RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 43090

Molecular fractionation of a soil fulvic acid (FA) and competitive sorption of trace metals (Cu, Zn, Cd, Pb) in hematite–solution systems: effect of the FA-to-mineral ratio†

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Understanding of the interactions occurring between fulvic acids (FAs) and trace metals in mineral–solution systems is a major issue for cycles of organic matter and micro-pollutants in surface media. Batch experiments and molecular-scale investigations were conducted to address the mechanisms regulating the molecular fractionation of a terrestrial FA and the competition between Cu, Zn, Cd and Pb during sorption onto hematite, a mineral ubiquitous in soils, with a focus on effects of FA-to-mineral ratio (*r*). A main result is that *r* controlled both the identity of the FA molecules preferentially sorbed on hematite and the sequence of the FA-promoted sorption of metals, at acidic pH. Data at moderate *r* evidenced that the sorption degree of a FA molecule increased with molecular acidity, supporting surface complex formation at hematite sites involving preferentially the most acidic and oxygenated FA molecules. FA-promoted sorption of strong Lewis acids such as Pb and Cu was favored (relative to Cd or Zn) by sorbed FA bearing multiple oxygenated functionalities. In contrast, preferential uptake of condensed aromatics and low oxygenated aliphatics/not-condensed aromatics prevailed at high *r*. A reduced FA-promoted sorption of Cu, which contrasted with an increased FA-promoted sorption of Cd, was observed too. Complex interactions must be invoked (competitive effects, hydrophobic forces, hydrogen bonding) to explain the striking results obtained in highly-competitive FA-concentrated systems. Our data highlight that (coupled) retention/mobilization of reactive organic molecules and of toxic metals like Cd and Pb is a function of the FA-to-metal oxide ratio of soils.

Received 19th June 2017
Accepted 31st August 2017

DOI: 10.1039/c7ra06838g

rsc.li/rsc-advances

1. Introduction

Humic substances (HSs) like humic acids and fulvic acids (FAs) are ubiquitous in all natural surface systems as mixtures of many organic compounds with various compositions and origins. HSs have been widely reported to have the ability to bind metals and hydrophobic compounds[1–3] and to sorb on the surfaces of (nano)minerals.[4,5] The latter process is expected to play an important role in the surface properties and sorption capacities of relevant minerals of soils such as Fe-/Al-oxyhydroxides or clays, as well as on the concentration and chemical reactivity of dissolved organic molecules of surface waters. HS–mineral surface interactions are therefore of interest for several environmental issues, *e.g.*, the geo-cycle of organic carbon, dissemination of natural or engineered nanoparticles in aquatic systems, and mobility and bioavailability of trace metal elements (TMEs) that have natural or anthropogenic origins and are potentially toxic at excess concentrations (*e.g.*, Cu and Zn) or at trace levels (*e.g.*, Cd or Pb). In particular, many field studies[6–10] have highlighted that HSs exert major control on the migration/retention behavior of TMEs in natural surface systems.

Considerable experimental work has been done over past decades to identify parameters and processes regulating the distribution of a TME between mineral surface and solution in ternary metal–HS–mineral systems, with the final aim of better understanding the impact of HS on the fate of trace metals in soils. It has been widely reported that the sorption of TMEs (Cu, Pb, Co, lanthanides…) on surfaces of metal (hydr)oxides and clays is reduced by the presence of HS at high pH values due to complexation of the metal by dissolved HS[11] and is promoted by the sorption of HS at low pH values due to specific interactions between organic matter and trace metal cations at mineral surfaces.[11,12] Experimental and spectroscopic evidences were

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† Electronic supplementary information (ESI) available: Complementary macroscopic data of pH-dependency of PPH sorbed onto hematite at $r = 1.4$ mg C per m^2 (Fig. S1), complementary molecular-scale data: ESI(−)-MS spectra of PPH native solution and of supernatants of PPH sorption experiments onto hematite at pH 3.9 (Fig. S2) and VK diagrams for PPH native solution (Fig. S3), and comparative results of experiments of single and competitive Cu sorption onto 0.375 g L^{-1} hematite for an initial PPH-to-mineral ratio of 0.1 mg C per m^2 (Fig. S4). See DOI: 10.1039/c7ra06838g

given for complexation of metals with the functional groups of sorbed organic matter[12–14] and/or formation of ternary surface–metal–HS complexes.[15,16] A few experimental studies have been devoted to the competitive sorption of TMEs in ternary metal–HS–mineral systems, too.[12,13,15,17] Elliott *et al.*[17] showed that the presence of HS is likely to change the affinity order of divalent metals for soil surfaces. The authors found that the affinity order of Cu, Pb, Cd and Zn for acidic soils corresponds to the order of p*K*s for the first metal hydrolysis products (*i.e.* Pb > Cu > Zn > Cd) in the absence of HS, whereas the retention of Cd is favored over that of Zn in the presence of HS. This was in agreement with experimental studies showing that the stability constants of dissolved metal–HS complexes increase in the order Pb and Cu > Cd > Zn[1–3] (this order being explained by differences in the sizes and electronic structures of the metal cations), supporting existence of specific interactions between metals and HS sorbed at surfaces of soil minerals. pH is not the only parameter reported to govern effect of HS on metal sorption, which has been shown to depend on solution characteristics such as ionic strength and concentration of metal[13,18,19] or on surface properties of mineral,[20] too. In contrast, the effects of the characteristics of HS on the sorption of TMEs in ternary metal–HS–mineral systems have seldom been investigated. An extensive batch study by Zuyi *et al.*[19] supported that the nature of the HS, its fractionation by sorption, and its coverage on the surface of mineral are key parameters of sorption of an inorganic cation. Further work providing in-depth insights into the effects of these parameters on HS sorption is needed for exploring main mechanisms controlling the sorption of a HS and for better understanding of their impacts on the retention behavior of TMEs. Such an approach conducted in well-constrained mineral–solution systems taken as models of soil sub-systems is of particular interest for advancing towards a better knowledge of (coupled) cycles of TMEs and organics in more-or-less humic geochemical systems.

In this study, we addressed the effects of a key parameter, the fulvic acid-to-mineral ratio on the mechanisms involved in the sorption of a terrestrial fulvic acid onto hematite taken as a model of iron oxihydroxides existing in soils, and on the competitive sorption of Cu, Zn, Cd and Pb at trace levels. It has long been known that the sorption of a HS on the surface of a metal oxihydroxide results in a chemical fractionation of HS between mineral surface and solution[21–23] – as HS are heterogeneous mixtures of thousands of organic compounds of various compositions, structures and reactivity of functional groups – that is to say that some compounds of HS are preferentially sorbed on the surface. Recently, descriptions of the mechanisms and molecular parameters governing the sorptive fractionation of an aquatic FA, an HA and two terrestrial FAs were provided by using ultra-high resolution mass spectrometry combined with electrospray ionization (ESI-FTMS) in studies of the identity of the HS compounds which are preferentially sorbed (and not sorbed) on an aluminum oxide surface.[24–26] Galindo and Del Nero[24] and Fleury *et al.*[26] have provided molecular scale evidence that, at acidic pH, the sorption degree of a FA molecule in a CO_2 series is positively correlated with its molecular acidity, for the highly reactive, oxygen-functionalized compounds sorbed *via* surface ligand exchange such as aliphatics, not-condensed aromatics (NCAs), and polycyclic aromatic compounds (PACs) of high atomic O/C ratio. Fleury *et al.*[26] have also revealed in their investigations using FAs rich in condensed aromatics, that both molecular acidity and hydrophobic character are involved for PACs and low O/C NCAs, and that sorption is the result of surface ligand exchange reactions or hydrophobic interactions according to the atomic O/C ratio of the molecules. Their results compared well with those reported for the sorption of the soluble fraction of an humic acid on alumina,[25] where there was observed a heightened contribution of the hydrophobic interactions due to the highest content in highly condensed aromatic compounds of this terrestrial humic substance. All these findings imply that sorptive fractionation mechanisms taking place on an alumina surface are similar for HA and FA, with extent of the various mechanisms being largely determined by the amount, nature and reactive ability of the molecules present in HS. However, no study has been focusing so far on the effect of FA-to-iron oxihydroxide ratio on the mechanisms involved in the sorptive fractionation of FA, nor on the FA-driven competitive sorption behavior of TMEs. It has long been known that mobility of TMEs in aquatic systems, sediments and soils is largely dependent on their interactions with mineral surfaces such as iron (hydr)oxides and clays.[27] Iron oxihydroxides are widespread in soils, sediments and aquatic systems,[28] where they are typically nanosized[29] and occur in many forms ranging from amorphous ferrihydrite to crystalline goethite and hematite.[30] They are widely reported to be excellent adsorbents for various anions, for organic matter[31,32] and for heavy metals[33,34] including cadmium, copper, lead and zinc.[35–37] They are therefore expected to influence largely the mobility of these species in various ecosystem compartments,[38] owing to their high specific surface area and high surface reactivity. Hematite has moreover been used in many studies of NOM/Fe-oxihydroxides/metal model systems.[39]

The approach used here for investigations of PPH–hematite–metal systems combined macroscopic studies of the (co)sorption of a terrestrial FA (noted PPH) and divalent metals with descriptions at the molecular scale of the FA sorption. Sorption isotherms of Cu, Zn, Cd and Pb onto hematite were derived from batch experiments of competitive metal sorption as a function of pH and at different PPH-to-mineral ratios. On-line electrophoretic mobility (EM) measurements of mineral suspensions were also performed for gaining insights into the surface charges of the particles. The use of a LTQ Orbitrap XL hybrid mass spectrometer with high resolution and high mass accuracy allowed detecting thousands of dissolved compounds constitutive of PPH, deriving the elemental composition of most of them, and identifying sorbing/not sorbing molecules by comparing ESI(−) mass spectra recorded before and after contact with the mineral surface of PPH solutions at acidic pH (∼4). Macroscopic and molecular-scale data were combined to elucidate the mechanisms and the chemical identity of the organic molecules involved in FA sorption and gain insights into the competitive sorption of TMEs in systems at various FA surface coverage of an iron oxide.

2. Materials and methods

2.1 Materials

All the solutions were prepared using reagent grade chemicals and ultra-pure water (purity >18 MΩ cm). The fulvic acid noted "PPH" was extracted from a sample of soil developed over sandstone under a beech forest and collected near La Petite-Pierre (Vosges Mountains, France) following the International Humic Substances Society (IHSS) standard method for isolation of soil fulvic acids. This method excerpted from Swift[40] uses XAD-8 resin adsorption to isolate fulvic acids. Stock solutions of PPH were prepared and stored frozen in the dark until used. Hematite nanoparticles were provided by US Research Nanomaterials, with a chemical purity >99.5%, a 30 nm particle size and a surface area of 40 ± 20 m^2 g^{-1}.

2.2 FA sorptive fractionation in binary FA–hematite systems

Batch experiments of PPH sorption onto hematite were carried out following the procedure described in a previous publication[26] at pH 3.9 ± 0.2 and at different FA-to-mineral ratios, r, leading to low or high FA surface coverage, s ($r = 0.1$, 0.6, or 1.4 mg C per m^2 leading to $s = 0.1$, 0.3 and 0.7 mg C per m^2, respectively). No attempt was made to fix the ionic strength of the initial experimental solutions, as background salts were previously observed to alter considerably the ESI-MS response. After shaking of the 10 mL samples for 24 hours at 298 K, the final pH of the suspensions were measured. The suspensions were then centrifuged at 8000 rpm during 2.5 hours for solution–colloid separation and the supernatants were collected. Aliquots were taken for measurements of dissolved organic carbon (DOC) using a Shimadzu TOC-V$_{CPH}$ analyzer, and all the remaining supernatant solutions were adjusted (using a 0.01 M HCl solution) to a pH value of 3.5 prior to ESI(−)-MS analysis. On-line measurements of the electrophoretic mobility (EM) of the particles in suspensions were also performed on aliquots of samples collected before centrifugation using dynamic light scattering (Malvern Zetasizer Nano ZS instrument). Values reported for EM correspond to mean values calculated from three measurement replicates.

An additional series of PPH batch sorption experiments was carried at different pH values ($3 < \text{pH} < 6.5$) and at $r = 1.4$, in order to determine the amount of PPH sorbed at the surface of hematite as a function of pH. Same procedure as that described above was used, and all remaining supernatant solutions were used for measurements of dissolved organic carbon (DOC) using a Shimadzu TOC-V$_{CPH}$ analyzer.

A Thermo Scientific LTQ Orbitrap hybrid mass spectrometer was used for the analysis of FA solutions in the ESI negative ionization mode. Analytical parameters are described in detail in a previous publication.[26] The samples were infused directly into the ESI source with a spray voltage of 3.5 kV at a flow rate of 10 μL min^{-1}. The source capillary was held at −50 V and 275 °C, and a voltage of −240 V was applied to the tube lens. For each acquisition, 100 scans (2 s per scan) were co-added using Xcalibur software. The Orbitrap MS was externally calibrated in negative ion mode on the 50–2000 m/z range using a LTQ/FT-Hybrid ESI Calmix solution, for a mass accuracy better than 3 ppm. All MS spectra were acquired on two separate ranges, 120–400 m/z and 400–798 m/z, to improve mass accuracy in the low mass region and signal-to-noise (S/N) ratio for high m/z ions. Chemical formulae were assigned to m/z values of peaks detected with S/N >4 using the Xcalibur software. All possible formulae attributable to a given odd m/z value were calculated by considering ^{12}C, ^{1}H and ^{16}O atoms (with upper limits for the number of atoms equal to 200, 600 and 50, respectively) and by rejecting all formulae having theoretical masses differing by more than 3 ppm from the measured mass. For even m/z values (odd masses), peaks corresponding to species including one ^{13}C isotope were rejected. Because of the low nitrogen content of HS, the remaining species were considered to contain at most one ^{14}N atom, in addition to ^{12}C, ^{1}H and ^{16}O atoms.

For identified compounds, calculation of the aromaticity index (A.I.) as defined by Koch and Dittmar[41] allowed to distinguish between three categories of compounds: PACs ($0.67 < \text{A.I.}$), NCAs ($0.5 < \text{A.I.} < 0.67$), and compounds with a pronounced aliphatic character ($\text{A.I.} < 0.5$). The chemical formulae were represented in Van Krevelen (VK) diagrams which plot the hydrogen/carbon (H/C) ratio *versus* the oxygen/carbon (O/C) ratio of the compounds. To derive the order of relative affinities of PPH compounds for the mineral surface, we used the parameter I defined by Galindo and Del Nero[24] and Fleury *et al.*[26] which is equal to the ratio of the normalized peak intensity of an ion in supernatant (after sorption) on the normalized peak intensity of the ion in initial solution (before sorption), with the normalization being made to the total ion current (TIC) of the considered solution. The lower the value of I of an ion, the higher its relative affinity for the mineral surface: ions with $I = 0$ are totally sorbed on the mineral surface, while ions with $I \neq 0$ are distributed between surface and solution.

It is well-known that the intensity of an ion on a mass spectrum not only depends on its concentration but also on its ionization efficiency and on the matrix.[26] The effect on the relative peak intensities of the ions (and thus on their values of I) induced only by the decrease in solution concentration upon PPH sorption at the surface of hematite was studied in a previous publication,[26] in order to differentiate it from the effect on I of the sorptive fractionation process itself. The results of this study showed that a value of I lower than 0.7 (or 0.9 for the range 400–798 m/z range at pH 3.8) indicates a rather good sorption of an ion on the mineral surface, while ions showing values comprised between 0.7 and 1 (or 0.9 and 1.2 for the range 400–798 m/z range at pH 3.8) are poorly sorbed or not sorbed at all. Ions showing values higher than 1 (or 1.2) are not sorbed at all during the experiment.

2.3 Metal sorption experiments in ternary metal–FA–hematite systems

Sorption isotherms of Cu, Zn, Cd and Pb onto hematite were obtained from series of multi-elemental batch experiments carried out as a function of pH ($3 < \text{pH} < 7$), with and without fulvic acids. Hematite suspensions were prepared in individual PEHD tubes with a mineral-to-solution ratio of 0.375 g L^{-1}. For experiments performed in the presence of fulvic acid, PPH was then added to obtain FA-to-mineral ratios of 0.10 ± 0.04 mg C per m^2 and 1.4 ± 0.1 mg C per m^2. Aliquots of a multi-elemental stock solution prepared from nitrate standards were introduced simultaneously in the tubes, to obtain initial concentrations of 0.8 ± 0.2 μM for each of Cu, Zn, Cd and Pb. The pH values of the solutions were adjusted using 0.1 M HNO_3 and NaOH solutions. After shaking of the 10 mL samples for 24 h at 298 K, final pH values were measured. The suspensions were centrifuged at 8000 rpm during 2.5 hours for solution–colloid separation and the supernatants were collected. Aliquots were taken for DOC measurements and remaining supernatant solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). No experimental replicates were made. Error bars shown on graphics correspond to analytical standard deviations calculated on the mean analytical values.

On-line measurements of the electrophoretic mobility (EM) of the particles in suspensions were performed on aliquots of samples collected before centrifugation using dynamic light scattering (Malvern Zetasizer Nano ZS instrument), following the same procedure as previously (*cf.* Section 2.2). Values reported for EM correspond to mean values calculated from three measurement replicates.

3. Results

3.1 Sorption behavior of FA in hematite–solution systems

Macroscopic and electrokinetic results. Fig. 1 and S1 in ESI† present the data obtained on the amount of PPH sorbed (*s*, in mg C per m^2 solid) at the surface of hematite as a function of the FA-to-hematite ratio of experiment (*r*, in mg C per m^2 solid) at pH 3.9, and as a function of pH, respectively, and compare them to previous data acquired by our team[26] for other FA–mineral–solution systems of interest (as mineral: α-Al_2O_3; as FA: Pahokee Peat Fulvic Acid, PPFA, supplied by International Humic Substances Society and a FA extracted from a soil under fir cover, PPC). At pH 3.9, the amount of sorbed FA was found to increase with an increasing of the FA-to-solid ratio (Fig. 1). The data show two main zones of FA-to-hematite ratio with regard to the sorption behaviour of PPH. The sorption was complete at very low values of *r* (≤0.2 mg C per m^2). The percent sorption was decreased to 50% since a low value of *r* (0.5 mg C per m^2). That the amount of fulvic acid sorbed increased within a narrow range of low *r* values whereas the percent sorption decreased drastically suggests that different types of sites of binding of PPH – including high-affinity sites in limited amount(s) – and/or different types of adsorption species of PPH were present on the surface of hematite. Table 1 compares the concentration of hematite sorption sites, *i.e.*, of surface hydroxyl groups ($[S]_{surf}$) estimated on the basis of a surface site density of 7.5 sites per nm^2 recommended by Peacock et Sherman,[42] with the concentration of functional groups of FA, mainly carboxyls ($[COOH]_{FA}$) and phenolic groups ($[Ph]_{FA}$) as measured by FA titrations following the procedure of Ritchie and Perdue,[43] for experiments at different *r*. On the basis of a very conservative – although not realistic-approach that one mole of carboxyl groups react with one mole of hematite surface sites, at most 18% of hematite sorption sites may be involved in binding of PPH molecules at $r = 0.1$ mg C per m^2. Phenolic groups are not considered to react at pH 3.9 as they are fully protonated (*cf.* acidity constants in Table 1 for carboxyl and phenolic groups of PPH, which were calculated to be equal to 1.1 and 9.27, respectively). In conditions of very low *r*, the concentration of hematite surface sites ($[S]_{surf}$) is thus estimated to be high compared to that of PPH functional groups. At the intermediate PPH-to-hematite ratio studied ($r = 0.6$ mg C per m^2), at most 41% of hematite surface sites are implicated in sorption. Possibly, surface sites are at near-saturation at the highest value of *r* studied, only ($r = 1.4$ mg C per m^2, *cf.* Table 1). A main result observable on Fig. 1 is the quasi-linear relation between the initial FA-to-mineral ratio of the experiments (*r*) and the amount of FA sorbed (corresponding to *ca.* 50% of FA sorption) for different terrestrial fulvic acids and for intermediate to high *r* values (0.5–1.4 mg C per m^2). This result suggests that, at acidic pH, main mechanisms controlling the sorption on the surfaces of Al-oxide and Fe-oxide of the various terrestrial FAs studied are similar under conditions where binding sites existing at the mineral surfaces were not fully saturated. Indeed, it is to be expected that a great difference between the types of surface sites implicated in binding of FA onto the minerals and/or between the sorbed FA species would result in different amounts of FA sorbed on the mineral surfaces, at equilibrium for a given initial FA-to-mineral ratio. The linear relation between *r* and amount of FA sorbed suggests almost comparable sorption mechanisms for the various metal oxides used. Fig. S1† shows that the percentage of PPH sorption decreases slightly with an increase of pH from 3 to 6, which is possibly due to an increase of the extent of deprotonation of functional groups of the FA (concomitantly to a slight increasing of deprotonation of surface hydroxyl groups). Fig. 2 reports EM data and shows positive values of electrophoretic mobility of the hematite particles over a wide pH range, in the absence of PPH and metals, which reflect the typical positive surface charge exhibited by hematite due to the protonation state of its ferrinol sites (isoelectric point, IEP = 9, data not shown). It was observed that the sorption of PPH imparts negative charges to the

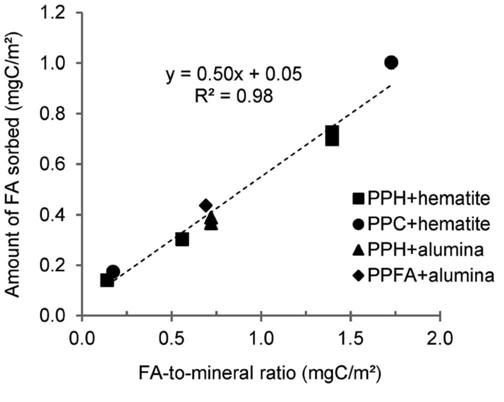

Fig. 1 Amount of PPH sorbed at pH 3.9 on the surface of hematite as a function of FA-to-mineral ratio of experiment, along with previous data acquired by our team[26] for other systems of interest (*cf.* text).

Table 1 Estimated parameters of sorption experiments of PPH performed at pH 4 and at different PPH-to-hematite ratios (*r*) leading to different percentages of FA sorption: concentrations ([ ]) and proton binding constants (log *K*) of carboxyl groups (COOH) and phenolic groups (Ph) of PPH calculated using the procedure of Ritchie et Perdue[43] and concentrations of hematite surface groups ($[S]_{surf}$, *cf.* text)

Mineral	*r* ratio (mg C per m^2)	FA sorption (%)	$[COOH]_{FA}$ (μeq L^{-1})	$\log K_{COOH}$	$[Ph]_{FA}$ (μeq L^{-1})	$\log K_{Ph}$	$[S]_{surf}$ (μmol$_{sites}$ L^{-1})
Hematite	0.1	100	33.6	1.1	12.1	9.27	190
	0.6	54	144		51.8		
	1.4	52	336		121		

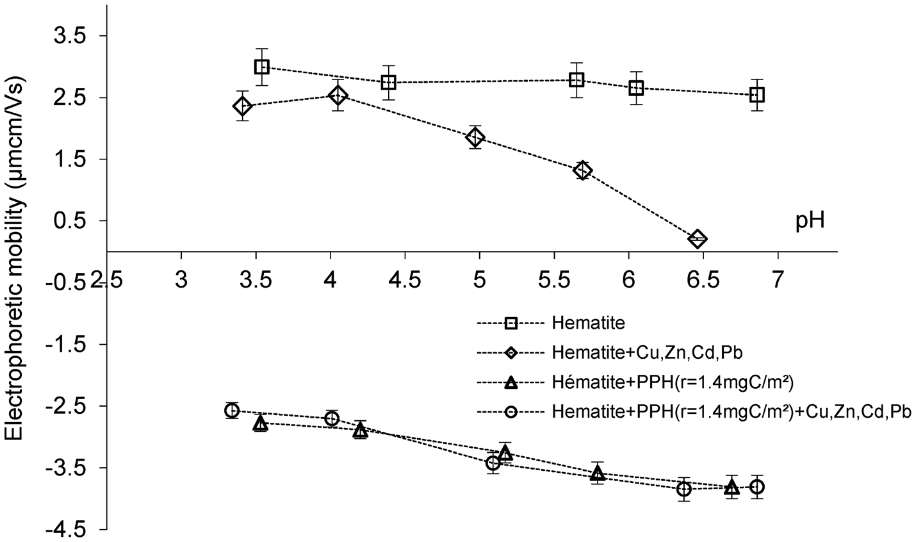

Fig. 2 Effects of sorption of PPH and/or of competitive sorption of trace level concentrations of Pb, Cu, Zn and Cd (at 0.8 ± 0.2 μM for each metal) on the surface charge of hematite as revealed by EM data recorded in suspensions of 0.375 g L^{-1} of hematite at different pHs.

hematite surface. At the highest FA-to-hematite ratio studied, the surface appears to be negatively charged throughout the pH range studied and the surface charge decreases slightly with an increase of pH from 3 to 7. Possibly, an increase with pH of the extent of de-protonation of functional groups of PPH molecules (sorbed and dissolved) can slightly affect the extent of PPH sorption by lowering the electrostatic attraction exerted by the FA-loaded α-Fe_2O_3 surface on aqueous PPH molecules and/or by reducing the formation of outer-sphere PPH–surface complexes. The reversal of sign of hematite surface charge induced by the sorption of PPH, at high surface coverage by the FA, is a main observation. This is a strong evidence that some molecules of FA were potential-determining molecules in hematite suspensions and that they reacted coordinatively with ferrinols groups onto hematite to induce a shift of IEP towards a very low value (IEP < 3, at high FA surface coverage). Indeed, formation of outer-sphere surface complexes can decrease surface charges, whereas only formation of inner-sphere species that takes place in Stern layer of the electrical double layer of the mineral–solution interface leads to IEP shift. Thus, IEP shift and reversal of surface charges evidenced the chemical sorption of PPH molecules. Formation of inner-sphere surface complexes involved ferrinol sites and functional groups of FA, as suggested by published spectroscopic or modeling studies[11,44,45] (probably carboxyl groups at acidic pH with an increasing contribution of phenolic groups with increasing pH[46]).

ESI(−) MS spectra. ESI(−) mass spectra were recorded in the ranges 120–400 *m*/*z* and 400–798 *m*/*z* for native solution of PPH and for supernatants collected at the end of PPH sorption experiments at pH 3.9. Effect of FA-to-solid ratio was examined (*cf.* Fig. 1) and the supernatants analyzed were taken from experiments at *r* values leading either to high/moderate surface coverage ($s \sim 0.7$ and 0.3 mg C per m^2 at $r = 1.4$ and 0.6, respectively) or low surface coverage ($s \sim 0.1$ mg C per m^2 at $r = 0.1$). The total ion currents (TIC) recorded for the latter were lower than for the former, due to sorption of PPH at mineral surfaces. Fig. S2† reports, as an example, spectra recorded for native solution of PPH and supernatants of experiments at high *r* (1.4). A noticeable feature is that many of the compounds detected on the spectra of native solution were no longer observable on supernatants' spectra or they displayed lower peak intensity in supernatants than in native solution. The magnitude of decrease in peak intensity varied from one compound to another. These features provide strong evidence for a process of fractionation of PPH during sorption, that is to say that some compounds of PPH were preferentially sorbed at the mineral surface. The term "compounds" apply here to FA subunits held together by weak forces or bonding which are disrupted during strong FA–mineral surface interactions, in accordance with the concept of supramolecular assembly proposed by several authors.[47–50]

Fractionation behavior of FA in hematite–solution systems. Chemical formula attributed to PPH compounds peaking on ESI(−) spectra of native solution with S/N >4 are represented on VK diagrams in Fig. S3.† The compounds distribute in a wide region of the diagrams and belong to three categories of molecules defined by aromaticity index, namely, PACs (polycyclic aromatic compounds), NCAs (not-condensed aromatics), and compounds of more or less aliphatic character. Fig. 3 reports VK diagrams in which PPH compounds are sorted as a function of their degree of relative sorption onto hematite. At the lowest FA-to-hematite investigated, which leads to a low FA surface coverage too, nearly all compounds are totally sorbed on

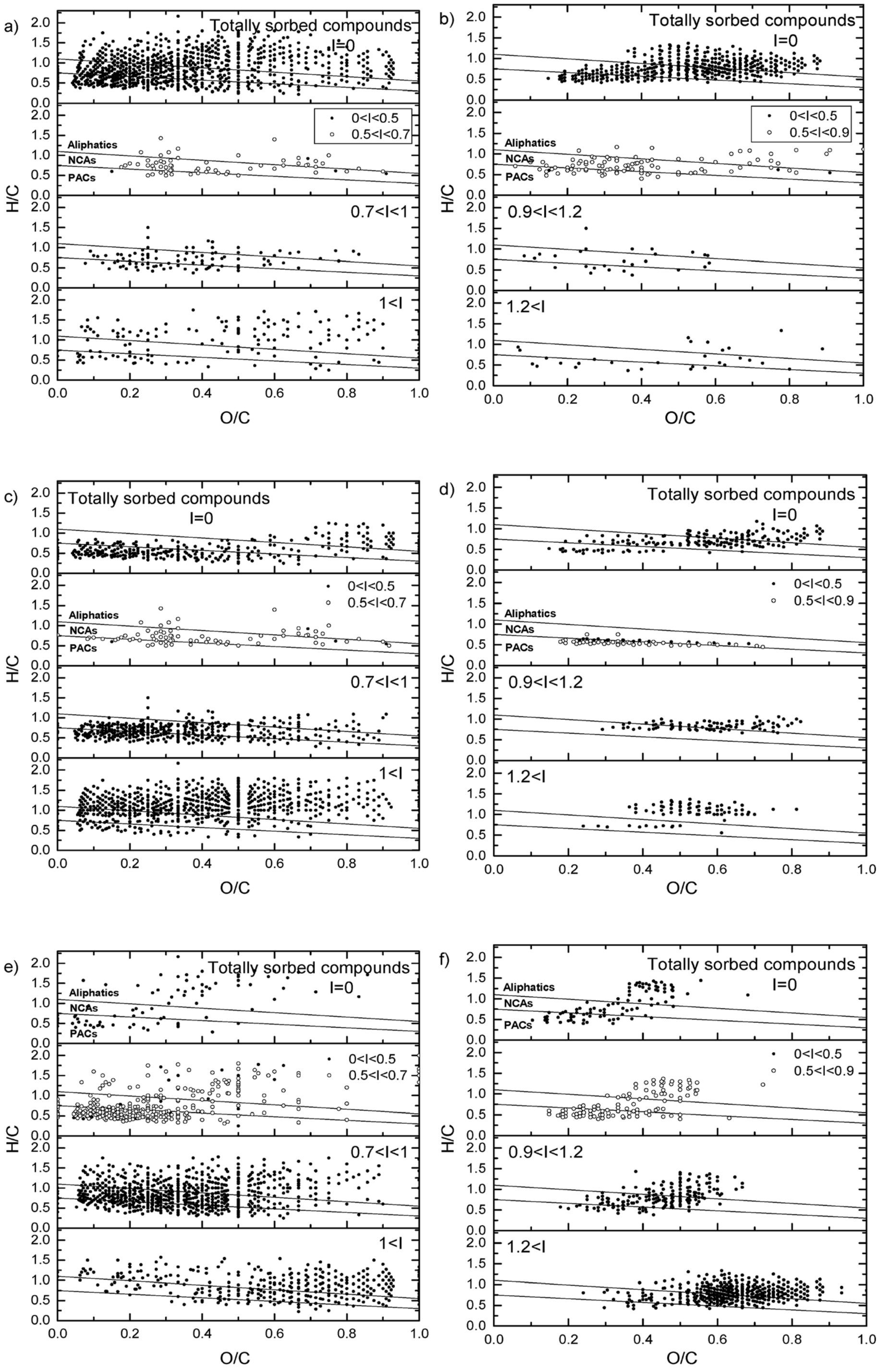

Fig. 3 VK diagrams for PPH compounds sorted as a function of their relative affinities at pH 3.9 for the surface of hematite at $r = 0.1$ mg C per m^2 (a, b), $r = 0.6$ mg C per m^2 (c, d), and $r = 1.4$ mg C per m^2 (e, f) and identified in the mass ranges 120–400 m/z and 400–798 m/z, respectively.

the surface, in good accordance with the macroscopic sorption results (100% of bulk FA sorbed at $r = 0.1$ mg C per m^2). At intermediate values of r and s, general trends in sorptive fractionation are as follows (Fig. 3c and d). First, the compounds totally sorbed ($I = 0$) belong to two clusters of molecules of specific chemical identities, which gather PACs and strongly oxygenated compounds (0.5 < atomic O/C ratio < 0.8) of the type of NCAs or of aliphatics of atomic H/C ratio <1.1, respectively. Second, aliphatics and NCAs show a decrease in their relative degree of sorption with a decrease of the O/C molecular ratio and an increase of the H/C ratio. The most hydrogenated molecules among the aliphatics (H/C > 1) are left in solution. Patterns in Fig. 3e and f, corresponding to the results obtained at $r = 1.4$ mg C per m^2, are discussed below. Fig. 4a reveals that the relative degree of sorption onto hematite of a PPH molecule in a $-CO_2$ homologous series (*i.e.*, in a series of molecules whose chemical formula differ by number of CO_2 only) is directly correlated to its number of carboxyl groups, *i.e.*, to its molecular acidity. An inverse and linear relation between value of I and number of carboxyls in a molecule was observed for $-CO_2$ series of aliphatics as well as of aromatics (except for PACs of low O/C). Fig. 4b refers to the results obtained for the $-CH_2$ homologous series. A sharp increase of I with nC is observable, indicating that the affinity for surface of a molecule within a $-CH_2$ series decreases with an increasing of length or of number of aliphatic chains. These findings evidence that the affinity order for the hematite surface of most of the PPH compounds follows the order of molecular acidity. Such results are comparable to those reported in recent molecular-scale studies[24,26] which revealed for FA/HA–Al_2O_3–solution systems the preferential sorption of the most acidic and highly oxygenated molecules bearing multiple carboxyl functionalities for each class of FA compounds, *via* a mechanism of surface ligand exchange. The most striking feature of the present study is that a quite different trend is observable in conditions of high r leading to both a high coverage of the hematite surface by FA and a high concentration of dissolved FA (Fig. 3e and f). The highly oxygenated compounds (0.5 < atomic O/C ratio < 0.8) of the type of aliphatics (with atomic H/C <1.1) or of NCAs display the weakest relative degrees of sorption among all PPH compounds, while PACs of O/C ≤0.4 show among the highest relative degrees of sorption. Even molecules such as aliphatics of high H/C ratio and low O/C – which show no peculiar affinity for metal oxide surface at moderate r – display higher relative degrees of sorption than the aliphatic/NCA molecules bearing multiple oxygenated functionalities. These features are well illustrated by the change in the relations existing between I and nC for CO_2 and CH_2 series of molecules belonging to aliphatic and NCA compounds with O/C >0.2 (*cf.* Fig. 4). It is striking that the relations found at a high value of r are diametrically opposed to those found at a low r value, reflecting a high relative degree of sorption of the most oxygenated PPH compounds at

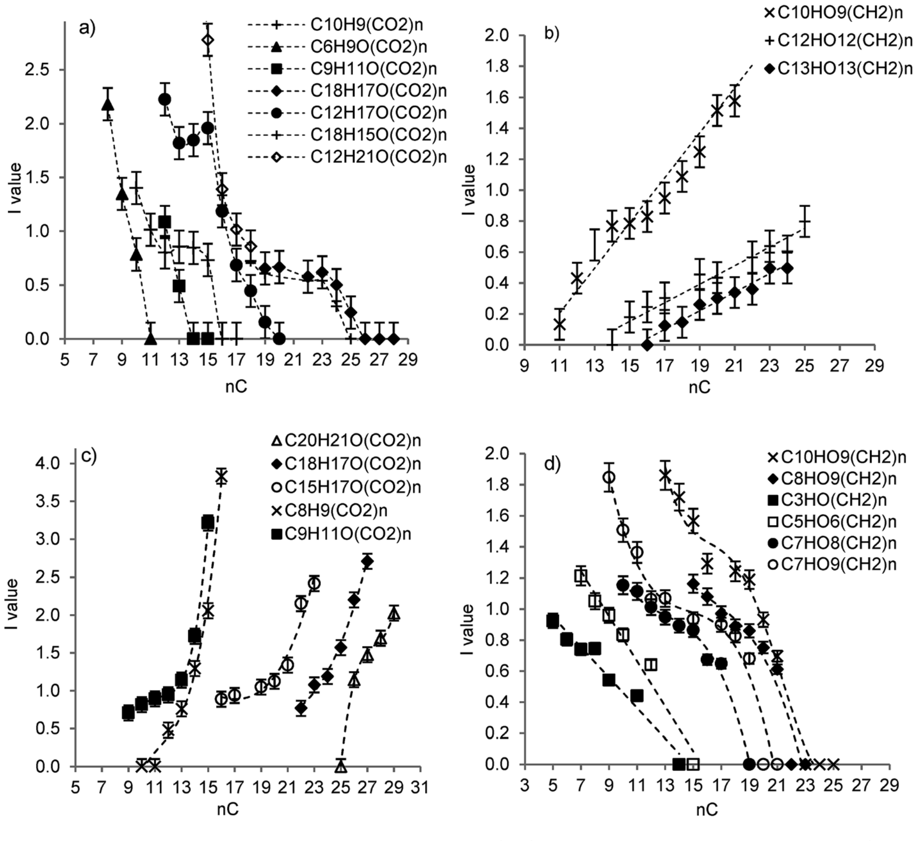

Fig. 4 Evolution of the value of I as a function of number of carbon atoms (nC) of aliphatic and NCA compounds (with O/C >0.2) in $-CO_2$ and $-CH_2$ series of PPH, after sorption of the FA in hematite–solution systems at pH 3.9 and at $r = 0.6$ mg C per m^2 (a and b, respectively) or $r = 1.4$ mg C per m^2 (c and d, respectively).

moderate r value ($r = 0.6$ mg C per m^2) and a low relative degree of sorption of these same molecules at high r value ($r =$ 1.4 mg C per m^2). Thus, we provide molecular-scale evidence that the fractionation behavior of a FA during its sorption at acidic pH on the hematite surface, and consequently the nature and the reactivity of the sorbed or dissolved organic molecules, strongly depends on FA-to-hematite ratio and cover rate of the surface by FA. On the one hand, our data confirm that the exchange of ligands on the surface of a metal oxide is a key mechanism which promotes the adsorption of highly acidic and oxygenated molecules, whatever the class of FA/HA molecules considered (PACs, NCAs or aliphatics), at a moderate surface coverage by HS, which is in good accordance with previously published results.[26] On the other hand, our results reveal that other processes or parameters must be envisaged to explain the dramatic fall, when the ratio FA-to-mineral increases, of the relative degree of sorption of these types of molecules bearing multiple oxygenated functionalities and having thereby the potential ability to bind at metal-oxide surfaces.

3.2 Sorption isotherms of metals in FA–hematite–solution systems

Binary hematite–metal systems. Major findings of the competitive sorption of Cu, Zn, Cd and Pb in hematite–metals–solution systems are as follows. In the absence of PPH (Fig. 5), the sorption of all metals increases with pH (S-shaped curve) and the values of pH$_{50}$ (*i.e.* pH at which 50% of metal is sorbed) follow the order of first metal hydrolysis constants, *i.e.*, Pb > Cu > Zn > Cd, consistently with previously published studies reporting a positive correlation between the tendency of metals to hydrolyze and their tendency to interact with hydroxylated surfaces.[17,51,52] The sorption of the metals induces a lowering of the isoelectric point of hematite (Fig. 2), evidencing the formation of inner-sphere metal surface complexes onto hematite.[53] Such a lowering may be well accounted for by the formation of uncharged/negative internal sphere (IS) surface species such as SO–MOH complexes (S denoting a metal center at surface) reported to exist for Cu,[54,55] Pb[56] and Cd[57] sorbed at low surface coverage onto Fe-oxihydroxides, and/or such as $(SOH)_2M(OH)_2^0$ and $(S_3O(OH)_2)M_2(OH)_3^0$ complexes reported for Cu sorbed at high coverage.[42]

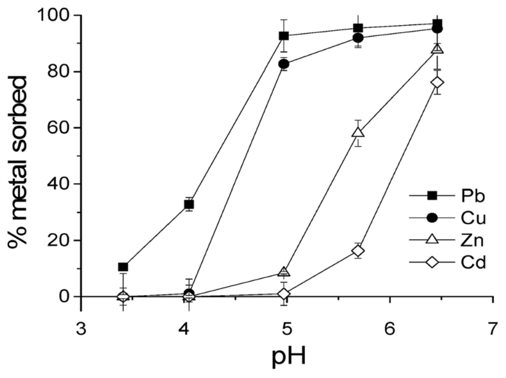

Fig. 5 Results of experiments of the competitive sorption of Pb, Cu, Zn and Cd at trace level concentrations (at 0.8 ± 0.2 μM for each metal) in suspensions of 0.375 g L^{-1} hematite at different pHs.

Ternary hematite–metal–PPH systems. Fig. 6 shows metal sorption isotherms obtained in the presence of PPH for different values of r. The sorption of PPH at a low r (0.1 mg C per m^2) promotes the sorption of metals on the surface of hematite at pH ≤5 in the order: Pb > Cu > Cd > Zn, with the behavior of Zn being only poorly impacted (Fig. 6). This sequence of promotion of metal sorption is in good agreement with the order in stability constants reported for metal–humic acid complexes in solution,[1,2,58] suggesting similar affinity order of metals for PPH in solution and for PPH when totally sorbed on the hematite surface. Probably, carboxyls are the main functional groups involved in the sorption of Pb/Cu at pH <5 owing to their high concentration in PPH and to their deprotonated state at acidic pH (*cf.* paragraph above), as already reported in literature for many HS.[1,59–61] Table 2 reports calculated values of the ratio K_{Me} at pH 4, which is defined as follows:

$$K_{Me} = \frac{[Me]_{surf}}{[COOH]_{surf} \times [Me]_{aqu}} \tag{1}$$

and where $[Me]_{surf}$ and $[Me]_{aqu}$ are concentrations of metal sorbed at the surface and remaining in solution at near-equilibrium, respectively, and $[COOH]_{surf}$ is the concentration of carboxyl groups of FA sorbed at the surface calculated on the basis of 16.02 meq per g C of COOH groups in bulk FA, as measured by FA titrations following the procedure of Ritchie and Perdue.[43] Values of K_{Me} obtained for Cu, Cd and Zn at a low value of r (estimated value of $[COOH]_{surf}$ equal to 33.6 μmol L^{-1} from data at $r = 0.1$ mg C per m^2 in Table 1) have the dimensions of conditional constants of formation of metallo-organic surface species, as sorption of FA is complete in these conditions and no metal sorption was observed at pH 4 in the absence of FA. It is to be noted that value of K_{Me} cannot be calculated for Pb from our experimental data as *ca.* 30% of Pb sorption was observed at pH 4 in the absence of FA (*cf.* Fig. 6). At the lowest value of r studied, the value of K_{Cu} is two orders of magnitude higher than those calculated for Cd and Zn, which illustrates well the strong tendency of this metal to co-adsorb with FA on surface of hematite at acidic pH. In conditions of high r (1.4 mg C per m^2) where *ca.* 50% of FA is sorbed in the pH range 3–7, the adsorption isotherms obtained in experiments of competitive metal sorption show a significant-to-high effect of PPH for promoting the sorption of all metals at acidic pH; more precisely, at pH ≤4 and 4.5 for Cu and Pb, respectively and at pH ≤5.5 and 6 for Zn and Cd, respectively (Fig. 6). A main result of present study is that the sequence of promotion of metal sorption by PPH (Pb > Cu > Cd > Zn at pH ≤5) is not observable anymore in the whole pH range 3–5 at a high value of r. The promotion of the sorption of Cd and Zn by FA is found to be greater than that of Cu in the pH range 4–5, and the promotion sequence is Pb > Cd ≥ Cu ≥ Zn at pH 4. The values of K_{Me} at high r reported in Table 2 were calculated by considering a simple hypothesis that the percentage of sorption for carboxyl groups of FA at pH 4 is similar to that of bulk FA, (which leads to an estimated value of $[COOH]_{surf}$ equal to 175 μeq L^{-1} from data

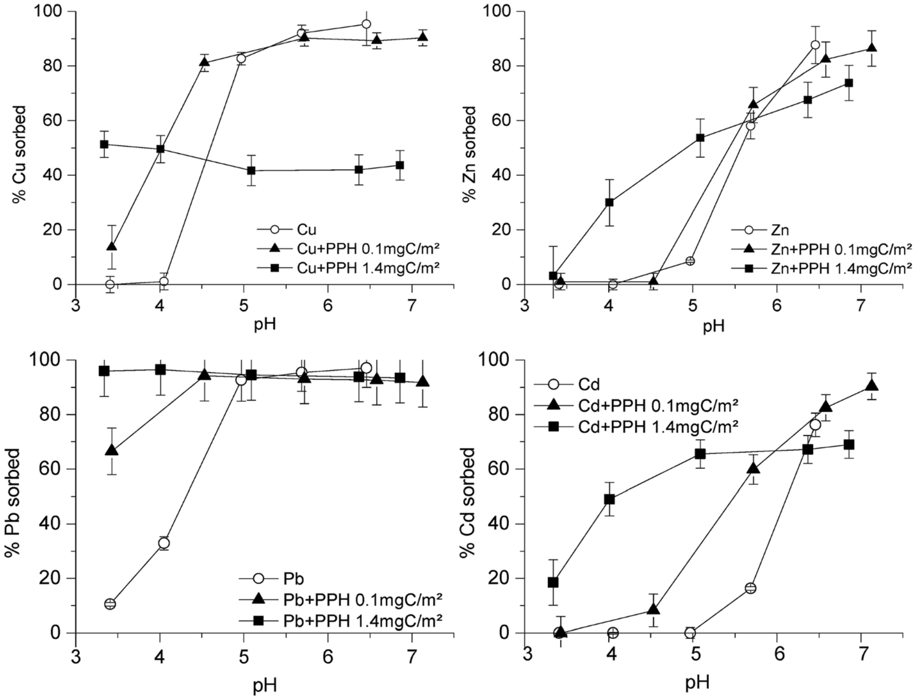

Fig. 6 Results of experiments of the competitive sorption of Pb, Cu, Zn and Cd at trace level concentrations (at 0.8 ± 0.2 μM for each metal) in suspensions of 0.375 g L^{-1} hematite at different pHs, in the absence of PPH or for initial PPH-to-hematite ratios of 0.1 mg C per m^2 or 1.4 mg C per m^2.

Table 2 Calculated values of the ratio K_{Me} (*cf.* text of paragraph 3.2) in experiments of competitive sorption of Pb, Cu, Zn and Cd onto hematite at pH 4 and at different FA-to-hematite ratios (*r*)

r ratio (mg C per m^2)	K_{Cu} (L mol^{-1})	K_{Zn} (L mol^{-1})	K_{Cd} (L mol^{-1})
0.1	1.25×10^5	1.65×10^3	1.85×10^3
1.4	5.08×10^3	2.45×10^3	5.72×10^3

in Table 1). That the value of K_{Cu} is lower at high *r* than at low *r* (and that the percentage of Cu sorption is lower at pH >4) is in accordance with what is expected of the general trend in behavior of a metal governed by a competition between surface complexation by FA and aqueous complexation. It has been widely reported in the literature that dissolved FA may interfere on metal sorption – or even prevent it – due to aqueous metal complexation,[1,2,58,62] whose extent increases with pH due to a progressive increase of the extent of deprotonation of functional groups of dissolved FA molecules and a decrease of the sorption of FA. That the percent sorption of Pb, Zn and Cd increases at acidic pH when *r* is increased from a low to a high value could be due to an increase of the amount of carboxyl groups sorbed (*cf.* Table 1) which would expectedly promote the binding of metals at the surface of hematite. However, a striking result is that the values of K_{Cd} and K_{Zn} obtained at high *r* are greater than those obtained at low *r*, which indicates that the increase observed in the percentages of sorption of Cd and Zn is greater than the expected effect of an increase of $[COOH]_{surf}$ (calculated on the basis of the sorption of bulk FA). In summary, the change in the sequence of promotion by FA of metal sorption observed with an increase of *r* at pH 4–5 cannot be explained solely by a competition between the formation of metallo-organic surface complexes in the order Pb > Cu > Cd > Zn (observable at low *r*) and the formation of aqueous metallo-organic complexes in the same order reported in several published studies.[2,58]

4. Discussion

A main finding of this study is that the FA-to-hematite ratio is a key parameter governing trends in sorption on hematite observed at acidic pH both of the molecules constitutive of a terrestrial fulvic acid and of divalent metals at trace level concentration. In particular, its effect on the sorptive fractionation of a fulvic acid had never been explored before. The ESI-MS data presented here provide new knowledge at molecular level that advances the in-depth description of the interactions occurring in complex FA–metal oxide–TME–solution systems.

4.1 FA fractionation behavior

Significant differences were found between the fractionation patterns obtained for the sorption of PPH at a high value and at a low value of the FA-to-hematite ratio, respectively, which addresses the underlying mechanisms. All the results obtained at the molecular scale for the hematite–solution system at moderate value of *r* and at moderate FA surface coverage indicate that the sorption behavior of PPH at pH 4 is mostly the result of a highly selective mechanism, which is a surface ligand exchange involving the high affinity ferrinol sites at the mineral surface and carboxyl groups of PPH molecules. The main molecular parameter governing selectivity is molecule acidity, as shown by the nC–I relations existing within CO_2 and CH_2 homologous series whatever the class of compounds to which a series belongs. Significance of the existence of such relationships has been widely discussed in our previously published studies.[25,26,63] The numerous homologous series accounting for the large number of different basic structures in PPH, and the wide range of I values observed, complied well with the concept that a FA is made up by small subunits held together by weak forces. It evidenced moreover that surface ligand exchange competed efficiently the cohesion forces of the supramolecular assembly to induce a disruption of the FA structure during the process of sorption. Uptake of the least oxygenated PACs and NCAs is probably driven by hydrophobic interactions between their hydrophobic moieties and those of the strongly sorbed PACs.[26,63]

Molecular acidity is not the only parameter to be taken into account to explain the PPH sorption behavior at high FA-to-hematite ratio. The dramatic FA fractionation schemes observed during FA sorption compare well with published studies reporting that hydrophobic fractions of FAs and/or the organic molecules with high contents in aromatic moieties activated by oxygenated functionalities are preferentially sorbed on the surfaces of Fe-oxide and Al-oxide minerals as compared to aliphatic fractions.[21,23,64,65] An important observation from our ESI-MS data is the much lower number of totally sorbed PPH molecules observable in the experiment at high value of r than in the experiment at moderate value of r, despite a higher FA coverage. These results attest for a strong competition of the PPH molecules for the sorption on the hematite surface at high FA-to-mineral ratio. We propose that two parameters beside molecular acidity contribute to the fractionation pattern in such a highly competitive and FA-concentrated system, namely, the amounts of ferrinol surface sites available for coordination of FA carboxyl groups and the rate of hematite dissolution.

A first hypothesis is that the strong competition for coordination at the ferrinol surface sites is in favor of the condensed aromatic structures carrying oxygenated functionalities (*cf.* values of I in Fig. 3e and f) because the latter may represent the most acidic of all organic components of terrestrial FA. Synergistic effects are expected to be induced by a high occupancy of the ferrinol sites by the most acidic PACs bearing multiple oxygenated functionalities. Their presence in the first sorption layer formed on the surface of hematite likely provides significant amounts of hydrophobic domains available for further interactions with the hydrophobic moieties of PACs of low O/C present in the solution, as well as with NCAs and aliphatics of intermediate and low O/C. Moreover, the large extent of deprotonation of the carboxyl groups (*i.e.*, of those not engaged directly in surface bonding) of the oxygenated PACs in the first layer of sorbed FA results in high negative charges at hematite–solution interface (*cf.* Fig. 2). As a consequence, the dielectric constant of water at the surface of hematite may be apparently lower than that of free water (because electric fields induced by surface charge influence its value as shown by Booth[66]), which favors the adsorption of hydrophobic molecules. Moreover, the negative surface charges may prevent the approach in the close proximity of hematite surface of dissolved molecules which are highly acidic (deprotonated) such as NCAs and aliphatics of high O/C ratio, due to electrostatic repulsion. All these effects may represent one of the causes for the increase of sorption degree with increase of number of CH_2 of a molecule in a $-CH_2$ series (*i.e.*, an increase of its aliphatic character and a decrease of its acidity) that was observed for NCAs and aliphatics in experiment at high r (Fig. 4d). Consistently, they may account for the observation that the degree of sorption of a PPH molecule in a CO_2-series is inversely correlated to its number of carboxyl groups, with such a trend being explained by a decrease in molecule acidity with nCO_2.[67] In summary, all the effects described above might have led to higher degrees of sorption (likely *via* H-bonding or hydrophobic effects) for the least acidic and least oxygenated molecules in these classes of compounds than for the most acidic ones.

A second hypothesis is that the highly oxygenated NCAs and aliphatics of PPH are preferentially kept in solution because they tend to participate in aqueous complex formation with Fe^{3+} released by dissolution of hematite. The inverse and linear correlation observed between degree of sorption of a PPH molecule (NACs and aliphatics) and nCO_2 at high r (Fig. 4c) may thus be interpreted by a partial control of PPH fractionation due to the increasing participation of a PPH molecule to chemical binding in solution with an increase of its acidity, through reactions of aqueous complex formation involving its oxygenated (carboxyl) groups and aqueous Fe. Previous studies have indeed shown that Fe ions participate to formation of strong metallo-organic complexes with HAs, either in solution or at mineral surfaces.[68,69] Moreover, it has long been known that presence of organic matter increases solubility and rates of dissolution of Fe-oxides.[70] Differences in sorptive fractionation trends of PPH observed with increasing FA-to-hematite ratio may thus be well accounted for by competitive effects between Fe^{3+} metallic centers at hematite surface and dissolved Fe^{3+} ions for coordination of the highly oxygenated NCAs and aliphatics bearing multiple functionalities. Actually, both characteristics of high FA-to-hematite ratio systems, *i.e.*, high dissolution rates of hematite and limited amounts of ferrinol surface sites available for ligand exchange with the high amounts of oxygenated functional groups of FA, may concur to the strong fractionation observed between the highly-sorbed oxygenated PACs and the poorly-sorbed oxygenated NCAs and aliphatics, owing to small differences in acidity and/or relative affinities for surface and aqueous Fe of these molecules which all have potentially strong metal binding properties.

4.2 Competitive sorption behavior of the metals

Few studies have reported so far experimental results on the competitive sorption of TMEs in ternary metal–HS–mineral systems. We provide evidence that the presence of a terrestrial FA not only changes the affinity order of the divalent metals for hematite surface at acidic pH but also that the affinity order is highly dependent on FA-to-hematite ratio and FA surface coverage. Processes leading to the change reported here in the order of metal sorption at high FA-to-mineral ratio are of primary interest in the mobility/retention behavior of metals in soils rich in humic substances.

The promotion sequence by PPH of metal sorption onto hematite (Pb > Cu > Cd > Zn) reported at low *r* (where PPH is totally sorbed) and at low pH (where no metal sorption occurs in the absence of PPH) was in good agreement with the results of Elliott *et al.*[17] In such conditions, it clearly reflects the overall order in metal–PPH–surface binding and it is similar to the order in stability constants reported for metal–humic substance complexes in several studies.[2,58] Some discrepancies however exist regarding relative stability of metal–fulvate complex between Pb and Cu. Unlike in the aforementioned studies, several authors have found a higher value of stability constant for Cu than for Pb.[1,71] It must be stressed that the reported values for metal–humic substances complexation are dependent on many experimental parameters, *e.g.*, pH, ionic strength, composition of humic/fulvic acid and metal loading, which often makes them not being directly comparable. For example, Town and Filella[62] made a collection of published lead-humic substances equilibrium quotients and they highlighted by taking into account metal ion loading that a linear relationship exists between metal complexation capacity of organic matter and log K value. This relationship evidenced that apparent stronger binding sites of humic substances are utilized at lower metal ion loadings and that progressively weaker sites contribute to metal complexation at higher loadings.[62] Nonetheless, there is a general agreement that metal–humic substance constants are higher for Cu and Pb than for Cd, then Zn, *e.g.*, Pb- and Cu-humate/fulvate complexes are much more stable than Cd–Zn-humate/fulvate complexes. On the basis of the literature, we can hypothesize similar general trends in the order of co-adsorption of the metals with PPH on the surface of the hematite (observed at low *r*) and the order of binding of the metals to dissolved PPH, which is: Pb and Cu > Cd > Zn. A change in the sequence of promotion of the adsorption of metals by FA can therefore not be explained only by a simple scheme of competition between the aqueous complexation and the surface complexation of the metals with bulk FA. Explaining the change in the promotion sequence with *r* observed in this study at pH 4–5, in particular the promoted sorption of Cd and Zn over that of Cu, requires considering the intervention of processes cooperating or competing with sorption (depending on the metal under consideration) which are closely linked to characteristics of the high FA-on-hematite ratio system, *e.g.*, solution containing dissolved FA and Fe^{3+} ions (high hematite dissolution rate), amounts of ferrinol sites available for coordination of carboxyl groups of FA and subsequent fractionation behavior of PPH, specific properties of the heavily FA-loaded surface.

A metal ion is expected to participate in formation of two main types of ternary inner-sphere metallo-organic sorption complexes on the surface of a mineral, namely, the metal tends to bind to functional groups of sorbed organic molecules to form surface–FA–metal complexes, and/or it makes a bridge between the surface and the sorbed organic molecules by binding directly to oxygen atoms of the hydroxyls groups present on hematite to form stable ternary surface–metal–FA complexes. Sorbed PPH molecules may occupy sorption sites of Cu under conditions of high *r* where the surface coverage of hematite by PPH is high ($s = 0.7$ mg C per m^2), preventing thereby the formation of surface–Cu–FA complexes. Although possible, such a process cannot account alone for the decrease in Cu sorption with *r*. Another important process to take into account is that Pb and Cu compete for the same sorption sites. This is revealed by our data of the single (Fig. S4†) or of the competitive sorption (Fig. 6) of Cu on hematite showing that the presence of Pb decreases the FA-promoted sorption of Cu at low FA-to-mineral ratio. In the multi-metal experiments at low *r*, a competition between Pb and Cu and PPH molecules for ferrinol sites is to be ruled out because ferrinols are available in large quantities with respect to the concentration of metals or functional groups of FA (*cf.* Table 1). Hence, it may be inferred that Cu participates in the absence of Pb to the formation of ternary surface–organic ligand–Cu complexes implying sorption sites present in very small quantities at hematite surface, probably multidentate sites. In multi-metal systems, Pb is likely to compete successfully for binding at such sites, owing to its marked affinity reported for the stronger binding sites of humic substances.[62] This is consistent with data on metal-humate, metal salicylate and metal benzoate of Kostic *et al.*[2] showing that there is a strong competition between Pb(II) ions and Cu(II) ions in the binding for carboxyl and phenolic binding sites of humate macromolecules. In the experiment at high *r*, both Pb and the Fe^{3+} ions released at acidic pH by the promoted dissolution of hematite are likely to compete against binding of Cu at the multidentate sites of the sorbed PPH fraction. It has been suggested in a published study of the effects of Fe competition on binding of rare earth elements to humic acid[68] that Fe^{3+} has a marked affinity for the few strong HA multidentate sites, as Fe was shown to be a strong competitor for heavy rare earth elements in low pH conditions at which Fe^{3+} binds to HA. Iron implication provides a valid explanation for the decrease in the FA-promoted Cu sorption on hematite observed here at acid pH (4–5) when the value of *r* is changed from low to high in the experiment, despite the number of functional groups of PPH sorbed is potentially increased concomitantly. Competitive phenomena between Pb, Fe and Cu for the small quantities of the multidentate sites of the sorbed organic matter would thus explain that the FA-promoted Cu sorption decreases with the presence of Pb or with a high FA-on-hematite ratio, favoring certainly the complexation of Cu with dissolved FA molecules at low pH. Moreover, the dissolved molecules in the studied system at high *r* have potentially strong binding properties for metals (*cf.* paragraph 4.1). Consistently, the sorption of Cu onto hematite observed at near-neutral pH value in the absence of FA is significantly reduced in the presence of dissolved PPH. The extent to which the sorptive fractionation of FA regulates the distribution of FA multidentate sites between the hematite surface and the solution is an important topic for further research to elucidating mineral–metal–humic interactions in soils rich in humic substances and the detailed effect of a difference in composition/reactivity between adsorbed and dissolved fractions of FA on the reduction of the FA-promoted Cu sorption at acidic pH.

The higher affinity of Cd and Zn for hematite observed at high *r* than at low *r* (at acidic pH 4–5) would necessarily imply differences in the reactivity and characteristics existing between a poorly PPH-loaded and heavily PPH-loaded surface of the hematite. First, as underlined before, the large extent of deprotonation of the carboxyl groups of the oxygenated PACs sorbed in a first sorption layer results in a heavily negatively charged surface of hematite, for a high value of *r* (*cf.* Fig. 2). This may favor the further adsorption of Cd^{2+} and Zn^{2+} as outer-sphere metal–fulvate surface complexes and/or the electrostatic attraction exerted on the metal ions by the strongly charged surface by FA may promote their placement at a certain distance of the solution–hematite interface in a diffuse layer of counter-ions compensating the surface charges. Second, the sorption of Zn and Cd is possibly favored at high *r* due to the higher degree of sorption of PPH molecules of intermediate O/C to which these metals tend to associate preferentially, owing to their low Lewis acidity. Further studies are needed to evaluate the exact role of preferential adsorption onto Fe oxides of NACs or aliphatic compounds of FA which display intermediate O/C ratios on the inversion of the order of the promotion of sorption of Cu and Cd (Zn) in conditions of high FA-to-mineral ratio.

5. Conclusions

The results presented here highlight that the fulvic acid-to-mineral ratio is a key parameter controlling the competitive sorption of both the organic molecules constitutive of a terrestrial fulvic acid and of divalent trace metals on the surface of hematite.

In particular, our ESI-MS data provide new knowledge at molecular level of the sorptive fractionation of a FA that improves greatly our understanding of the mechanisms of the FA–Fe oxide–solution interactions. Whereas molecular acidity is the main parameter driving the sorption of a FA molecule in weakly FA-concentrated hematite–solution systems, this molecular parameter has the reverse effect of promoting the mobility of aliphatics and not-condensed aromatics in the highly competitive FA-concentrated systems. In the latter conditions, a series of complex interactions are to be considered, – *e.g.*, strong competitive effects between most acidic molecules, hydrophobic effects, hydrogen bonding – to explain the preferential sorption of all PACs and of the low oxygenated FA molecules. These results emphasize that a thorough study of the chemical characteristics of individual HS components, such as acidity, hydrophobicity, and functional groups, and of relationships between molecular characteristics and sorptive fractionation of HS, is powerful for acquiring detailed knowledge of HS sorption mechanisms; knowledge on which our comprehensive understanding of the behavior of complex mixtures such as HS in geochemical systems can be built.

The data on the competitive sorption of divalent metals in hematite–FA solution systems support that a potentially highly toxic metal as Pb is strongly retained on Fe-oxides owing to its peculiar affinity for a few multidendate sorption sites of sorbed FA molecules bearing multiple oxygenated functionalities. In contrast, it is suggested that sorption of Cu on such sites is competed successfully at acidic pH by the presence and the preferential sorption of Pb, and by that of Fe^{3+} ions in conditions of high FA-to-mineral ratio favoring the enhanced dissolution of iron oxides and the subsequent release of Fe in solution. Competitive effects between surface complexation of Cu and aqueous complexation of Cu involving the highly acidic NACs and aliphatics left in solution in FA-concentrated systems may also concur to a decrease in FA-promoted retention of Cu on the metal oxide. Unlike for Cu, the highly FA-rich systems display enhanced ability for retardation of Cd, another metal highly toxic, owing to the characteristics of the heavily FA-loaded mineral surfaces, including a possible role of the specific retention of the FA compounds (aliphatics and NACs) of intermediate O/C ratios in these conditions. Further studies combining macroscopic and molecular-scale information are needed to precise the exact role of a possible difference in metal affinity order between the FA molecules preferentially sorbed (PACs and less oxygenated FA molecules) and those preferentially left in solution (acidic and oxygenated NACs and aliphatics) on the competitive behavior of divalent metals in high FA-to-mineral ratio conditions. Valuable insights into the role of sorptive fractionation pattern of HS on the competitive sorption of TEMs on iron oxides may also be provided by combined macroscopic and molecular investigations using supramolecular assemblies such as humic acids, which are known to display at low HS-to-metal oxide ratio a heightened contribution of hydrophobic interactions as compared to FA, due to their highest content in PACs.[25] More information on relationships between HS molecular characteristics, HS fractionation and competitive metal sorption on iron oxides is of interest to better comprehend the coupled cycles of metals and organic matter in geochemical surface systems rich in Fe-oxyhydroxides, owing to their high specific surface area and high surface reactivity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank IPHC and the Alsace Region for their financial support. We also gratefully acknowledge the reviewers for their helpful comments and for improvement of the manuscript.

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