutions and the synthesis and binding experiments, respectively.

### 2.2. Goethite synthesis and characterization

Goethite (GOE) was synthesized following the procedure described by Atkinson et al. (1967). Briefly, 5 M NaOH was added dropwise to a 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution with vigorous stirring, and N<sub>2</sub> was bubbled through the solution to prevent contamination with carbon dioxide. The precipitate thus obtained was then aged for 72 h at 60 °C, cooled at room temperature, dialyzed until the conductivity was below 10 μS/cm and freeze-dried to obtain a powder, which was then homogenized and stored.

In order to determine the surface charge properties of the goethite, potentiometric acid-base titrations were carried out following the method proposed by Antelo et al. (2005). The titrations were conducted using a Crison microBU 2031 autoburette, a Crison 2002 pH meter and a Radiometer GK2401C pH electrode (Ag/AgCl reference). The surface charge was determined at three different ionic strengths (0.01, 0.1, and 0.5 M), with KCl as inert electrolyte and with standard 0.1 M KOH and 0.2 M HCl solutions as titrants. The surface area was obtained by the BET N<sub>2</sub> sorption method, in a Micromeritics ASAP 2000 analyser (V3.03). X-ray powder diffraction (XRD, Phillips PW1710 diffractometer) was used to confirm that the resulting particles were goethite.

### 2.3. Humic acid extraction and characterization

Peat samples were taken from an ombrotrophic peat bog in Galicia (NW Spain, 43° 28' 5.10" N, 7° 32' 6.53" W). The site and soil characteristics and the proton binding properties of the peat soil have been described in detail by López et al. (2011). The peat soil was acid-washed to remove the inorganic ions present, following a method similar to that proposed by Smith et al. (2004). This peat was then dialyzed, freeze-dried and stored. The humic acid was extracted from the peat by the method described by the International Humic Substances Society (Swift, 1996). The solid-state CPMAS (cross-polarization magic angle spinning) <sup>13</sup>C NMR spectrum of the humic acid was recorded using a Varian INOVA-750 spectrophotometer. The elemental analysis was conducted with a LECO CHN-1000 analyser.

The chemical characteristics of the extracted HA (Table 1) are similar to those reported for other humic acid materials (Gondar et al., 2005). The solid-state CPMAS <sup>13</sup>C NMR data of the HA revealed an abundance of functional acid groups, mainly carboxylic, which represent 12% of the total C and are mainly responsible for the sorption reactivity, although phenolic groups were also present (4%). Furthermore, the high proportions of aromatic C (17%) and alkyl groups (34%) confirm that the HA is very structurally complex.

### 2.4. Preparation and characterization of OM-mineral composites

HA-coated goethite containing different proportions of C (FeC2, FeC4, FeC7 and FeC8) were prepared following the procedure described by Iglesias et al. (2010). Briefly, aqueous solutions of ionic strength 0.1 M (with KCl as electrolyte) and concentrations of HA ranging between 40 and 1500 mg/L were added to a goethite suspension, yielding final solid concentrations of 4 g/L. As low pH values favour HA sorption on goethite (Weng et al., 2006), the pH was adjusted to 4.0 by addition of 0.1 M HCl and KOH solutions under continuous stirring. Because of the different proportions of C in the four HA-coated goethite

**Table 1**  
Humic acid composition.

% C	% N	% O	% H	% C-Calkyl	% C-Oalkyl	% C-Arom	% C-Phenol	% C-COOH
51.2	3.4	36.2	5.4	34	37	17	4	12

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