

ADSORPTION OF SOIL-DERIVED HUMIC ACID BY SEVEN CLAY MINERALS: A SYSTEMATIC STUDY

REBECCA A. CHOTZEN, TAMARA POLUBESOVA*, BENNY CHEFETZ, AND YAEL G. MISHAEL*

Department of Soil and Water Sciences, Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem,
P.O. Box 12, Rehovot 7610001, Israel

Abstract—Humic acid (HA)-clay complexes are well known for their contribution to soil structure and environmental processes. Despite extensive research, the mechanisms governing HA adsorption are yet to be resolved. A systematic study was conducted to characterize the adsorption of a soil-derived HA to seven clay minerals. Clay surfaces affected HA adsorption directly due to structural differences and indirectly by altering solution pH. The following order of HA removal was obtained for the clay minerals at their natural pH: illite >> palygorskite > kaolinite > sepiolite > montmorillonite = hectorite >> talc. Removal of HA (precipitation and adsorption) by kaolinite and illite was attributed to the low pH they induce, resulting in protonation of the clay and HA surfaces. In spite of the low pH, the zeta potential for HA remained negative, which promoted HA adsorption to the protonated clay surfaces by ligand exchange. Ionic strength did not affect HA adsorption to clay minerals with low zeta potentials, indicating that charge screening is not a major mechanism of HA adsorption for these minerals, and supporting the suggestion that ligand exchange is the main adsorption mechanism to pH-dependent sites. The increase in ionic strength did, however, promote HA adsorption to clay minerals with high zeta potentials. At pH 8–9 the order of HA affinity for clay minerals was: palygorskite > sepiolite > montmorillonite = hectorite > kaolinite > illite > talc, emphasizing strong HA interactions with the fibrous clays. This strong affinity was attributed to their large surface areas and to strong interactions with OH groups on these clay surfaces. Results indicated that HA did not enter the intracrystalline channels of the fibrous clays but suggested that their macro-fiber structure facilitates HA adsorption. The sorption of HA to kaolinite further increased in the presence of Cu^{2+} , and the sorption of Cu^{2+} increased in the presence of HA, due to a number of synergistic effects. This study emphasizes the diverse effects of clay structure and solution chemistry on HA adsorption.

Key Words—Adsorption, Copper, Hectorite, Humic Acid, Illite, Kaolinite, Montmorillonite, Palygorskite, Sepiolite, Talc.

INTRODUCTION

Soil clay minerals have very large surface areas available for sorption (Grim, 1968; Sposito, 1984; Yapar *et al.*, 2015). In soil, these surfaces are rarely bare but instead coated with organic matter, thus altering the clay-mineral physicochemical properties. Even a small amount of soil organic matter (~1%) can influence significantly the surface chemistry of minerals (Bertsch and Seaman, 1999). Many studies (Kerndorff and Schnitzer, 1980; Sparks, 2003) have examined sorption of contaminants to clays and/or to soil organic matter; to understand these processes better, exploration of the interaction between clay minerals and soil organic matter is required.

One of the most prevalent components of humic substances are humic acids (HAs), which are polyelectrolytes formed by secondary synthesis reactions during the decay process of soil organic matter that undergoes microbial transformation (Stevenson, 1994). The HAs

are heterogeneous agglomerations containing varying functionalities ranging from non-polar polymethylene chains to highly polar carboxylic acid fractions (Ghosh *et al.*, 2009). The HAs derived from soils tend to be larger and more aromatic in nature than aquatic HAs (Stevenson, 1994). Due to greater aromaticity, polyfunctionality, and hydrophobicity, HAs are more likely to form coatings on soil minerals than other humic substances (Zhou *et al.*, 1994). Adsorption of HA by mineral surfaces is influenced mostly by solution pH, ionic strength, and the type of exchangeable cations. These factors also affect HA conformational changes (Vermeer *et al.*, 1998; Essington, 2015).

Complexes of HA and clay contribute to soil structure and water-holding capacity, and are involved in reductive and oxidative reactions, playing a major role in the cycling of various nutrients and pollutants (Sparks, 2003). Interactions between HA and clay have been studied widely, and the reported mechanisms include

* E-mail address of corresponding author:
tamara.polubesoava@mail.huji.ac.il;
yael.mishael@mail.huji.ac.il
DOI: 10.1346/CCMN.2016.064027

This paper is published as part of a special section on the subject of 'Clays in the Critical Zone,' arising out of presentations made during the 2015 Clay Minerals Society-Euroclay Conference held in Edinburgh, UK.

ligand exchange, cation and water bridging, van der Waals forces, and entropy-driven hydrophobic interactions. Inner-sphere adsorption by ligand exchange is considered to be one of the most significant HA sorption mechanisms (Gu *et al.*, 1994; Zhou *et al.*, 1994; Kretzschmar *et al.*, 1997). Ligand exchange occurs between polar organic functional groups of HA and mineral hydroxyls. Ligand exchange is significant mainly on Fe and Al oxides or on kaolinite where an abundance of hydroxyl edge surface sites are available for adsorption (Murphy *et al.*, 1994; Kleber *et al.*, 2007). The adsorption of HA on 2:1 clay minerals occurs mainly on the large basal surfaces; electrostatic interactions and interactions such as hydrogen bonding and cation bridging account for the formation of organic coatings on the clay particles (Zhou *et al.*, 1994; Sutton and Sposito, 2006; Wang *et al.*, 2012). The dominant interactions are, on the one hand, determined by the nature of the HA molecules and, on the other, by the properties of the mineral surfaces.

Despite extensive research on HA–clay interactions in recent decades (Greenland, 1971; Baham and Sposito, 1994; Zhou *et al.*, 1994; Spark *et al.*, 1997a; Vermeer *et al.*, 1998; Ghosh *et al.*, 2009; Wang *et al.*, 2012), the chemical properties of HA and the mechanisms and factors governing its adsorption are still debated (Sutton and Sposito, 2005). The effects of ionic strength and solution pH on HA adsorption to clays have been studied, but the effect of the clay ‘natural’ pH (pH of aqueous solutions equilibrated with clays) has not been addressed. Most artificially induced pH does not describe accurately the conditions occurring in the proximity of soil clay particles due to the buffer properties of clays. Furthermore, most studies only examined the adsorption of HA to one or two clay minerals (montmorillonite and kaolinite) under specific conditions. Correlation of the results of various studies and conclusions regarding the combined effects of mineral type and soil solution on sorption are difficult to establish, therefore (Spark *et al.*, 1997a). One of the important factors affecting sorption of HA to minerals is heavy metals, and, in particular, copper (Spark *et al.*, 1997b; Liu and Gonzalez, 1999; Arias *et al.*, 2002; Sparks, 2003; Komy *et al.*, 2014). Copper, which in acid media is mostly presented as the cation Cu^{2+} (Arias *et al.*, 2002), can form complexes with HA (Kholodov *et al.*, 2014). The HA can also promote adsorption of copper on minerals (Arias *et al.*, 2002; Hizal and Apak, 2006). To understand interactions in a Cu-HA-clay system, different combinations of these components, as well as their simultaneous and non-simultaneous addition, should be investigated.

The objective of the present study was, therefore, to conduct a systematic study of the adsorption of a soil-derived HA to clay minerals: montmorillonite, illite, and kaolinite which are abundant in soil, and palygorskite, hectorite, sepiolite, and talc, which are less common and have not been studied widely in this regard.

The affinity of HA to a wide range of clay minerals was investigated and compared. The impact of ionic strength and the clay ‘natural’ pH on HA adsorption was studied. The effect of clay-surface structure on HA adsorption was also investigated. In addition, Cu^{2+} and HA were found to have mutual effects on their adsorption to the acidic clay kaolinite.

MATERIALS AND METHODS

Humic acid

Humic acid was extracted from the soil of a citrus orchard (Rhodoxeralf) (Basra, Israel) as described by Drori *et al.* (2008). The HA elemental composition was measured using a Flash EA 1112 CHNS-O elemental analyzer (Thermo Scientific, Milan, Italy), and found to be: C 53.4%; N 5.4%; O 35.6%; H 5.2%; S 0.4%. The ash content was 8.93%.

The HA solutions were prepared by dissolving HA in 0.05 M NaOH (Sigma-Aldrich, Rehovot, Israel) to obtain a 60 mg L⁻¹ stock solution with 0.1 M NaCl (Sigma-Aldrich, Rehovot, Israel) as the background electrolyte, and re-adjusted with HCl (Sigma-Aldrich, Rehovot, Israel) to pH 7. The stock solution was further diluted with 0.1 M NaCl to obtain solutions ranging from 1 to 53 mg L⁻¹. The bulk (initial) HA and unbound HA solutions were analyzed by UV-Vis spectroscopy using an Evolution 300 UV-Vis Spectrophotometer (Thermo Scientific, Madison, Wisconsin, USA) in the wavelength range 200–800 nm. Calibration curves for the sorption isotherms were created by plotting optical absorbance (at 254 nm) vs. HA concentration (Zhou *et al.*, 1994). Stock solutions were stored in refrigeration (4°C) under nitrogen atmosphere.

Clays

Wyoming Na-montmorillonite (SWy-2), palygorskite (PFI-1), and hectorite (SHCa-1) were obtained from the Source Clays Repository of The Clay Minerals Society. ‘Supreme’ kaolinite was obtained from English China Clays (now Imerys) (St. Austell, United Kingdom). Commercial baby powder of talc (Johnson & Johnson Consumer Companies Inc., Skillman, New Jersey, USA) was used; XRD analysis indicated no admixtures to the talc. ‘Pansil’ sepiolite was purchased from Tolsa Group (Madrid, Spain), and Fithian illite was obtained from Ward’s Natural Science Establishment (Rochester, New York, USA). Clays were used as provided without further purification. The physico-chemical characteristics of the clays are listed in Table 1.

The cation exchange capacity (CEC) of the clays was determined with BaCl_2 (J.T. Baker Chemical Co., Phillipsburg, New Jersey, USA) (Hendershot and Duquette, 1986). X-ray diffraction was used for mineral identification and for measuring changes in basal spacing after HA adsorption. For XRD analysis, clay suspensions (1–2 mL) were placed on a ground-glass

Table 1. Physicochemical properties of clays (SA = surface area; CEC = cation exchange capacity).

Mineral	Structure	BET SA (m ² g ⁻¹)	CEC measured (meq/100 g)	pH	Zeta potential (mV)
Hectorite	2:1	63 ^a	43.9 ^a	9.3	-35.4
Illite	2:1	85 ^c	41.97	4	-15
Kaolinite	1:1	16	11.84	4.7	-26.6
Montmorillonite	2:1	32 ^a	76.4 ^a	9.1	-44.2
Palygorskite	Fibrous	136 ^a	19.5 ^a	8.9	-18.4
Sepiolite	Fibrous	203 ^b	35.66	9.3	-14
Talc	2:1	2.9 ^d	7.33	10.1	-35.4

^a van Olphen and Fripiat (1979)

^b Campelo *et al.* (1987)

^c Seabaugh *et al.* (2006)

^d Chiem *et al.* (2006)

slide and left for 1 day to air dry and sediment, in order to obtain oriented samples. X-ray powder diffraction measurements were performed using a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a horizontal single-axis goniometer, radius 217.5 mm, secondary graphite monochromator, 2° Soller slits, and a 0.2 mm receiving slit. The XRD patterns over the range 2–13°2θ were recorded at room temperature using CuKα radiation (λ = 1.5418 Å) with the following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 0.02°2θ, and counting time of 1 s/step.

Copper

The CuCl₂·2H₂O, purchased from Merck (Darmstadt, Germany), was of analytical reagent grade. Stock solutions (0.05–0.25 mmol L⁻¹) were prepared by dissolving CuCl₂ in double-distilled water.

HA adsorption by clays

Batch adsorption experiments were performed by adding clay suspensions (0.5 mL) to Eppendorf tubes containing 1 mL of HA (1–53 mg L⁻¹). The clay concentration in all tubes was 3.33 g L⁻¹ with 0.1 M NaCl solution as a background electrolyte. Based on preliminary kinetics experiments, the equilibration time was 48 h for all adsorption experiments. The samples (three replicates for each HA concentration) were equilibrated on a rotary shaker at room temperature (24°C). The tubes were then centrifuged in an MPW 351RH Universal Table Top Centrifuge (MPW Med. Instruments, Warsaw, Poland) at 18,228 × g for 30 min; the supernatants were analyzed for HA remaining in the solution by UV absorption at 254 nm, as described above. Supernatant pH values were measured.

Preliminary experiments indicated no adsorption of HA to the centrifuge tubes and no precipitation of HA due to centrifugation, in the absence of clay. A control experiment containing mineral particles in 0.1 M NaCl showed a small residual absorbance after centrifugation

due to incomplete removal of mineral particles. To obtain true free HA concentrations, the absorbance of the supernatant from the tubes with the smallest initial HA concentration (1 mg L⁻¹) was subtracted from all supernatant absorbance values (Zhou *et al.*, 1994).

The zeta potentials and particle sizes of the clays, HA, and HA-Cu complexes were measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, UK) with Dynamic Light Scattering (DLS).

The effect of ionic strength on the adsorption of HA (at an initial concentration of 23 mg L⁻¹) was studied for all clays using NaCl at ionic strengths of 0.001, 0.01, 0.1, 0.5, and 1 M. In order to evaluate the effect of pH on HA adsorption, clay suspensions were adjusted to pH values of 4 and 9 with either HCl or NaOH. Low pH values (pH 5 and lower) led to HA precipitation, the extent of which could not be estimated with the methods used; removal of HA by illite and kaolinite from solution was described, therefore, as ‘removal’ and not ‘adsorption.’

In order to evaluate HA adsorption in the intracrystalline channels of sepiolite and palygorskite, adsorption isotherms and kinetics experiments were conducted on clays which were heated at 500°C before adsorption measurements. The experiments were performed on the previously heated clays, and on unheated clays, over a period of 50 h at 25°C.

Copper–HA–kaolinite interactions

Copper-sorption isotherms were measured by equilibrating CuCl₂ solutions (in a range from 3.17 to 15.87 mg L⁻¹, pH 5.4–5.7) and HA (20 mg L⁻¹) solutions with kaolinite suspensions (3.33 g L⁻¹). The suspensions were agitated in 40 mL centrifuge tubes on a reciprocating shaker for 48 h (to reach equilibrium). After equilibration, the tubes were centrifuged at 30,600 × g for 30 min and aliquots of the supernatant were decanted and analyzed for Cu²⁺ and HA content. The concentrations of Cu²⁺ were measured using radial

inductively coupled plasma atomic emission spectrometry (ICP-AES), ('ARCOS', SPECTRO Analytical Instruments GmbH, Kleve, Germany). The measurements were performed according to the EPA Standard Method 6010c (2007). The HA concentrations were determined using a VCSH total organic carbon (TOC) analyzer (Shimadzu, Japan). Prior to TOC measurements, supernatant solutions with pH >5 were acidified slightly with HCl, and N₂ was bubbled through all solutions for 5 min to remove oxygen.

The low pH of the kaolinite-HA suspension (~5) was maintained throughout the experiments with Cu²⁺. Cu²⁺-HA complexation was evaluated by mixing CuCl₂ solutions with HA solutions for 48 h at the same concentrations as were used in the experiments with kaolinite. Following equilibration, the complexes were centrifuged, and HA and Cu²⁺ concentrations in supernatants were measured as described above.

The desorption of HA was checked for the HA-kaolinite complexes in the presence of Cu²⁺ at the same solid:liquid ratios. The supernatant remaining after HA adsorption experiments was removed, and solutions containing Cu²⁺ were added to the HA-kaolinite complexes; the tubes were agitated for 48 h. The TOC concentrations were measured as described above. The HA desorption was found to be insignificant.

The morphology of palygorskite, sepiolite, and HA at pH 4 and 7, and of the HA-Cu²⁺ complexes, was studied by scanning electron microscopy (SEM). The HA samples, before and after Cu²⁺ sorption, were lyophilized. The samples were mounted on brass blocks, coated with Au/Pd (Quorum SC7620), and examined using a JSM-5410LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). The backscattered electron images were acquired at an accelerating voltage of 20 kV, with tungsten emitter, at low vacuum mode (28 Pa).

Data analysis

Isotherms of HA adsorption on the different clay minerals were fitted by the Freundlich equation:

$$q = K_F \times C_e^N \quad (1)$$

where q is the amount sorbed (mg g⁻¹), C_e is the HA equilibrium concentration (mg L⁻¹), K_F (mg g⁻¹) (mg L⁻¹)^{-N} is the Freundlich coefficient, and N

(dimensionless) indicates the isotherm linearity. Single-point distribution coefficients (K_d) were calculated as ratios of amounts adsorbed to the equilibrium concentrations of 0.5, 2, and 5 g/L.

RESULTS AND DISCUSSION

Adsorption of humic acid

The isotherms of HA adsorption (removal for illite and kaolinite) to seven clay minerals were obtained at the 'natural' pH of the various clays and are presented as the amount of HA adsorbed per clay (g) or per clay surface area (m²) (Figure 1a,b, respectively). The adsorption/removal isotherms of HA to most of the clay minerals are H- and C-shaped with the affinity order of illite >> palygorskite > sepiolite > hectorite = montmorillonite >> talc.

The HA sorption isotherms were fitted to the Freundlich equation for all minerals (except illite and kaolinite, in which HA precipitated due to the low pH). Freundlich coefficients were calculated for HA adsorption on the different clay minerals at their natural pH (Table 2). The values of K_F coefficients demonstrate HA adsorption affinities to clays, with K_F represented from strong to weak affinity. The K_d calculated at 0.5, 2, and 5 mg/L showed the same order as K_F values; K_d values decreased with increase in equilibrium concentrations, which indicates stronger HA affinity to the high-energy surface sites of clay minerals.

Normalizing HA adsorption/removal to the surface areas of the clays (Figure 1b) emphasizes the low coverage of montmorillonite, palygorskite, hectorite, and sepiolite by HA in comparison with the high coverage of talc, kaolinite, and illite.

Effect of pH on HA adsorption. Addition of HA to clays did not affect the pH of aqueous solutions equilibrated with clays (referred to as 'clay natural pH') due to the buffer properties of clays. The strong affinity of HA to illite and kaolinite, both of which have a low pH, might be attributed to adsorption, in addition to a certain degree of HA precipitation induced by the low pH of these clay minerals. The issue of separating HA adsorption to minerals at low pH from precipitation requires further investigation.

Table 2. Parameters for HA adsorption on clays.

Clay	K_F	N	r^2	$K_{d\ 0.5}$ ^(a)	$K_{d\ 2}$ ^(b)	$K_{d\ 5}$ ^(c)
Palygorskite	4.37 ± 0.09	0.68 ± 0.02	0.99 ± 0.41	5.46	3.49	2.60
Sepiolite	2.06 ± 0.08	0.76 ± 0.02	0.99 ± 0.32	2.43	1.75	1.41
Montmorillonite	1.48 ± 0.09	0.63 ± 0.03	0.97 ± 0.45	1.91	1.15	0.82
Hectorite	0.89 ± 0.04	0.86 ± 0.02	1.00 ± 0.18	0.98	0.81	0.71
Talc	0.37 ± 0.05	0.69 ± 0.05	0.94 ± 0.28	0.46	0.30	0.22

^a, ^b, ^c are single-point distribution coefficients at the HA equilibrium concentrations 0.5 mg/L^a, 2 mg/L^b, and 5 mg/L^c.

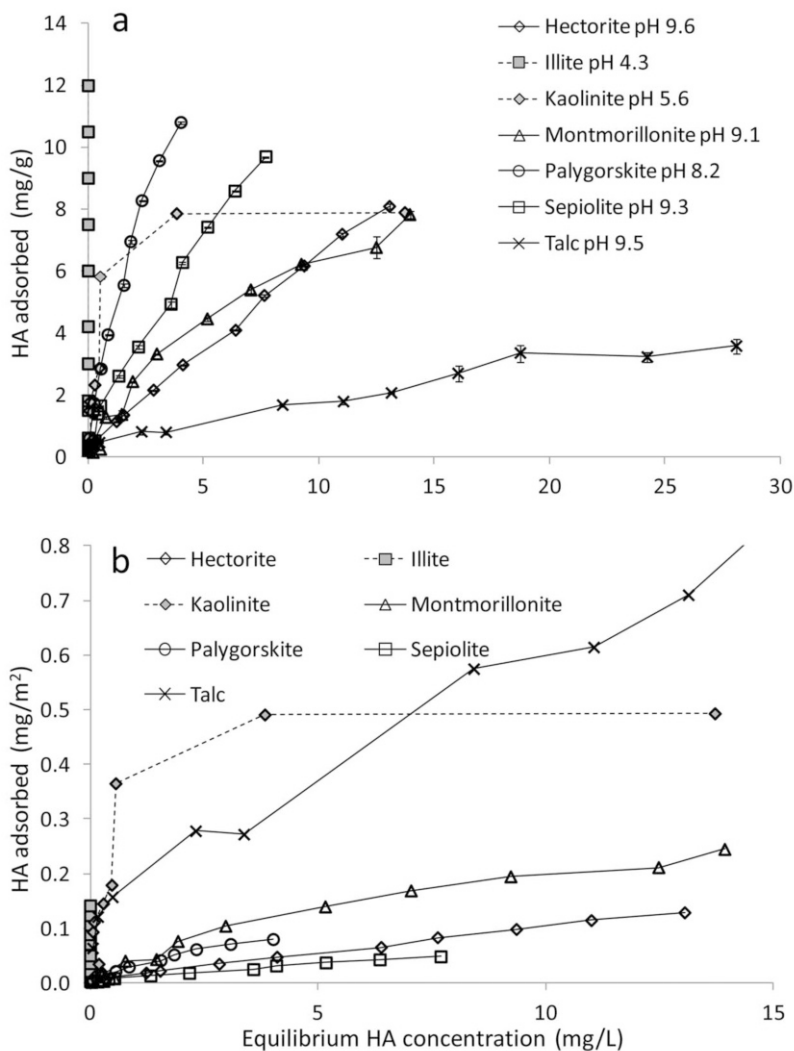


Figure 1. Isotherms of HA adsorption to clay minerals at natural clay pH: (a) per mg of clay sorbent; and (b) normalized to clay BET surface area (Table 1).

The adsorption of HA on illite and kaolinite at basic pH, and adsorption of HA on montmorillonite at pH 4, were investigated (Figure 2a). As expected, HA adsorption to the three clay minerals was greater at low pH due to protonation of the negatively charged HA and mineral surfaces, reducing the repulsion between the two colloids.

The effect was most pronounced in the case of illite. The low pH values measured for the illite were probably caused by hydrolysis of Fe constituents of the mineral. Fithian illite, used in the present study, contained 0.84 mmol Fe/g sample (Seabaugh *et al.*, 2006); its sorption properties are significantly pH-dependent, therefore. Analysis by XRD revealed traces of jarosite ($\text{KFe}_3^+(\text{OH})_6(\text{SO}_4)_2$) in the illite (results not shown). In addition, Mössbauer spectroscopy performed by Seabaugh *et al.* (2006) showed Fe(III) associated with

jarosite, illite, and Fe oxides and Fe(II) associated with illite. The presence of Fe may also assist with HA adsorption, rendering the zeta potential of Fithian illite more positive (-15 mV) compared to other types of illite, which have more negative zeta potentials (-30 to -22 mV) (Chorom and Rengasamy, 1995; Hussain *et al.*, 1996).

The greater HA loadings at a low pH (in the cases of kaolinite and illite) are an indication of ligand exchange between protonated surface hydroxyls and HA carboxylic groups (Sposito, 1984; Murphy *et al.*, 1992; Zhang and Sparks, 1989; Heidmann *et al.*, 2005). The zeta potential of the HA remained negative at this low pH, indicating that not all carboxylic groups were protonated.

The pH affects not only the protonation state of HA, but also its configuration (Ghosh and Schnitzer, 1980).

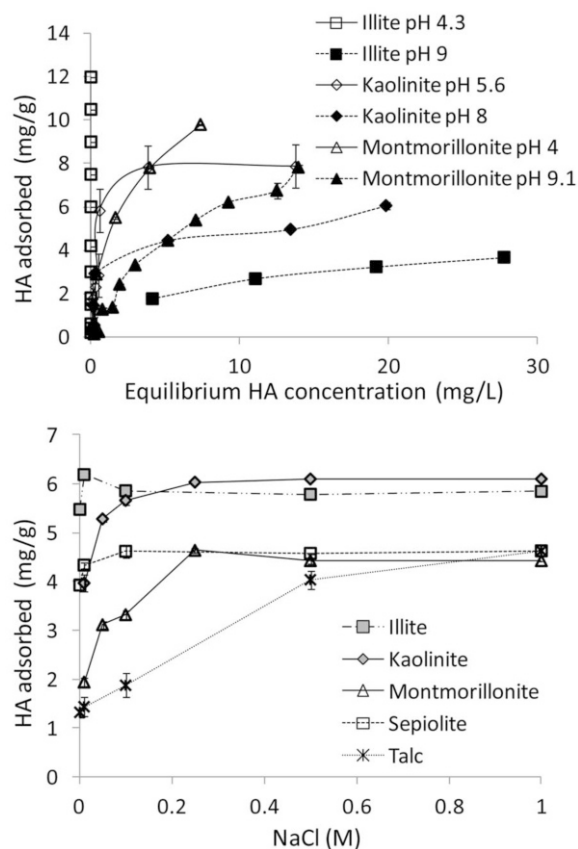


Figure 2. HA adsorption on clays – effect of: (a) pH; and (b) of ionic strength. HA concentration was 23 mg/L.

The configuration of the HA adsorbed was described by Vermeer *et al.* (1998) as a “dynamic layer, protruding into the solution.” At high pH, HA molecules are negatively charged, and adsorb flat onto the clay in chain configuration with hydrophilic groups extended into solution (Vermeer *et al.*, 1998). This results in poor HA adsorption to the negatively charged surfaces. A low pH generates an opposite effect: HA is less charged and more hydrophobic and, therefore, adopts a coiled conformation, protruding further into the solution with loops and tails and creating a thicker layer with fewer attachment points (Vermeer *et al.*, 1998).

Effect of ionic strength on HA adsorption. Increasing ionic strength screens the negative charges within the HA macromolecules, causing them to coil (Ghosh and Schnitzer, 1980). In turn, the closed configuration enables more HA molecules to be adsorbed. The effect of ionic strength on HA adsorption was studied at the natural pH of the clay minerals. Increasing the ionic strength enhanced, to some extent, HA adsorption to kaolinite and increased HA adsorption to montmorillonite and talc, but did not affect HA adsorption to illite and sepiolite (Figure 2b). This indicates that charge screening did not affect HA adsorption on clay minerals with

low zeta potentials, and supports the hypothesis that ligand exchange is the dominant adsorption mechanism at pH-dependent sites. In addition, HA–illite interactions are governed by low pH; hence, the effect of ionic strength on HA adsorption on illite can be concealed by the influence of pH. Accordingly, an increase in ionic strength promoted the adsorption of HA to montmorillonite and talc, both of which have large negative zeta potentials.

Recent studies (*e.g.* Burdukova *et al.*, 2007) have reported that talc is negatively charged not only due to the presence of pH-dependent SiOH and MgOH groups on the edge surfaces, but also due to the substitution of Si^{4+} ions by Al^{3+} , which results in a negative charge on the basal planes. In the current study, the zeta potential measured for talc was -35.4 mV, which explains the strong effect of ionic strength on HA adsorption.

Effect of clay-mineral structure on HA adsorption. In addition to the ionic strength and pH effects on adsorption, some of the phenomena observed are related to the clay structure and chemistry. The clay minerals which exhibited the greatest affinity for HA adsorption at their natural pH are illite, palygorskite, sepiolite, and kaolinite. These are also the clays with the least negative charges (zeta potential of -14 to -26.6 mV) in comparison with montmorillonite, *e.g.* with zeta potential of -44.2 mV. The significant adsorption to illite and kaolinite was attributed to the low ‘natural’ pH values of those minerals. Significant adsorption to palygorskite and sepiolite was observed, however, in spite of their natural pH of ~ 9 (Figure 3).

The strong affinity of HA for palygorskite and sepiolite can be explained by strong chemical bonds between the HA and surface silanol groups (Galán and Singer, 2011). Open-channel defects in the palygorskite and sepiolite structure (Krekeler and Guggenheim, 2008), and large BET surface areas can also promote HA adsorption. Palygorskite and sepiolite are fibrous clay minerals which have both external and intracrystalline channel surfaces available for adsorption. Humic

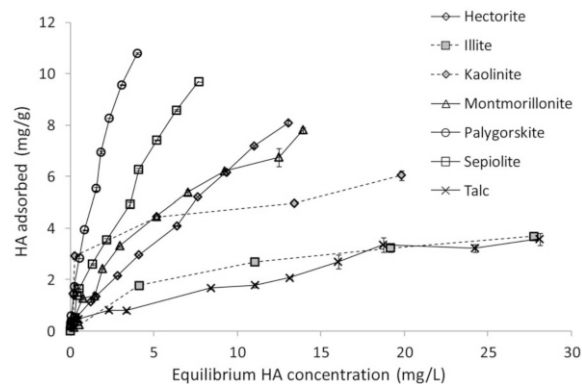


Figure 3. HA adsorption on clays at pH 8–9.

acid macromolecules have equivalent radii ranging from ~ 4.8 to 22 \AA (Barak and Chen, 1992) while sepiolite channel dimensions are $3.7 \text{ \AA} \times 10.6 \text{ \AA}$ and palygorskite $3.7 \text{ \AA} \times 6.4 \text{ \AA}$ (Galán, 1996). The adsorption of HA in the intracrystalline channels is feasible, therefore, especially for sepiolite, though restricted to small, high-polarity components of HA (Singer and Huang, 1989). Adsorption of HA molecules into the intracrystalline channels can be assessed by comparing HA adsorption to untreated and heated (500°C) clays. During the heating process, the clay minerals lose zeolitic water, undergo dehydroxylation, and the lattice collapses (Galan and Singer, 2011). Indeed, reduction in HA adsorption was observed for both fibrous clays upon heating to 500°C (Figure 4) due to channel collapse. A larger reduction of $\sim 50\%$ and also slightly slower kinetics were observed for palygorskite. The pH of the clays before and after heating remained unchanged, and thus the reduction in adsorption cannot be attributed to pH change. The small reduction in sepiolite adsorption differs from the phenomena described by Singer and Huang (1989), who showed a 35% decrease in adsorption upon heating sepiolite to 300°C , and a less significant reduction for palygorskite. The slight decrease in HA adsorption to sepiolite obtained in the current study suggests that only a small fraction of the

HA molecules enters the channels. Palygorskite channels are narrower than sepiolite channels; thus, HA is less likely to enter the palygorskite structure and the reduction in adsorption observed cannot be explained by channel collapse.

The significant reduction in HA adsorption to palygorskite upon heating can, however, be explained by the fibrous macro-structure of the mineral. Scanning electron microscopy images have shown the fine, long fibers of palygorskite to form a less dense aggregate mass than those of sepiolite (Figure 5), making possible the absorption of more HA between the fibers. Upon heating, the palygorskite macro-structure can be suggested to collapse, resulting in the slower kinetics and lower HA adsorption observed (Figure 4). The thicker and shorter, lath-shaped fibers of sepiolite form a denser aggregate mass (Grim, 1968) and, therefore, the macro-structure may undergo less dramatic changes upon heating. Hence, a smaller reduction in adsorption was observed (Figure 4a). Further investigation is required.

Montmorillonite has the largest surface area (including inner surfaces) amongst the clay minerals tested, but it has a relatively low sorptive capacity for HA due to the negative charge of mineral surfaces. Measurements by XRD showed no changes in montmorillonite d spacing after HA adsorption (data not shown), indicating that HA did not intercalate into the montmorillonite interlayer spaces.

Cu^{2+} -HA-kaolinite interactions

Kaolinite and Cu^{2+} were used as a model clay and heavy metal to study interactions in the system Cu^{2+} -HA-kaolinite. To elucidate Cu^{2+} -HA-clay interactions, sorption of Cu^{2+} by kaolinite (Cu+Kln), HA by kaolinite (Kln+HA), Cu^{2+} by kaolinite with pre-adsorbed HA (Cu[Kln+HA]), and co-sorption of Cu^{2+} and HA by kaolinite (Kln+Cu+HA) were studied. In addition, the complexation of Cu^{2+} with HA (Cu+HA) and the sorption of the HA+ Cu^{2+} complex by kaolinite ([Cu+HA]Kln) were explored.

HA- Cu^{2+} complexation. The complexation of Cu^{2+} with HA at various conditions is well documented (Kerndorff and Schnitzer, 1980; Spark *et al.*, 1997c; Christl *et al.*, 2001; Arias *et al.*, 2002; Tipping, 2002). In the current study, HA precipitation from solution due to complexation with Cu^{2+} increased from 46% to a maximum of 87% HA with the increase in Cu^{2+} concentrations (Figure 6a).

The HA- Cu^{2+} complexes were characterized by zeta potential and hydrodynamic radius measurements as a function of Cu^{2+} concentration (Figure 7). The zeta potential of the HA (-23 mV) became less negative with the increase in Cu^{2+} concentration. Accordingly, the HA particle size increased from 300 to 1300 nm as HA-Cu complexes were formed. These measurements suggested that HA complexation with Cu^{2+} neutralized the

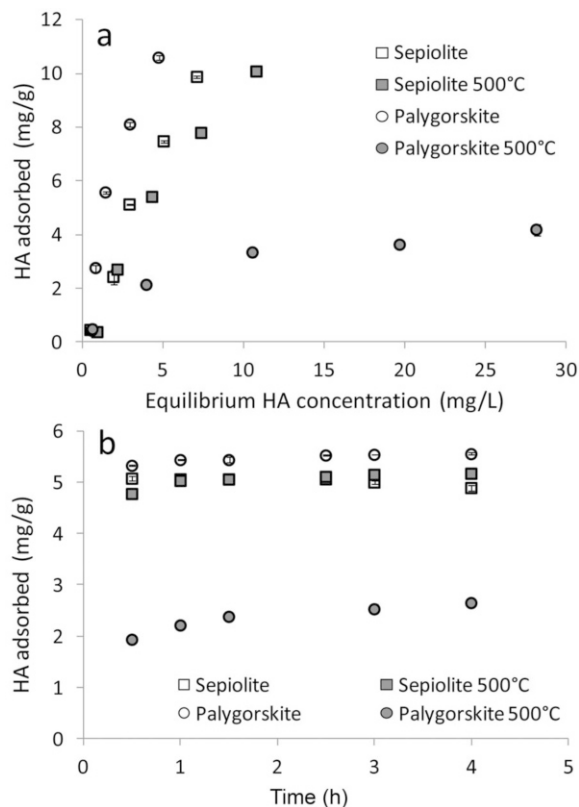


Figure 4. HA adsorption on palygorskite and sepiolite before and after heating the clays at 500°C : (a) isotherms, and (b) kinetics.

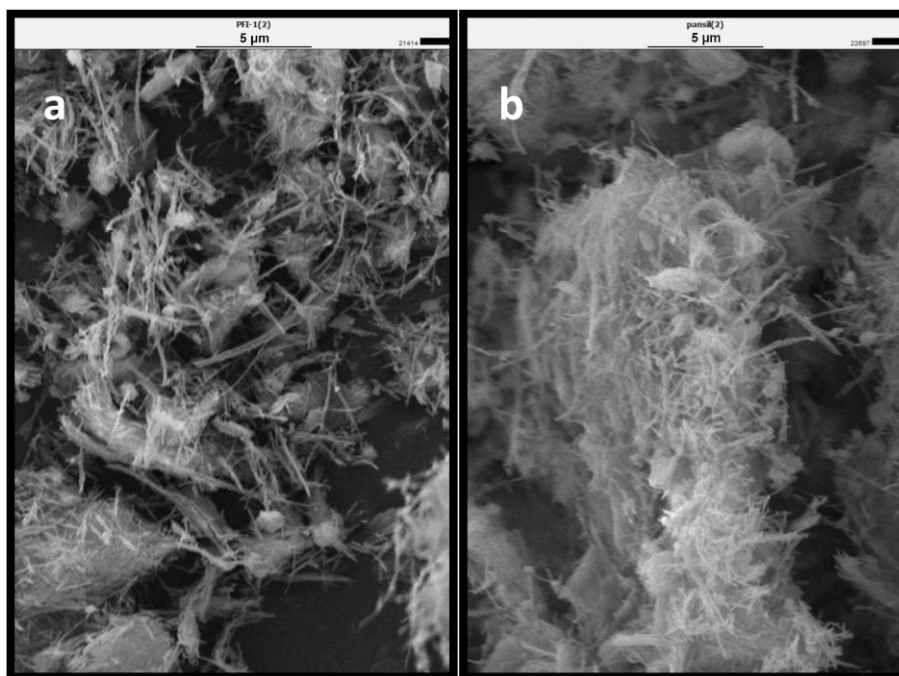


Figure 5. Morphology of (a) palygorskite and (b) sepiolite (fibers).

negatively charged sites on the HA molecules, reducing the intermolecular repulsion, and inducing aggregation. In addition, at high Cu^{2+} concentrations, CuCl_2 hydrolysis lowers the solution pH. This results in increased

HA hydrophobicity and a coiled configuration, which renders HA more likely to be adsorbed to clay-mineral surfaces (Vermeer *et al.*, 1998; Balcke and Kulikova, 2002). The complexes, stable in solution, are less negative than HA molecules, and more likely, therefore, to adsorb on the kaolinite surfaces and edges.

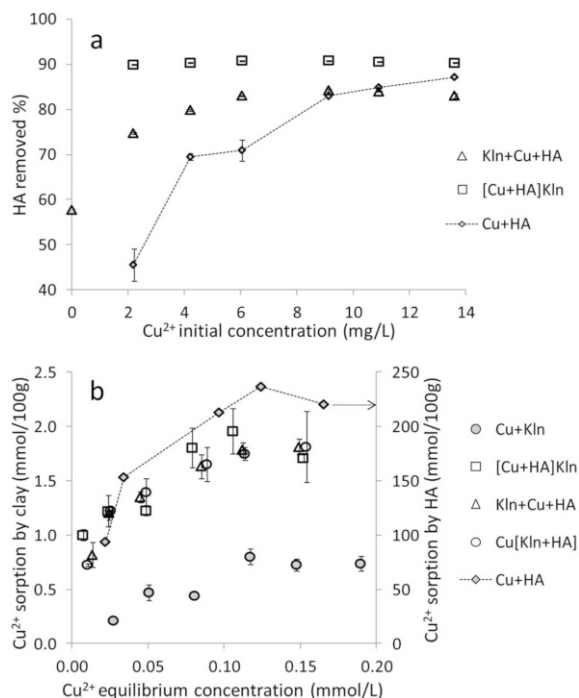


Figure 6. (a) HA sorption in the presence of Cu^{2+} and kaolinite; (b) sorption isotherm of Cu^{2+} by kaolinite (left) and HA (right).

Effect of Cu^{2+} on HA sorption to kaolinite. Sorption of the Cu+HA complex to kaolinite ([Cu+HA]Kln) resulted in greater HA sorption than any other scenario, with a constant sorption capacity of 90% regardless of the Cu^{2+} concentration added (Figure 6a). The sorption of HA on kaolinite was also studied in the presence of Cu^{2+} added simultaneously (Kln+Cu+HA). Sorption of HA in the case of simultaneous addition of kaolinite, Cu^{2+} , and HA (Kln+Cu+HA) was almost as high as for the Cu+HA complex; sorption increased with the addition of Cu^{2+} , however. In this scenario (Kln+Cu+HA), HA can be sorbed to kaolinite by means of different pathways: (a) direct adsorption of HA to the kaolinite; (b) direct adsorption of Cu^{2+} to the kaolinite followed by HA sorption by the metal cation (type-A ternary complex) (Davis, 2002); or (c) creation of Cu^{2+} and HA complexes which are then sorbed onto the clay.

Increased HA sorption by minerals in the presence of heavy metals has been reported by Vermeer *et al.* (1998) in a system of HA, Cd, and hematite. Similar results were shown by Heidmann *et al.* (2005a) in a system of fulvic acid, Pb, and kaolinite. The stereochemistry of metals such as Cu^{2+} -humate complexes allows bridging between the two adsorbents (Davis, 2002). Metal

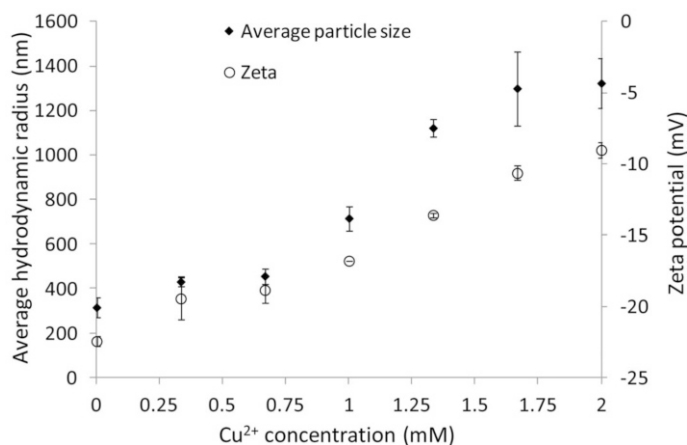


Figure 7. Average particle radius (nm) and zeta potential (mV) of HA titrated with CuCl_2 .

complexation with HA diminishes electrostatic repulsion in the adsorbed HA layer, increasing the ability of HA to bind to the negatively charged clay surfaces. In addition, adsorbed cations on the clay surface increase the electrostatic attraction between the clay mineral and the HA, forming type-A ternary surface complexes (Davis, 2002).

Effect of HA on Cu^{2+} sorption to kaolinite. Sorption of Cu^{2+} to kaolinite increased, with its concentration reaching 0.8 mmol/100 g of clay (Figure 6b). On the other hand, the complexation of Cu^{2+} by HA reached 240 mmol/100 g of HA. Three scenarios of Cu^{2+} sorption to kaolinite in the presence of HA were tested: (a) simultaneous addition of kaolinite, Cu^{2+} , and HA (Kln+Cu+HA); (b) Cu^{2+} adsorbed on the HA-kaolinite complex $\text{Cu}[\text{Kln}+\text{HA}]$; and (c) Cu^{2+} -HA complex adsorbed on kaolinite $[\text{Cu}+\text{HA}]\text{Kln}$. In all cases Cu^{2+} sorption to kaolinite increased drastically compared with Cu^{2+} sorption to untreated kaolinite reaching ~1.75 mmol/100 g clay.

The mechanisms, which enable greater sorption of HA on kaolinite in the presence of Cu^{2+} , are also responsible for increasing Cu^{2+} sorption to kaolinite in the presence of HA. In addition, the CEC of HA is much greater than that of clay minerals, ranging from 200 to 400 meq/100 g (Posner, 1966). The coating of clays with HA has been reported to increase their sorption and retention capacity for a variety of cations (Spark *et al.*, 1997b; Tipping, 2002). In the current study, the presence of HA in the system promoted significant Cu^{2+} sorption for all scenarios, not just for pre-adsorbed clay, due to the effect of Cu^{2+} -HA interactions occurring in all the systems studied.

The changes in HA morphology at pH 7 and 4, as well as after Cu^{2+} complexation, are clearly visible in the SEM images (Figure 8). Humic acid at pH 7 displays irregular, non-uniform aggregates and long ribbon or string-like structures (Figure 8a). At pH 4, when HA is more protonated and more aggregated, no ribbon or

string-like structures are visible (Figure 8b). The HA- Cu^{2+} complexes, at pH 5, display globular, uniform aggregates not visible in the absence of Cu^{2+} at the same low pH (Figure 8c), providing visual confirmation for the creation of metal-humate complexes.

CONCLUSIONS

This systematic study has enabled comparison of the affinity of soil-derived HA to a wide range of clay minerals, for the first time in some cases. The clay-mineral surfaces affected HA adsorption directly, due to their unique structural and surface properties, and indirectly, by altering the solution pH.

Previous studies reported HA adsorption on clays at different solution pHs which were adjusted to determine the impact of this factor on HA adsorption; the 'natural' mineral pH was overlooked. The present study has demonstrated that clay minerals display a strong buffer capacity to pH change. Mineral pH is suggested here to play a crucial role regarding surface reactions, in the vicinity of the mineral within the soil.

The order of HA removal from solution and adsorption to the clay minerals at the 'natural' pH of the clays was: illite >> palygorskite > kaolinite > sepiolite > montmorillonite = hectorite >> talc. Illite and kaolinite have naturally acidic pH values, enhancing HA adsorption by ligand exchange.

Ionic strength did not affect HA adsorption to kaolinite, illite, and sepiolite, indicating that charge screening is not a major mechanism in the case of clay minerals with low surface charge and supporting the suggestion that ligand exchange is the dominant adsorption mechanism to pH-dependent sites. Increasing the ionic strength promoted HA adsorption on clays with significant negative zeta potentials, *i.e.* montmorillonite and talc.

The strong affinity of HA for the fibrous clays, and especially palygorskite, was explained by HA adsorption between the particles of a complex macro-fibrous structure, which collapses upon heating.

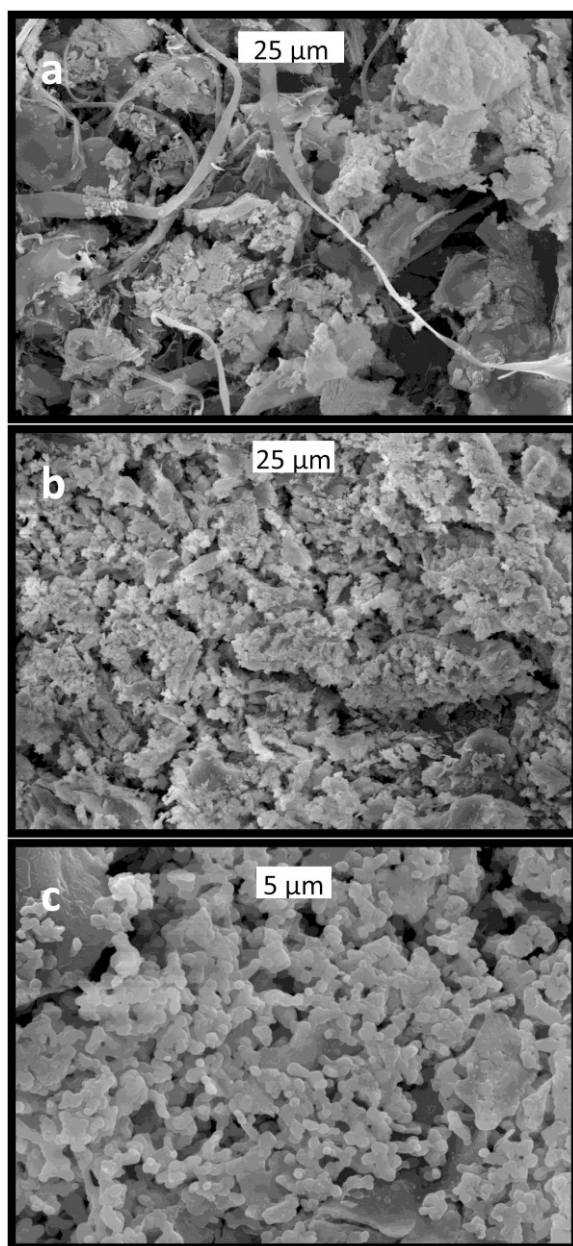


Figure 8. SEM images of HA morphology: (a) HA pH 7; (b) HA pH 4; and (c) Cu^{2+} -HA complexes at pH 5.

The presence of both HA and Cu^{2+} mutually increased their sorption to kaolinite due to their interactions, resulting in enhanced affinity of both components to kaolinite. The adsorption of HA to kaolinite was greater when a Cu^{2+} -HA complex was added to kaolinite, than simultaneous mixing of HA, Cu^{2+} , and kaolinite. Three scenarios of Cu^{2+} adsorption to kaolinite in the presence of HA were studied; in all experiments HA enhanced Cu^{2+} adsorption similarly.

The present study has emphasized the diverse effects of clay structure and properties on adsorption of HA.

When studying the interactions of organic matter with soils, not only should soil texture (% of sand, silt, and clay) be considered, but the clay mineralogy should also receive special attention. The effects of HA-clay complexes on contaminant binding can vary with the clay-mineral type, thus affecting the fate of contaminants in soils.

REFERENCES

- Arias, M., Barral, M.T., and Mejuto, J.C. (2002) Enhancement of copper and cadmium adsorption on kaolin by the presence of humic acids. *Chemosphere*, **48**, 1081–1088.
- Baham, J. and Sposito, G. (1994) Adsorption of dissolved organic carbon extracted from sewage sludge on montmorillonite and kaolinite in the presence of metal ions. *Journal of Environment Quality*, **23**, 147–153.
- Balcke, G. and Kulikova, N. (2002) Adsorption of humic substances onto kaolin clay related to their structural features. *Soil Science Society of America Journal*, **66**, 1805–1812.
- Barak, P. and Chen, Y. (1992) Equivalent radii of humic macromolecules from acid-base titration. *Soil Science*, **154**, 184–195.
- Bertsch, P.M. and Seaman, J.C. (1999) Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, **96**, 3350–3357.
- Burdukova, E., Becker, M., Bradshaw, D.J., and Laskowski, J.S. (2007) Presence of negative charge on the basal planes of New York talc. *Journal of Colloid and Interface Science*, **315**, 337–342.
- Campelo, J.M., Garcia, A., Luna, D., and Marinas, J.M. (1987) Surface properties of sepiolites from Vallecas-Madrid, Spain, and their catalytic activity in cyclohexene skeletal isomerization. *Reactivity of Solids*, **3**, 263–272.
- Chiem, L.T., Huynh, L., Ralston, J., and Beattie, D.A. (2006) An in situ ATR-FTIR study of polyacrylamide adsorption at the talc surface. *Journal of Colloid and Interface Science*, **297**, 54–61.
- Chorom, M. and Rengasamy, P. (1995) Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type. *European Journal of Soil Science*, **46**, 657–665.
- Christl, I., Milne, C.J., Kinniburgh, D.G., and Kretzschmar, R. (2001) Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 2. Metal binding. *Environmental Science & Technology*, **35**, 2512–2517.
- Davis, A.P. (2002) Adsorption of metal complexes at oxide and related surfaces. P. 5642 in: *Encyclopedia of Surface and Colloid Science* (A.T. Hubbard and P. Somasundaran, editors). Marcel Dekker, Inc., New York.
- Drori, Y., Aizenshtat, Z., and Chefetz, B. (2008) Sorption of organic compounds to humin from soils irrigated with reclaimed wastewater. *Geoderma*, **145**, 98–106.
- EPA Method 6010c (2007) Inductively coupled plasma-atomic emission spectrometry. <<http://www.epa.gov/osw/hazard/testmethods/sw846/>> (28 September 2014).
- Essington, M.E. (2015) *Soil and Water Chemistry: An Integrative Approach*. 2nd edition. CRC Press, Boca Raton, Florida, USA, 656 pp.
- Galán, E. (1996) Properties and applications of palygorskite-sepiolite clays. *Clay Minerals*, **31**, 443–453.
- Galán, E. and Singer, A. (editors) (2011) *Developments in Palygorskite-Sepiolite Research*. Developments in Clay Science, Elsevier, Amsterdam, p. 500.

- Ghosh, K. and Schnitzer, M. (1980) Macromolecular structures of humic substances. *Soil Science*, **129**, 266–276.
- Ghosh, S., Wang, Z.-Y., Kang, S., Bhowmik, P.C., and Xing, B.S. (2009) Sorption and fractionation of a peat derived humic acid by kaolinite, montmorillonite, and goethite. *Pedosphere*, **19**, 21–30.
- Greenland, D. (1971) Interactions between humic and fulvic acids and clays. *Soil Science*, **111**, 34–41.
- Grim, R.E. (1968) *Clay Mineralogy*. 2nd edition. International Series in the Earth and Planetary Sciences, McGraw-Hill, New York, 596 pp.
- Gu, B., Schmitt, J., Chen, Z., Liang, L., and McCarthy, J.F. (1994) Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environmental Science & Technology*, **28**, 38–46.
- Heidmann, I., Christl, I., and Kretzschmar, R. (2005) Sorption of Cu and Pb to kaolinite-fulvic acid colloids: Assessment of sorbent interactions. *Geochimica et Cosmochimica Acta*, **69**, 1675–1686.
- Hendershot, W. and Duquette, M. (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Science Society of America Journal*, **50**, 605–608.
- Hizal, J. and Apak, R. (2006) Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. *Journal of Colloid and Interface Science*, **295**, 1–13.
- Hussain, S.A., Demirci, Ş., and Özbayoğlu, G. (1996) Zeta potential measurements on three clays from Turkey and effects of clays on coal flotation. *Journal of Colloid and Interface Science*, **184**, 535–541.
- Kerndorff, H. and Schnitzer, M. (1980) Sorption of metals on humic acid. *Geochimica et Cosmochimica Acta*, **44**, 1701–1708.
- Kholodov, V.A., Kiryushin, A.V., Yaroslavtseva, N.V., and Frid, A.S. (2014) Copper(II) binding by free and kaolinite-sorbed humic substances. *Eurasian Soil Science*, **47**, 662–669.
- Kleber, M., Sollins, P., and Sutton, R. (2007) A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry*, **85**, 9–24.
- Komy, Z.R., Shaker, A.M., Heggy, S.E.M., and El-Sayed, M.E.A. (2014) Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid. *Chemosphere*, **99**, 117–124.
- Krekeler, M.P.S. and Guggenheim, S. (2008) Defects in microstructure in palygorskite-sepiolite minerals: A transmission electron microscopy (TEM) study. *Applied Clay Science*, **39**, 98–105.
- Kretzschmar, R., Hesterberg, D., and Sticher, H. (1997) Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. *Soil Science Society of America Journal*, **61**, 101–108.
- Liu, A. and Gonzalez, R.D. (1999) Adsorption/desorption in a system consisting of humic acid, heavy metals, and clay minerals. *Journal of Colloid and Interface Science*, **218**, 225–232.
- Murphy, E.M., Zachara, J.M., Smith, S.C., and Phillips, J.L. (1992) The sorption of humic acids to mineral surfaces and their role in contaminant binding. *The Science of the Total Environment*, **117/118**, 413–423.
- Murphy, E.M., Zachara, J.M., Smith, S.C., Phillips, J.L., and Wietsma, T.W. (1994) Interaction of hydrophobic organic compounds with mineral-bound humic substances. *Environmental Science & Technology*, **28**, 1291–1299.
- Posner, A.M. (1966) The humic acids extracted by various reagents from a soil. *Journal of Soil Science*, **17**, 65–78.
- Seabaugh, J.L., Dong, H., Kukkadapu, R.K., Eberl, D.D., Morton, J.P., and Kim, J. (2006) Microbial reduction of Fe(III) in the Fithian and Muloorina illites: Contrasting extents and rates of bioreduction. *Clays and Clay Minerals*, **54**, 67–79.
- Singer, A. and Huang, P.M. (1989) Adsorption of humic acid by palygorskite and sepiolite. *Clay Minerals*, **24**, 561–564.
- Spark, K., Wells, J., and Johnson, B. (1997a) Characteristics of the sorption of humic acid by soil minerals. *Australian Journal of Soil Research*, **35**, 103–112.
- Spark, K., Wells, J., and Johnson, B. (1997b) Sorption of heavy metals by mineral-humic acid substrates. *Australian Journal of Soil Research*, **35**, 113–122.
- Spark, K., Wells, J., and Johnson, B. (1997c) The interaction of a humic acid with heavy metals. *Australian Journal of Soil Research*, **35**, 89–101.
- Sparks, D.L. (2003) *Environmental Soil Chemistry*. Academic Press, San Diego, California, USA, 352 pp.
- Sposito, G. (1984) *The Surface Chemistry of Soils*. Oxford University Press, Oxford, UK, 234 pp.
- Stevenson, F.J. (1994) *Humus Chemistry: Genesis, Composition, Reactions*. 2nd edition. John Wiley & Sons, Inc., New York, 496 pp.
- Sutton, R. and Sposito, G. (2005) Molecular structure in soil humic substances: The new view. *Environmental Science & Technology*, **39**, 9009–9015.
- Sutton, R. and Sposito, G. (2006) Molecular simulation of humic substance–Ca–montmorillonite complexes. *Geochimica et Cosmochimica Acta*, **70**, 3566–3581.
- Tipping, E. (2002) *Cation Binding by Humic Substances*. Cambridge University Press, New York, 434 pp.
- van Olphen, H. and Fripiat, J.J. (editors) (1979) *Data Handbook for Clay Materials and Other Non-Metallic Minerals*. Pergamon Press, Oxford, UK, xiv + 346 pp.
- Vermeer, A., Riemsdijk, W. van, and Koopal, L. (1998) Adsorption of humic acid to mineral particles. 1. Specific and electrostatic interactions. *Langmuir*, **14**, 2810–2819.
- Wang, M., Liao, L., Zhang, X., and Li, Z. (2012) Adsorption of low concentration humic acid from water by palygorskite. *Applied Clay Science*, **67–68**, 164–168.
- Yapar, S., Özdemir, G., Fernández Solarte, A.M., and Torres Sánchez, R.M. (2015) Surface and interface properties of lauroyl sarcosinate-adsorbed CP+–montmorillonite. *Clays and Clay Minerals*, **63**, 110–118.
- Zhang, P.C. and Sparks, D.L. (1989) Kinetics and mechanisms of molybdate adsorption/desorption at the goethite/water interface using pressure-jump relaxations. *Soil Science Society of America Journal*, **53**, 1028–1034.
- Zhou, J.L., Rowland, S., Fauzi, R., Mantoura, C., and Braven, J. (1994) The formation of humic coatings on mineral particles under simulated estuarine conditions – A mechanistic study. *Water Research*, **28**, 571–579.

(Received 26 September 2015; revised 13 July 2016; Ms. 1038; AE: B. Lanson)