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A universal adsorption behaviour for Cu uptake by iron (hydr)oxide organo-mineral composites.

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ABSTRACT

Organo-mineral composites formed by the association of iron (hydr)oxides and organic matter are widespread in natural environments and play an important role as scavengers of bioessential elements and contaminants. To better understand the mobility and fate of Cu in natural soils and sediments we precipitated ferrihydrite and goethite organo-mineral composites using humic acid as an analogue for natural organic matter, with organic carbon content in the composites ranging from 2 to 16 wt% C. We then measured the adsorption of Cu to the end-member mineral and organic phases and the composites as a function of pH and Cu concentration. We determined the molecular mechanisms of Cu adsorption to the end-member phases and the composites, and used this information to develop molecularly constrained thermodynamic surface complexation models to quantify Cu adsorption. By combining our work here with previous work on the adsorption of Cu to ferrihydrite-bacteria composites, we provide insight into the predominance of Cu-carboxyl binding for Cu adsorption to iron (hydr)oxide organo-mineral composites, and the nature of Cu adsorption behaviour across a range of iron (hydr)oxide composites composed of different minerals and different types of organic matter. Taken as a whole our results show that Cu adsorption to the carboxyl group present in organic matter coatings on iron (hydr)oxides is likely common to most iron (hydr)oxide composites, such that Cu-carboxyl binding provides a key control on the fate and mobility of Cu in soils and sediments. Our work also suggests there is a universal adsorption behaviour for Cu adsorption to ferrihydrite organo-mineral composites, in which the mineral:organic mass ratio is a crucial parameter for determining Cu uptake. Overall we show that ferrihydrite composites composed of different types of organic matter and containing a wide range of organic mass ratios, but where the mineral is the dominant composite fraction, possess additive Cu adsorption behaviour which can be predicted using a component additivity surface complexation model.

Keywords: Iron (hydr)oxides; ferrihydrite; goethite; organic matter; humic acid; adsorption; trace elements; copper; EXAFS; surface complexation model.

1. INTRODUCTION

In natural soils and sediments iron (hydr)oxides are typically coated with organic matter in the form of humic substances and/or microbial cells (e.g., Davis, 1982; Sposito, 1984; O'Melia, 1989; Fortin and Langley, 2005). Similar to pure iron (hydr)oxides these organo-mineral composites are potent sorbents of a range of natural and contaminant species, and can provide a first order control on the mobility and fate of bioessential elements and contaminants alike (e.g., McCarthy and Zachara, 1989; Murphy and Zachara, 1995). In contrast to pure iron (hydr)oxides however, the adsorption behaviour of iron (hydr)oxide organo-mineral composites can significantly differ from their pure, end-member mineral and organic components (e.g., Murphy and Zachara, 1995). This is demonstrated for the macroscopic adsorption of Cu onto a range of iron (hydr)oxide organo-mineral composites, where Cu adsorption to iron (hydr)oxides that posses a surface coating of sorbed humic substances or bacterial cells is enhanced in the low-mid pH regime, and is attributed to the presence of additional binding sites associated with the organic fraction and/or new high-affinity sites created when the organics adsorb to the (hydr)oxide surfaces (e.g., Tipping et al., 1983; Murphy and Zachara, 1995; Alcacio et al., 2001; Christl and Kretzschmar, 2001; Buerge-Weirich et al., 2003; Flogeac et al., 2004; Saito et al., 2005; Jönsson et al., 2006; Weng et al., 2008; Zhu et al., 2010; Moon and Peacock, 2012, 2013). Only a very limited number of studies however, directly observe the microscopic mechanisms responsible for Cu adsorption onto iron (hydr)oxide organo-mineral composites. For composites consisting of ferrihydrite and bacterial cells, Cu adsorption is seen to occur onto both the mineral and organic composite fractions, with inner-sphere bidentate surface complexes on the mineral fraction and inner-sphere monodentate complexes via the carboxyl functional groups on the bacteria fraction (Moon and Peacock, 2012). The complexation of Cu by the carboxyl or phenolic functional groups present on iron (hydr)oxide organo-mineral composite surfaces is also observed for goethite-humic composites (Alcacio et al., 2001) and natural soil particles with organic matter coatings (Flogeac et al., 2004; Weng et al., 2008; Qu et al., 2017). Moon and Peacock (2012) take their ferrihydrite-bacteria composite data and combine this with the few other microscopic studies of Cu adsorption to iron (hydr)oxide organo-mineral composites and natural soil particles cited above, to propose that Cu adsorption to the carboxyl group present in organic matter coatings might be common to most iron (hydr)oxide composites, such that Cu-carboxyl binding provides a key control on the fate and mobility of Cu in soils and sediments.

The adsorption of Cu to both the mineral and organic fractions of iron (hydr)oxide organo-mineral composites also means it is difficult to predict Cu adsorption behaviour, and thus the concentration of Cu in natural and contaminated environments (Christl and Kretzschmar, 2001; Moon and Peacock, 2013). The adsorption behaviour of trace species taken up by organo-mineral composites can be described as being either additive, where the sum of the adsorption on the individual end-member composite fractions equals that of the composite (Zachara et al., 1994), or non-additive, where the sum of the adsorption on the individual end-member composite fractions does not equal that of the composite (Vermeer et al., 1999). Work to date for Cu adsorption to iron (hydr)oxide composites is limited but shows contrasting adsorption behaviour, where, for example, assuming linear additivity, the predicted adsorption of Cu to hematite-humic systems is consistently under-estimated compared to that observed, i.e., sorption on the composites is more than expected assuming additivity (Christl and Kretzschmar, 2001), while for goethite-humic systems and some natural soils adsorption is more than expected in the mid-high pH regime but less than expected at the mid-low pH regime (Ali and Dzombak, 1996; Robertson, 1996; Saito et al., 2005; Weng et al., 2008; Antoniadis and Golia, 2015). For ferrihydrite-bacteria composites, Moon and Peacock (2013) show that Cu adsorption is additive in composites composed predominantly of the ferrihydrite fraction, and non-additive in composites composed predominantly of the bacteria fraction. These authors suggest that the adsorption behaviour of ferrihydrite-bacteria composites is determined by the mineral:bacteria mass ratio in the composites, with composites composed predominantly of mineral behaving additively and predominantly of bacteria behaving non-additively (Moon and Peacock, 2013). The non-additive behaviour is attributed to a change in the surface charge of one or both of the composite fractions as a result of their close spatial association, where the proximity of a significant quantity of negatively charged organic to positively charged mineral will reduce the positive charge of the mineral resulting in enhanced cation adsorption to the mineral fraction in the mid-high pH regime, while simultaneously reducing the negative charge of the organic resulting in decreased cation adsorption to the organic fraction in the mid-low pH regime (e.g., Vermeer et al., 1999; Ferris et al., 1999). Taking their ferrihydrite-bacteria composite data and combining this with the few other studies of Cu adsorption to iron (hydr)oxide organo-mineral composites cited above, Moon and Peacock (2013) suggest that the mineral:organic mass ratio in iron (hydr)oxide organo-mineral composites might provide a common parameter for understanding Cu adsorption behaviour in these systems, where composites composed predominantly of the mineral fraction behave additively and Cu concentrations in associated natural and contaminated waters can be predicted using a linear additive approach.

To further understand Cu adsorption behaviour on iron (hydr)oxide organo-mineral composites, we augment the ferrihydrite-bacteria work by Moon and Peacock (2012, 2013) and investigate Cu adsorption to ferrihydrite-humic acid and goethite-humic acid organo-mineral composites. We determine the molecular adsorption mechanisms of Cu to the end-member mineral and organic phases and the composites, and develop molecularly constrained thermodynamic surface complexation models to investigate the nature of the Cu adsorption behaviour. Combined with the work of Moon and Peacock (2012, 2013) the objective of our work here is twofold. Firstly, we investigate the predominance of Cu-carboxyl binding in a range of iron (hydr)oxide organo-mineral composites, composed of different iron (hydr)oxide minerals (ferrihydrite and goethite) and different types of organic matter coatings (bacteria and humic substances). Secondly, we investigate the additive vs. non-additive nature of Cu adsorption to this range of composites in order to provide insight into Cu adsorption behaviour in natural environments where iron (hydr)oxides are coated with organic matter.

2. MATERIALS AND METHODS

2.1. Ferrihydrite, goethite and humic acid preparation and characterisation

Ferrihydrite (Fh) was prepared following the method of Schwertmann and Cornell (2000) for the precipitation of 2-line ferrihydrite via hydrolysis of Fe(III) salt solution. Goethite (Gt) was synthesized following a similar procedure to that described by Atkinson et al. (1967). Briefly, Fh was prepared by rapid hydrolysis of 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$ (aq) with 1 M NaOH at pH 7, while Gt was prepared by hydrolysis of 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$ (aq) with 5 M NaOH and the obtained precipitate was aged for 72 h at 60 ºC. Both Fh and Gt were washed several times over a week in equivalent volumes of 18.2 MΩ·cm MilliQ water, after which Fh was stored as a slurry at 4ºC, and Gt was freeze-dried, following standard protocols to maintain mineralogical integrity (Schwertmann and Cornell, 2000). Plastic labware and AR grade reagents were used throughout the preparations.

Mineral identity and purity of the precipitates was confirmed by X-ray powder diffraction (XRD) using a Bruker D8 Advance powder diffractometer and Cu–Kα radiation (λ = 1.5406 Å). The BET surface area of the precipitates was determined in triplicate using a Micromeritics Gemini V surface area analyser, with samples dried and degassed at room temperature for 24 h using N_2 (g) (<1 ppm CO_2 (g)). We report Fh and Gt surface areas of 300 ± 12 and 103 ± 3 m^2/g, respectively, which are in good agreement with literature values (Schwertmann and Cornell, 2000).

Humic acid (HA) was obtained from an ombrotrophic peat soil in Galicia (NW Spain, 43° 28′ 5.10″ N, 7° 32′ 6.53″ W) (López et al., 2011). Preparation and characterisation of the HA is reported in López et al. (2012). Briefly, the soil was acid-washed to remove inorganic components following Smith et al. (2004), and then HA was extracted following Swift (1996). Peat samples in the same geographical region are reported to contain 0.001 – 0.004 wt% Cu (Olid et al., 2010).

2.2. Organo-mineral composite preparation and characterisation

Five Fh and one Gt organo-mineral composites with different wt% adsorbed C were prepared following the method suggested by Iglesias et al. (2010a, b). Briefly, Fh slurries and Gt dry powder were prepared as mineral suspensions in distilled water and were then amended with 0.1 M $NaNO_3$ or KCl, respectively, and concentrations of HA ranging between 40 and 1700 mg/L were added to obtain final solid concentrations between 4-8 g/L. Low pH values favour HA adsorption onto iron (hydr)oxides (Weng et al., 2006; Xiong et al., 2015), thus the pH was adjusted to 4.0 by addition of 0.1-0.2 M HCl. The resulting slurries were shaken for 7 days after which they were centrifuged at 12000 rpm for 10-20 minutes (Centronic BL-II). The composites were washed with distilled water until the presence of HA in the supernatant was negligible, as determined by UV-Vis performed at 280 nm. The Fh composites were stored as a slurry at 4ºC, and the Gt composite was freeze-dried. The BET surface area of the precipitates was determined as above. The C contents of the Fh and Gt composites were determined with a Eurovector EA 3000 series combustion analyser, and a LECO CHN-1000 analyser, respectively. The five Fh composites and one Gt composite contained 2, 5, 8, 12, 16 and 7 wt% C, respectively, and are hereafter referred to as Fh_HA_2wt%C, Fh_HA_5wt%C Fh_HA_8wt%C, Fh_HA_12wt%C, Fh_HA_16wt%C and Gt_HA_7wt%C, respectively. The BET surface area of the precipitates was determined as above, and we report surface areas for the Fh organo-mineral composites with 2, 5, 8, 12 and 16wt% C as 254 ± 9, 214 ± 9, 154 ± 8, 104 ± 7 and 36 ± 3 m^2/g, respectively, and the Gt organo-mineral composite with 7wt% C as 63 ± 4 m^2/g. These 1-sigma errors are larger than those generated for the end-member Fh and Gt, and this likely reflects a degree of heterogeneity in the spatial association of the HA with the mineral particles, where organic matter coatings on mineral particles are well known to be heterogeneous (e.g., Mayer, 1999).

2.3. Cu adsorption experiments

Adsorption experiments were conducted following Moon and Peacock (2012, 2013) using AR grade reagents and 18.2 MΩ·cm MilliQ water. pH measurements were calibrated to ± 0.05 pH units using Whatman NBS grade buffers. Adsorption pH edges were prepared from pH ~ 3 – 8 so that adsorbents contained 0.7wt% Cu at 100% adsorption. Briefly, we prepared a $Cu(NO_3)_2{\cdot}3H_2O$ stock solution at 2.09 x 10^{-3} mol/L and a $NaNO_3$ background electrolyte at 0.1 M, after which adsorption samples were prepared by suspending 0.02 g dry weight of adsorbent in 29 mL of background electrolyte, and then amending with 1 mL of Cu stock solution to give a total volume of 30 mL, a solid-solution ratio of 0.67 g/L and a total Cu concentration of 7.0 x 10^{-5} mol/L. The resulting suspensions were shaken and the pH was measured while stirring, and adjusted by dropwise addition of either dilute HNO_3 or NaOH. Samples were then shaken continuously for 48 h to ensure equilibrium (Saito et al., 2005; Zhu et al., 2010), readjusting the pH when necessary to keep it constant at ± 0.1 pH units of the set pH value (total acid or base addition did not exceed 1 mL). At the end of the experiments the solids were separated from the supernatants by centrifugation (4000 rpm for 10 min), obtaining an adsorption sample (thick paste) for spectroscopic analysis and a clear supernatant for determination of total Cu concentration. Supernatants were filtered using 0.02 μm polycarbonate membrane filters, acidified with 1 % HNO_3 and analysed for Cu by inductively coupled plasma mass spectrometry (ICPMS). All the adsorption experiments were performed in triplicate.

The data for the adsorption of Cu to Fh was taken from Moon and Peacock (2013), where adsorption pH edges were performed at 0.7 and 2.2 wt% Cu. In this work we prepared adsorption pH edges for Gt at 0.7 and 0.2 wt% Cu, HA at 0.7 wt% Cu, and the Fh organo-mineral composites with 2, 5, 8, 12 and 16 wt% C, and Gt_HA_7wt%C, all at 0.7 wt% Cu (wt% Cu all given for 100 % adsorption). EXAFS data for Fh was taken from Moon and Peacock (2012) where EXAFS was performed on a specific sample at pH 6.25 (100 % Cu adsorbed). For Gt and HA, EXAFS was performed here on specific samples at pH 6 and pH 5, respectively (each 100 % Cu adsorbed). These samples are referred to hereafter as Fh_0.7wt%Cu_pH6.25, Gt_0.7wt%Cu_pH6 and HA_0.7wt%Cu_pH5. For the Fh_HA_8wt%C, Fh_HA_12wt%C and Gt_HA_7wt%C organo-mineral composites EXAFS was performed here at pH 4.3, 5 and 6 (representing a range of wt% Cu adsorbed). These samples are referred to hereafter as Fh_HA_8wt%C_0.7wt%Cu_pH4.3, Fh_HA_12wt%C_0.7wt%Cu_pH4.3 and Gt_HA_7wt%C_0.7wt%Cu_pH4.3 (or pH 5 / pH 6 as appropriate).

Experimental solution speciation was calculated with PHREEQC (Parkhurst and Appelo, 1999) using the MINTEQ.V4 database (Charlton and Parkhurst, 2002) and is shown in Fig. S1 as a function of pH. Until pH ~7 Cu speciation is dominated by Cu^{2+} (aq), while after pH ~7 $Cu(OH)_2$ (aq) becomes the dominant hydrolysis product and after pH ~8 precipitation of $Cu(OH)_2$ (s) accounts for ~20 % of the Cu total. In our adsorption experiments Cu therefore principally adsorbes as Cu^{2+} (aq).

2.4. X-ray absorption spectroscopy

2.4.1. EXAFS data collection

EXAFS standards for hydrated Cu, Cu-phosphoryl and Cu-carboxyl coordination environments are represented by solutions of Cu-perchlorate, Cu-phosphate and Cu-acetate, respectively, and were collected in Moon and Peacock (2011). In our Cu-phosphoryl and Cu-carboxyl solutions Cu is complexed with either P or C, respectively (where the calculated average number of ligands (either P or C) bound to the Cu ion is 0.9, with solution speciation determined with PHREEQC (Parkhurst and Appelo, 1999) using the MINTEQ.V4 database (Charlton and Parkhurst, 2002)) (Moon and Peacock, 2011). EXAFS of Fh_0.7wt%Cu_pH6.25 was collected in Moon and Peacock (2012), while data for Gt_0.7wt%Cu_pH6 and HA_0.7wt%Cu_pH5, and the Fh_HA_8wt%C_0.7wt%Cu, Fh_HA_12wt%C_0.7wt%Cu and Gt_HA_7wt%C_0.7wt%Cu organic-mineral composites at pH 4.3, 5 and 6 were collected here at the Cu K-edge (8.979 keV) at Diamond Light Source Ltd., UK, Beamlime B18. The data for Fh, Gt and HA were used as model samples. During data collection, storage ring energy was 3.0 GeV and the beam current was approximately 250 mA. EXAFS spectra were collected in fluorescence mode using a Ge 30-element detector. Before data collection, a series of XANES and EXAFS scans on test samples were performed to monitor potential photo reduction and X-ray beam damage on the sample. Test scans indicated no photo-reduction or drying of the adsorption sample wet pastes after 25 EXAFS scans to $k = 12$ Å^{-1}. Adsorption samples were presented to the X-ray beam as a thick paste held in a 2 mm-thick Teflon slide with a 4 x 10 mm sample slot. Small sheets of 250 µm-thick Mylar were placed either side of the Teflon slide and sealed with a small amount of vacuum grease to hold the pastes in place and prevent drying. Energy calibration was achieved by assigning the first inflection point of Au (L3) foil to 11.919 keV.

2.4.2. EXAFS data analysis

EXAFS data reduction was performed using ATHENA (Ravel and Newville, 2005) and the Cu spectra were fit using DL_EXCURV (Tomic et al., 2004). Spectra were fit in k-space over 3-12 Å^{-1}, and the fitting included full multiple scattering as coded in EXCURV98 (Binsted, 1998). Multiple scattering calculations require specification of the full three-dimensional structure of the Cu coordination environment (i.e., bond angles in addition to bond lengths). This was done using hypothetical model clusters with C1 symmetry (Fig. S2). The number of independent data points (N_{ind}) was determined using Stern's rule (Stern, 1993) as $2\Delta k\Delta R/\pi + 1$ (Booth and Hu, 2009) where Δk and ΔR are the range in k- and R-space actually fitted; as such, $N_{ind} = 16$. The fits for the hydrated Cu and Cu-phosphoryl solution standards were generated in Moon and Peacock (2011) by refinement of clusters representing these different coordination environments. The fit to the Cu-carboxyl solution standard is updated here using a modified model cluster to that presented in Moon and Peacock (2011) that is consistent with the immediate coordination environment of Cu bound to carboxyl ligands in a monodentate or chelated ring configuration. Briefly, in our Cu-carboxyl solution standard Cu is complexed to carboxyl ligands in a monodentate configuration but in natural humic substances recent work shows that Cu is most likely complexed to carboxyl ligands in a more complex chelated ring structure (Karlsson et al., 2006; Manceau and Matynia, 2010). Both monodentate and chelated ring configurations however, have very similar immediate Cu coordination environments that result in Cu-C distances between ~2.7 and 3.3 Å (e.g., for monodenate: Koizumi et al., 1963; Cingi et al., 1977; Hoang and Valach, 1992; for 5- and 6-membered chelated rings: Lenstra and Kataeva, 2001; Zhang, 2007), and a shoulder feature at ~6 Å^{-1} which manifests in the Fourier transform at ~4 Å (e.g., Karlsson et al., 2006; Manceau and Matynia, 2010; Moon and Peacock, 2011). This shoulder feature results from multiple scattering associated with the co-linear arrangement of the Cu, C and non-bonding O of the ≡RCOO(H) groups in either monodentate or chelated ring configuration (Karlsson et al., 2006; Manceau and Matynia, 2010; Moon and Peacock, 2011). As such, despite the fact that our Cu-carboxyl solution standard is relatively simple, it reproduces the essential features of Cu-carboxyl complexation reported for natural humic substances. The fit to the HA_0.7wt%Cu_pH5 model sample was then generated here by refinement of the optimised Cu-carboxyl solution standard cluster (with 15 refined parameters: Fermi energy (EF), 6 Cu–O distances, 1 Cu–C distance, and 7 Debye-Waller factors (DWF's)). The fits to the Fh_0.7wt%Cu_pH6.25 model sample were generated in Moon and Peacock (2012) and to the Gt_0.7wt%Cu_pH6 model sample were generated here by refinement of clusters representing a range of possible Cu coordination environments, including bidentate edge-sharing (with 13 refined parameters: EF, 4 Cu–O distances, 1 Cu–Fe distance, 5 DWF's, the coordination number for the Fe atom, and the theta bond angle for the Fe atom) and bidentate corner-sharing (with 15 refined parameters: EF, 4 Cu–O distances, 2 Cu–Fe distance, 6 DWF's, the coordination number for the Fe atoms, and the theta bond angle for the Fe atoms). Fits to the organo-mineral composite samples at pH 4.3 were generated here by refinement of the optimised HA_0.7wt%Cu_pH5 model sample, while fits to the organo-mineral composite samples at pH 5 and 6 were generated here by linear combination of the optimised HA_0.7wt%Cu_pH5 and either Fh_0.7wt%Cu_pH6.25 or Gt_0.7wt%Cu_pH6 model samples as coded in EXCURV98. The linear combination fit was performed over the k-range 3-12 Å^{-1} with a linear combination of the k^3-weighted $\chi(k)$ for the two appropriate clusters. In the linear combination, only the correction to the EF applied in ATHENA and relative site occupancies were optimised.

Fit quality was assessed using the EXAFS R-factor (as coded in EXCURV98) and the EXAFS Fit Index (as coded in Binsted, 1998), with an absolute index of goodness of fit given by the reduced χ^2 function, where the reduced χ^2 values provide a measure of the suitability of single site models vs. multiple site models for a given experimental spectrum. Typical errors associated with EXAFS modelling over the k-range used here are 15 % and 25 % for first and second shell coordination numbers, respectively, ±0.02 and 0.05 Å for first and second shell distances, respectively, and 15 % and 25 % for first and second shell DWF's, respectively (Binsted, 1998). For the linear combination fits, the error associated with the optimised site occupancies was evaluated by assuming that manual changes to the optimised site occupancies were not significant until they generated >10 % increase in the Fit Index, equivalent in all cases to >10 % increase in the reduced χ^2 function (Peacock, 2009).

2.5. Surface complexation modelling

The adsorption behaviour of Cu on Fh, Gt and HA and the organo-mineral composites was fit to a thermodynamic surface complexation model using the program EQLFOR (Sherman et al., 2008; Moon and Peacock, 2013). The fit to Fh was taken from Moon and Peacock (2013). The composites were fit adopting a linear component additivity approach where we combined the end-member models for Cu-adsorbed humic acid and either Cu-adsorbed Fh or Gt. In the end-member models and the combined composite models, the basic Stern model (BSM) (Westall and Hohl, 1980) was used to account for the surface electrostatics. Activity corrections to the stability constants for aqueous species were made using the Davies equation. Detailed discussion on the development of the Fh model is available in Moon and Peacock (2013), and for the Gt, HA and organo-mineral composite models in Section 3.3 below.

3. RESULTS AND DISCUSSION

3.1. Copper adsorption on iron (hydr)oxides, humic acid and organo-mineral composites

The adsorption of Cu to Fh, Gt and HA is plotted in Fig. 1 as a function of pH and for each adsorbent we observe a sigmoid adsorption edge that is in good agreement with previous studies of Cu adsorption onto iron (hydr)oxides (e.g., Dzombak and Morel, 1990; Peacock and Sherman, 2004) and humic substances (Liu and González, 2000; Li et al., 2010). The adsorption of Cu to the organo-mineral composites is plotted in Fig. 2 as a function of pH and although we observe a generally sigmoidal shape, the adsorption edges are intermediate between the end-member iron (hydr)oxide and HA, with significantly enhanced adsorption in the low-mid pH regime. In particular, at pH ~3.5, Fh and Gt show no adsorption while Fh and Gt composites show ~10 % and ~40 % adsorption, respectively (Fig. 2). This macroscopic adsorption behaviour is similar to that reported for other iron (hydr)oxide organo-mineral composites, where Cu adsorption to iron (hydr)oxides that posses a surface coating of sorbed humic substances or bacterial cells is enhanced in the low-mid pH regime, and is attributed to the presence of additional binding sites associated with the organic fraction and/or new high-affinity sites created when the organics adsorb to the (hydr)oxide surfaces (e.g., Tipping et al., 1983; Murphy and Zachara, 1995; Alcacio et al., 2001; Christl and Kretzschmar, 2001; Buerge-Weirich et al., 2003; Flogeac et al., 2004; Saito et al., 2005; Jönsson et al., 2006; Weng et al., 2008; Zhu et al., 2010; Moon and Peacock, 2012, 2013). In particular however, Fig. 3 shows the adsorption of Cu to the Fh-HA composites with 2, 5, 8, 12 and 16wt% C together with the adsorption of Cu on Fh-bacteria (Bacillus subtilis) composites taken from Moon and Peacock (2012, 2013), where, other than the different adsorbents, the experimental adsorption conditions are identical. Comparing the data for Cu adsorption on these different types of Fh organo-mineral composites it is apparent that the macroscopic Cu adsorption behaviour appears to be independent of the nature of the organic matter (HA or bacteria) and the wt% C present in the composite (with wt% C ranging from 2 to 32 wt%). To the authors' knowledge, this is the first time that this commonality in Cu macroscopic adsorption behaviour on several types of Fh organo-mineral composites has been observed, and it suggests there is a universal adsorption behaviour for Cu in these composite adsorption systems.

3.2. XAS of Cu adsorption on iron (hydr)oxides, humic acid and organo-mineral composites

The EXAFS data for the hydrated Cu, Cu-phosphoryl and Cu-carboxyl solution standards, and for the adsorption of Cu to the Fh, Gt and HA model samples, and the Fh and Gt organo-mineral composites is shown in Fig. 4 (for Fh) and Fig. 5 (for Gt). Fitted parameters for the model samples and organo-mineral composites are shown in Table 1.

3.2.1. Solution standards and end-member ferrihydrite, goethite and humic acid model samples

The data and fits for the hydrated Cu and Cu-phosphoryl solution standards and the Fh model sample are taken from Moon and Peacock (2011) and Moon and Peacock (2012), respectively, while the fit to the Cu-carboxyl solution standard is updated here using the modified model cluster for the immediate coordination environment of Cu bound to carboxyl ligands in a monodentate or chelated ring configuration. Briefly, in the hydrated Cu solution standard the Cu immediate coordination environment consists of four equatorial O's in square planar configuration and one axial O (e.g., Pasquarello et al., 2001; Benfatto et al., 2002; Frank et al., 2009; Moon and Peacock, 2011). While in the Cu-phosphoryl and Cu-carboxyl solutions standards there are additional P or C ligands representing Cu complexed to phosphoryl and carboxyl ligands, respectively, with the Cu immediate coordination environment consistent with monodentate configuration (Cu-phosphoryl), and monodentate or chelate configurations (Cu-carboxyl), respectively. The Fh model sample represents Cu adsorbed to Fh via a bidentate edge-sharing complex, and consists of 4.0 O at 1.90-2.03 Å and 1 Fe at 3.01 Å (Moon and Peacock, 2012).

The Gt model sample is fit following the same procedure as in Moon and Peacock (2012) for Cu adsorbed to Fh. Several model clusters representing different Cu coordination environments were tested, including bidentate edge-sharing and bidentate corner-sharing surface complexes (Section 2.4.2). The best fit to the data is provided by refinement of the bidentate corner-sharing cluster, resulting in 4 O at 1.90-2.00 Å and 2 Fe at 3.03 and 3.28 Å (Table 1). The fit is in good agreement with previous studies of Cu adsorption on Gt (e.g., Peacock and Sherman, 2004) and cannot be statistically improved by including the formation of any other Cu adsorption complex.

The HA model sample is fit following the same procedure as in Moon and Peacock (2011) for Cu adsorbed to bacteria. We initially made a visual comparison of the HA data in k- and R-space (magnitude and imaginary parts) with the solution standard data, and we observe significant visual similarities with the Cu-carboxyl solution standard, and a significant misfit with the hydrated Cu and Cu-phosphoryl solution standards (Fig. 4). In particular, the HA spectrum shows a very similar structure to the Cu-carboxyl spectrum at k ~4-5 $Å^{-1}$ and ~6-7 $Å^{-1}$ and at R ~4 Å (Fig. 4), consistent with multiple scattering associated with the co-linear arrangement of the Cu, C and non-bonding O of the ≡RCOO(H) groups in either monodentate or chelated ring configuration (Karlsson et al., 2006; Manceau and Matynia, 2010; Moon and Peacock, 2011). The HA spectrum also displays a prominent peak in the Fourier transform at ~2.9 Å, which matches the Cu-carboxyl solution standard, and is consistent with the Cu-C distance in monodentate or chelated ring Cu-carboxyl compounds. The best fit to the HA model sample is provided by refinement of the Cu-carboxyl solution standard cluster, resulting in 4 O at 1.92-2.00 Å, an axial O at 2.31 Å, 1 C at 2.79 Å and the non-bonding O of the ≡RCOO(H) group at 4.12 Å (Table 1). This fit is in excellent agreement with Cu adsorbed to Bacillus subtilis bacteria (Moon and Peacock, 2011), and both the Cu-C distance and the orientation of the ≡RCOO(H) group with respect to the square planar $(CuO_4H_n)^{n-6}$ ion (Fig. S2) are also in good agreement with EXAFS studies of Cu sorbed to natural humic substances where Cu is complexed with carboxyl ligands that form 5- or 6-membered chelate rings (e.g., Karlsson et al., 2006; Manceau and Matinya, 2010). Since carboxyl ligands comprise the majority of reactive sites in humic substances below pH 7 and are well known to form a huge array of synthetic complexes with Cu, the strongest bonds between humics and Cu are expected to occur via the carboxyl groups (Sposito et al., 1979; Boyd et al., 1981). Some empirical modelling studies however, suggest that phenolic ligands present in HA are also important, and possibly provide higher affinity sites for Cu complexation (e.g., Tipping 1998; Milne et al., 2003). Whilst we cannot rule out the minor presence of Cu-phenol complexation in our HA model sample, our EXAFS data display the unique characteristics of Cu-carboxyl complexation with the presence of the multiple scattering features associated with the co-linear arrangement of the Cu, C and non-bonding O of the ≡RCOO(H) groups.

3.2.2. Ferrihydrite and goethite organo-mineral composites

The Fh and Gt organo-mineral composite samples are fit following the same procedure as in Moon and Peacock (2012) for Cu adsorbed to Fh-bacteria composites, where the composites can be visually compared to the solution standards and model samples to determine whether the composite spectra are the result of a single or multiple Cu coordination environment (Fig. 4 and 5).

In the first instance we observe significant visual similarities between our HA model sample and the Fh and Gt composites prepared at pH 4.3; notably the composite samples display the similar weak shoulder feature at k ~6 Å^{-1}, and the peaks in the Fourier transform at ~2.9 Å and ~4 Å, attributable to complexation between Cu and ≡RCOO(H) functional groups (Section 3.2.1.). Importantly, these spectra do not appear to display a peak in the Fourier transform at ~3 Å, attributable to complexation between Cu and Fe (Section 3.2.1.). These spectra are therefore likely the result of Cu complexation in a single coordination environment in which Cu is adsorbed to carboxyl functional groups present on the HA fraction of the composites. Accordingly, the best fit to the Fh_HA_8wt%C_0.7wt%Cu_pH4.3, Fh_HA_12wt%C_0.7wt%Cu_pH4.3 and Gt_HA_7wt%C_0.7wt%Cu_pH4.3 spectra are provided by minimal refinement of the HA model sample cluster, resulting in 4 O at 1.92-2.00 Å, an axial O at 2.34-2.35 Å, 1 C at 2.79 Å and the non-bonding O of the ≡RCOO(H) group at 4.09-4.11 Å (Table 1). The fits cannot be statistically improved by including the formation of any other Cu adsorption complex, either in addition to carboxyl complexation on the HA fraction of the composite, or also including complexation on the mineral fraction of the composite.

The remaining Fh and Gt composites prepared at pH 5 and 6 display features common to both the HA and Fh or Gt model samples; notably the weak shoulder feature at k ~6 Å^{-1}, which diminishes in prominence from the composites prepared at pH 4.3, the peaks in the Fourier transform at ~2.9 Å and ~4 Å, but in addition a small peak in the Fourier transform at ~3 Å. This latter peak is absent in the composites prepared at pH 4.3 and suggests the presence of Cu complexation to Fe. These spectra are therefore likely the result of Cu complexation in a multiple coordination environment in which Cu is adsorbed to carboxyl groups of the HA fraction and ≡Fe(OH) groups of the mineral fraction in the composites. The best fit to these spectra were generated via a linear combination of the model spectra for Cu adsorption to HA and Fh or Gt (Table 1). The binding of Cu to carboxyl or phenolic groups present on iron (hydr)oxide organo-mineral composite surfaces has also been observed for Gt-humic composites (Alcacio et al., 2001) and natural soil particles with organic matter coatings (Flogeac et al., 2004; Weng et al., 2008; Qu et al., 2017). Our work here on Cu adsorption to Fh and Gt composites made with HA, combined with previous work on Cu adsorption to Fh composites made with bacteria (Moon and Peacock, 2012), Cu adsorption to bacteria (Moon and Peacock, 2011), and Cu adsorption to humic substances (e.g., Davies et al., 1997; Xia et al., 1997; Karlsson et al., 2006; Strawn and Baker, 2008; Manceau and Matynia, 2010; Kulikowska et al., 2015; Yang et al., 2015; Qi et al., 2017) further demonstrates the universal importance of Cu-carboxyl binding for Cu mobility and fate in natural environments (Moon and Peacock, 2012).

3.3. Surface complexation models for Cu adsorption on iron (hydr)oxides, humic acid and organo-mineral composites

We develop surface complexation models for the adsorption of Cu on our Fh, Gt and HA, and our Fh and Gt organo-mineral composites, that are consistent with the molecular mechanisms of Cu adsorption as determined by EXAFS. The organo-mineral models are then used to probe the nature of the Cu adsorption behaviour on the organo-mineral composites. Through comparison with previous work on the adsorption of Cu to Fh-bacteria composites by Moon and Peacock (2013) we provide an overarching insight into the general adsorption behaviour of Cu on iron (hydr)oxide organo-mineral composites.

3.3.1. End-member Cu surface complexation models

The model for Cu adsorption on Fh is taken from Moon and Peacock (2013), while the models for Cu adsorption on Gt and HA are developed here based on the model for Cu adsorption on Fh by Moon and Peacock (2013), and the model for Cu adsorption on bacteria by Moon and Peacock (2011), respectively; the model input parameters are reported here in Table 2 and the model fits to the data are shown in Fig. 1. Briefly, we use the Basic Stern Model (BSM) (Westall and Hohl, 1980) to model the adsorbent electrostatics, with a 3-site 1 pK formalism for the protonation of the Fh surface (consisting of singly coordinated $\equiv FeOH^{-0.5}$ sites that are split into those that are able to adsorb cations in edge-sharing $\equiv FeOH^{-0.5}(e)$ and corner-sharing $\equiv FeOH^{-0.5}(c)$ configuration, and triply coordinated $\equiv Fe_3O^{-0.5}$ sites (e.g., Hiemstra et al., 1989; Hiemstra and van Riemsdijk, 2009)), a 2-site 1 pK formalism for the protonation of the Gt surface (consisting of singly coordinated $\equiv FeOH^{-0.5}$ sites, and triply coordinated $\equiv Fe_3O^{-0.5}$ sites (e.g., Hiemstra et al., 1996; Antelo et al., 2005), and a 2-site 1 pK formalism for the protonation of the HA (involving carboxylic $\equiv RCOO^-$ and phenolic $\equiv RO^-$ sites) where the stability constants for the protonation of these sites and the site densities are constrained using the NICA-Donnan model (Kinniburgh et al., 1999), calibrated on multiple data sets (López et al. (2012). The input parameters for the models are generated by fitting potentiometric titration data for the adsorbent acid-base behaviour, or determined via direct measurement of the adsorbent physiochemical characteristics, and are detailed in Moon and Peacock (2013) for Fh, Otero-Fariña

(2017) for Gt, and López et al. (2012) for HA; the input parameters are summarised here in Table 2. The adsorption data are then fit by iteration of the log K for the complexation reaction that represents the formation of the Cu-Fh, -Gt or -HA complexes as identified by EXAFS. The Fh and Gt adsorption data for Fh_0.7wt%Cu and Fh_2.2wt%Cu, and Gt_0.2wt%Cu and Gt_0.7wt%Cu, respectively, were fit simultaneously. The best fit log K values for the adsorption of Cu to Fh via the bidentate edge-sharing surface complex as determined via EXAFS is log K_{Fh} 8.61 (Moon and Peacock, 2013), to Gt via the bidentate corner-sharing surface complex as determined by EXAFS is log K_{Gt} 12.93, and to HA via the carboxyl complex as determined by EXAFS is log K_{HA} 2.49. The sensitivity of the models to the input parameters is determined via a sensitivity analysis in which these parameters are varied over a full range of reasonable experimental or theoretical values (Moon and Peacock, 2011, 2013); details of the sensitivity analysis are provided in the SI. This procedure results in a variation of ±0.9, ±0.7 and ±1.0 log units for the fitted Fh, Gt and HA log K's, respectively. This analysis provides a rigorous estimate for the range over which the log K values may vary due to inherent uncertainties in the parameterisation of the Fh, Gt and HA adsorption properties in the models. The log K values of 8.61±0.9 (Moon and Peacock, 2013), 12.93±0.7 and 2.49±1.0 for the adsorption of Cu to Fh, Gt and HA, respectively, are therefore used in the work here.

3.3.2. Organo-mineral surface complexation models

Our adsorption edge data shows that the adsorption of Cu on our organo-mineral composites is intermediate between the end-member iron (hydr)oxide and HA (Fig. 2). Our EXAFS data shows that Cu adsorption onto the composites occurs via the same molecular mechanisms as onto the isolated, end-member composite fractions (Fig. 4 and 5). This suggests that the Cu adsorption behaviour of the composites shows a degree of additivity, where the sum of the individual end-member adsorptivities on isolated Fh and HA, or Gt and HA, equals that of the composites. As such we use a component additivity approach to fit the Fh and Gt composite adsorption data, in which the models for Cu adsorption to Fh and HA, or Gt and HA, respectively, are linearly combined to produce a single adsorption model for each composite (Moon and Peacock, 2013); the model input parameters are reported here in Table 3 and the model fits to the data are shown in Fig. 6 and 7. As the additive combination of the Fh and HA, or Gt and HA models, the Fh and Gt composite models use the BSM (Westall and Hohl, 1980) to model the composite electrostatics, and for the Fh composite adopt a 5-site 1 pK formalism (consisting of the 3 Fe sites, $\equiv FeOH^{-0.5}$(e), $\equiv FeOH^{-0.5}$(c) and $\equiv Fe_3O^{-0.5}$, plus the

2 HA sites, ≡RCOO$^-$ and ≡RO$^-$), while for the Gt composite adopt a 4-site 1 pK formalism (consisting of the 2 Fe sites, ≡FeOH$^{-0.5}$ and ≡Fe$_3$O$^{-0.5}$, plus the 2 HA sites, ≡RCOO$^-$ and ≡RO$^-$). In this component additivity approach log K's for the protonation and binding of electrolyte ions to these sites, and absolute site densities, are fixed to the values of the Fh or Gt and HA models. Operational site densities for each site, and a surface area and Stern layer capacitance for each composite, are then calculated from the end-member values weighted to the appropriate Fh:HA or Gt:HA mass ratio (Table 3). In the first instance the adsorption of Cu to the composites is modelled using the exact best-fit log K values derived for the Fh and HA, or Gt and HA, adsorbents (Fig. 6a and 7a). The end-member log K values are then iterated whilst keeping all other parameters constant (Fig. 6b and 7b). If the composites behave in an additive manner then the optimised log K values should fall within the uncertainties on the end-member values. In addition, the predicted distribution of the Cu between the end-member fractions in the composites should reflect the Cu distributions as directly determined by the EXAFS.

3.3.3. Ferrihydrite organo-mineral composite surface complexation model

The fits to the Fh organo-mineral composites with 2, 5, 8, 12 and 16 wt% C using the exact end-member log K's for Cu adsorption on Fh (log K_{Fh} 8.61) and HA (log K_{HA} 2.49) are shown in Fig. 6a, and the fits after iterating the end-member log K's are shown in Fig. 6b. The fits using the exact end-member log K's somewhat underestimate total Cu adsorption across almost the entire pH regime for all of the Fh composites, i.e., adsorption onto the composites is more than expected assuming strict additivity (Fig. 6a). Iteration of the end-member log K's however, results in optimised log K's that are within the uncertainty on the end-member values (log K_{Fh} 8.61±0.9 and log K_{HA} 2.49±1.0; see section 3.3.1), with an average log K_{Fh} 9.27 and log K_{HA} 3.31. These optimised log K's produce very good fits for all the Fh composites, in which the models are able to approximate the total Cu adsorbed (Fig. 6b), and also the distribution of the adsorbed Cu between the Fh and HA fractions (Table 4). As such our Fh organo-mineral composites can be modelled assuming a component additivity approach. This adsorption behaviour is in excellent agreement with some of the Fh-bacteria composites investigated by Moon and Peacock (2012, 2013). The Fh-HA composites here, and the similarly behaving Fh-bacteria composites in the previous work, all represent composite adsorption systems in which the composites are comprised predominantly of the mineral fraction (where our Fh composites with 2, 5, 8, 12 and 16 wt% C are composed of ~96, 90, 84, 77 and 69 % mineral, respectively, and the similarly behaving Fh-bacteria composites are composed of ~82 and 65 % mineral) (Fig. 3). Moon and Peacock (2013) show that Fh-bacteria composites comprised predominantly of the bacteria fraction (with ~67 % bacteria) cannot be modelled in a component additivity approach, and thus do not behave additively. These authors suggest that the adsorption behaviour of Fh-bacteria composites is determined by the mineral:bacteria mass ratio in the composites, with composites composed predominantly of mineral behaving additively and predominantly of bacteria behaving non-additively (Moon and Peacock, 2013). This behaviour is attributed to a change in the surface charge of one or both of the composite fractions as a result of their close spatial association (e.g., Vermeer et al., 1999; Ferris et al., 1999; Christl and Kretzschmar, 2001), that is more pronounced with a greater fraction of bacteria (Moon and Peacock, 2013). It is well known that when organics are associated with iron (hydr)oxide surfaces the positive charge of the mineral surface is significantly reduced (e.g., Tipping and Cooke, 1982; Hunter, 1983; Beckett and Le, 1990; Day et al., 1994; Verneer and Koopal, 1998; Wang et al., 2015; Otero-Fariña et al., 2017). As a result these composites can display enhanced cation adsorption to the mineral fraction, compared to the isolated mineral counterpart (e.g., Vermeer et al., 1999). When a composite is composed predominantly of the mineral fraction then the electrostatic effect is mild, and a somewhat enhanced adsorption, underestimated by a strictly additive approach as seen for the Fh-bacteria composites, can be accommodated by the uncertainties inherently present in the parameterisation of the mineral and bacteria adsorption properties in the models (Moon and Peacock, 2013). On the other hand when a composite is composed predominantly of bacteria then the effect is pronounced and the adsorption behaviour cannot be predicted in an additive approach (Moon and Peacock, 2013). Our work here on Fh composites made with HA, combined with the previous work on Fh composites made with bacteria (Moon and Peacock, 2013), points towards a universal adsorption behaviour for Fh organo-mineral composites, in which the mineral:organic mass ratio is a crucial parameter for determining Cu adsorption behaviour. Overall we show that Fh composites composed of humic or microbial organic matter and containing a wide range of organic mass ratios but where the mineral is the dominant composite fraction, possess additive Cu adsorption behaviour which can be predicted in a component additivity approach.

3.3.4. Goethite organo-mineral composite surface complexation model

The fit to the Gt organo-mineral composite with 7 wt% C using the exact end-member log K's for Cu adsorption on Gt (log K_{Fh} = 12.93) and HA (log K_{HA} = 2.49) is shown in Fig. 7a, and the fit after iterating the end-member log K's is shown in Fig. 7b. Similar to the Fh composites, the fit using the exact end-member log K's somewhat underestimates total Cu adsorption in the mid-upper pH regime, but significantly underestimates adsorption in the mid-lower pH regime, and in this region adsorption onto the composite is significantly more than expected assuming strict additivity (Fig. 7a). Iteration of the end-member log K's results in an optimised log K for the organic fraction that is outside the uncertainty on the end-member value (log K_{HA} = 2.49±1.0; see section 3.3.1) at log K_{HA} 4.86 and log K_{Gt} 12.10. These optimised log K's produce a very good fit to the Gt composite, in which the model is able to approximate the total Cu adsorbed (Fig. 7b), but the model fails to accurately predict the distribution of the adsorbed Cu between the Gt and HA fractions (Table 4). As such our Gt organo-mineral composite cannot be modelled assuming a component additivity approach. Given that this Gt composite is composed predominantly of the mineral fraction (~86 % mineral), the non-additive Cu adsorption behaviour is at odds with the additive behaviour of Fh composites similarly dominated by the mineral phase. This behaviour might be understood in light of the significant difference in surface area between Gt and Fh, where Gt and Fh as measured here, and generally in agreement with typical Gt and Fh surface areas, are ~103 and ~300 m^2/g, respectively (Section 2.1). With a significantly lower surface area, and for an approximately equivalent amount of HA, the HA surface loading on a Gt composite will be more than double that on a Fh composite (where, for example, Gt_HA_7wt%C and Fh_HA_8wt%C have 1.33 mg HA/m^2 and 0.52 mg HA/m^2, respectively). As such, in the mid-lower pH regime, where adsorption onto the HA fraction dominates, the Cu adsorption behaviour of our Gt composite will more closely resemble the adsorption of Cu onto isolated HA, and will not follow additive adsorption behaviour.

4. CONCLUSIONS

By combining our work with previous studies on Fh composites made with bacteria, we suggest there is a universal adsorption behaviour for Cu on Fh organo-mineral composites, in which the mineral:organic mass ratio is a crucial parameter for determining whether Cu uptake adheres to additivity. We show that in composites dominated by the mineral fraction, Cu adsorption behaviour is additive, where the sum of the adsorption on the individual end-member composite fractions equals that of the composite, while in composites dominated by the organic fraction, Cu adsorption behaviour is non-additive. For Fh composites dominated by the mineral fraction the Cu adsorption behaviour can be modelled in a component additivity approach. Overall we show that Fh composites composed of different types of organic matter and containing a wide range of organic mass ratios but where the mineral is the dominant composite fraction, possess additive Cu adsorption behaviour which can be predicted using a component additivity surface complexation model.

We also find that Cu-carboxyl binding plays an important role in the adsorption of Cu to HA and the HA fraction of Fh and Gt organo-mineral composites. Our work here combined with previous work on the adsorption of Cu to other types of iron (hydr)oxide organo-mineral composite, humic substances and bacteria, further demonstrates the universal importance of the carboxyl group for Cu adsorption, mobility and fate in natural environments.

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TABLE 2: Input parameters for the surface complexation models for Cu adsorbed to ferrihydrite (reproduced here from Moon and Peacock, 2013), goethite and humic acid.

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FIGURE 2: Adsorption of Cu to a) ferrihydrite, humic acid and ferrihydrite organo-mineral composites, and b) goethite, humic acid and goethite organo-mineral composite, as a function of pH. Symbols are data points, lines are model fits (data and fits for ferrihydrite taken from Moon and Peacock, 2013). In all cases X axis error bars are not visible as the standard deviation in pH is ≤0.1 pH units. For clarity Y axis error bars are not shown but in all cases the standard deviation in % Cu adsorbed is ≤5 %.

FIGURE 3: Adsorption of Cu to ferrihydrite, humic acid, Bacillus subtilis bacteria and ferrihydrite organo-mineral composites, made from humic acid and Bacillus subtilis bacteria. Symbols are data points, lines are model fits (data for Bacillus subtilis (B) and ferrihydrite-bacteria composites (Fh-B) are taken from Moon and Peacock, 2011; 2013, respectively). In all cases X axis error bars are not visible as the standard deviation in pH is ≤0.1 pH units. For clarity Y axis error bars are not shown but in all cases the standard deviation in % Cu adsorbed is ≤5 %.

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FIGURE 6: Component additivity approach surface complexation model fits for Cu adsorbed to ferrihydrite organo-mineral composites. a) Fits are those generated using the exact end-member log K_{CuHA} = 2.49 and log K_{CuFh} = 8.61. b) Fits are those generated by optimising the exact end-member log

K_{CuHA} = 3.31 and log K_{CuFh} = 9.27. Symbols are data points, lines are model fits where solid lines = total predicted Cu adsorbed, dotted lines = $\equiv RCOOCu^+$ and dashed lines = $\equiv (FeOH)_2Cu^+$. Error bars are calculated as the standard deviation in pH and % Cu sorbed of triplicate data sets. In all cases X axis error bars are not visible as the standard deviation in pH is ≤0.1 pH units. For clarity Y axis error bars are not shown but in all cases the standard deviation in % Cu adsorbed is ≤5 %.

FIGURE 7: Component additivity approach surface complexation model fits for Cu adsorbed to goethite organo-mineral composite. a) Fits are those generated using the exact end-member log K_{CuHA} = 2.49 and log K_{CuFh} = 12.93. b) Fits are those generated by optimising the exact end-member log K_{CuHA} = 4.86 and log K_{CuFh} = 12.10. Symbols are data points, lines are model fits where solid lines = total predicted Cu adsorbed, dotted lines = $\equiv RCOOCu^+$ and dashed lines = $\equiv (FeOH)_2Cu^+$. Error bars are calculated as the standard deviation in pH and % Cu sorbed of triplicate data sets. In all cases X axis error bars are not visible as the standard deviation in pH is ≤0.1 pH units. For clarity Y axis error bars are not shown but in all cases the standard deviation in % Cu adsorbed is ≤5 %.