Pb, Cu, and Zn Distributions at Humic Acid-Coated Metal-Oxide Surfaces

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Abstract

Mineral surfaces are often coated by natural organic matter (NOM), which has a major influence on metal-ion sorption and sequestration because of the abundance of binding sites in such coatings and the changes they cause in local nanoscale environments. The effects of NOM coatings on mineral surfaces are, however, still poorly understood at the molecular level due to the complexity of these systems. In this study, we have applied long-period x-ray standing wave-florescence yield (LP-XSW-FY) spectroscopy to measure the partitioning of naturally present Cu(II) (0.0226%), Zn(II) (0.009%), and Pb(II) (~0.0004%) between Elliott soil humic acid (ESHA) coatings and three model single-crystal metal-oxide substrates: α -Al₂O₃(0001), α -Al₂O₃(1-102), and α -Fe₂O₃(0001). The competitive sorption effects among these metal ions for binding sites in the ESHA coatings and on the metal-oxide surfaces were investigated as a function of reaction time, calcium content, and solution pH. Pb(II) ions present in the ESHA coatings were found to redistribute to reactive α -Al₂O₃ (1-102) and α -Fe₂O₃ (0001) surfaces after 3 hours of reaction (pH = 6.0, [Ca(II)] = 2 mM). Pb(II) partitioning onto these reactive metal-oxide surfaces increased with increasing reaction time (up to 7 d). In addition, the partitioning of Cu(II) and Zn(II) from the ESHA coating to the α -Fe₂O₃ (0001) substrate increased slightly with reaction time (2.4% and 3.7% for Cu(II) and Zn(II), respectively, after 3 hours and 6.4% and 7.7% for Cu(II) and Zn(II), respectively, after 72 hours of reaction time). However, no changes in the partitioning of Cu(II) and Zn(II) onto the α -Al₂O₃ (1-102) surface were observed with increasing reaction time, suggesting that these ions strongly complex with functional groups in the ESHA coatings. Similar results were obtained for Cu(II) and Zn(II) on the ESHA-coated α -Al₂O₃ (1-102) surfaces in samples without the addition of calcium. However, the amounts of Pb(II) mobilized from the ESHA coatings onto the α -Al₂O₃ (1-102) surfaces increased from 40% (no added Ca) to 58% (with 2 mM Ca) after 72 hours of reaction time, possibly due to displacement of Pb(II) by Ca(II) from binding sites in the ESHA coatings. In contrast, Pb(II), Cu(II), and Zn(II) present in the ESHA coatings were found to be unreactive with the α -Al₂O₃ (0001) surface. The observed reactivities of the three ESHA-coated metal-oxide surfaces with respect to metal-ion sorption are consistent with the trend observed for the uncoated metal-oxide surfaces: α -Fe₂O₃(0001) > α -Al₂O₃(1-102) > α -Al₂O₃(0001). In addition, Pb(II) partitioning onto α -Al₂O₃ (1-102) surfaces increased with increasing pH from 4.0 to 9.0 as a result of the increasing negative surface charge. These results show that intrinsic properties (nature of binding

sites, binding affinities, and surface charge) of the ESHA coatings and metal-oxide surfaces, as well as external parameters such as pH and competing ions, are key factors governing the distribution and speciation of metal ions at complex NOM/mineral interfaces.

1. INTRODUCTION

NOM is ubiquitous in terrestrial and aquatic ecosystems, and humic substances are the predominant species of NOM in water, soils, and sediments (Leenheer et al., 1994; Aiken and Cotsaris, 1995; Benedetti et al., 1995; Gu et al., 1996a; Kinniburgh et al., 1999; Tipping, 2002; Koopal et al., 2005). The properties and concentrations of humic substances vary significantly with source because they are heterogeneous mixtures of biochemical degradation products from plant and animal residues (Aiken and Cotsaris, 1995; Tipping, 2002). For example, the concentration of humic substances in groundwater can vary from 1 to 70 mg/L (Thurman et al., 1982; Herbert and Bertsch, 1995) as dissolved organic carbon (DOC), whereas the DOC concentration in surface waters can range from 0.5 to 100 mg/L with an average concentration of 5 mg/L; the DOC concentration in ocean water is found to be 1 mg/L at the surface and 0.5 mg/L at depth (Tipping, 2002). The content of humic substances in soils can vary from less than 1% in some sandy soils to essentially 100% in peats (Tipping, 2002). The effective concentration of humic substances (mass of humic matter per unit volume of soil water) can be as high as 60 g/L in B horizons of forest soils to 5 g/L in the typical marine sediment (Lofts et al., 2001; Tipping, 2002). These results show that humic substances can be present in very high concentrations in soils and sediments, and thus can potentially influence metal-ion distributions in natural environments (Tipping, 2002).

Humic substances are complex mixtures of organic macromolecules containing various reactive functional groups such as carboxylic (-COOH), phenolic (-OH), amino (-NHR, -NH₂), and thiol (-RS) (Tipping, 1993; Leenheer et al., 1994; Gu et al., 1996a; Gu et al., 1996b; Kinniburgh et al., 1999; Tipping, 2002; Koopal et al., 2005; van Riemsdijk et al., 2006; Rey-Castro et al., 2009). Anionic functional groups (e.g., carboxylic) introduce negative charges and have a strong affinity for positively charged mineral surfaces, and thus often partially coat fine-grained minerals such as the common metal-(oxy)hydroxide minerals in soils (Neihof and Loeb, 1974; Davis, 1984; Ransom et al., 1997; Au et al., 1999; Mayer, 1999; Bonneville et al., 2009;

Lalonde et al., 2012). Neihof and Loeb (1974) introduced the concept known as the “effective monolayer hypothesis”, which postulates that most particles in marine environments are coated by thin films (effective monolayers) of organic matter. This hypothesis led to the notion that adsorption properties of marine particles are controlled by organic coatings (Balistrieri et al., 1981; Davis, 1984), which was followed by the notion that most particles in soils and aquatic systems are coated by a thin organic film (Mayer, 1994; Au et al., 1999). However, Ransom et al. (1997) found that most organic matter and microbial coatings in continental margin sediments are patchy in distribution and discontinuously associated with clay minerals, thus refuting the effective monolayer hypothesis. In a subsequent study, Mayer (1999) concluded that less than 15% of particle surfaces are covered by organic matter in marine aluminosilicate sediments with low to moderate loadings of organic matter ($< 3 \text{ mg organic carbon/m}^2$). Mayer and Xing (2001) further suggested that the organic carbon content in B and C horizons of acidic soil samples is at the monolayer equivalent level ($\sim 1 \text{ mg organic carbon/m}^2$), whereas the organic carbon content in surficial A and O horizons exceeds that level. Soil organic matter is often closely associated with mineral surfaces (Mikutta et al., 2009; Lalonde et al., 2012). For example, Lalonde et al. (2012) reported that 21.5 ± 8.6 percent of organic carbon is directly bound to reactive iron-oxide phases in sediment samples from a wide range of depositional environments, suggesting that reactive iron-oxide phases serve as an “extremely efficient rusty sink” for organic carbon.

The presence of such organic coatings on mineral surfaces, even discontinuous patchy ones, could potentially induce steric and electrostatic changes that modify the physicochemical properties of colloidal mineral particles such as surface charge and colloidal stability, and substantially alter the sorptive capacity of metal-(oxy)hydroxide minerals (e.g., Davis, 1984; Tipping, 2002; Gu et al., 1996b). In addition, various reactive functional groups present in humic substances are known to form strong complexes with metal contaminants such as Cu, Zn, Pb, and Hg, making them potentially important environmental sorbents and a major influence on the fate and transport of metal contaminants in environmental systems (Benedetti et al., 1995; Kinniburgh et al., 1999; Tipping, 2002). A recent study of the speciation of airborne Pb using x-ray adsorption spectroscopy demonstrated that the major species of Pb in air is primarily Pb-humate, suggesting that the Pb is from soils (Pingitore et al., 2009). Understanding how metal ions interact with NOM and minerals in the soil is essential for evaluating the transport and fate of metal ions in the environment.

There have been extensive studies of the interaction of humic substances with aqueous metal ions and mineral surfaces in contact with aqueous solutions (Benedetti et al., 1995; Kinniburgh et al., 1999; Wightman and Fein, 2001; Tipping, 2002; Tipping et al., 2002; Tombacz et al., 2004;). However, the potential effects of organic coatings on mineral surface reactivity and their influence on metal-ion sorption and cycling are largely unverified experimentally due to the complexity of the systems and the lack of appropriate analytical tools. As a result, qualitative and quantitative information about metal-ion partitioning between mineral surfaces and organic coatings is required for better understanding of metal cycling under realistic environmental conditions.

The availability of high intensity synchrotron light sources has resulted in the development of new analytical methods that can provide quantitative information on the partitioning of metal ions between mineral surfaces and NOM or microbial biofilm coatings. Batterman, Golovchenko and co-workers introduced x-ray standing wave spectroscopy on surfaces in several classic papers (Batterman, 1964; Batterman and Cole, 1964; Golovchenko et al., 1974; Cowan et al., 1980) and pointed out the utility of both long-period and short-period (or Bragg) x-ray standing wave fluorescent yield spectroscopy for probing the distribution of metal ions at buried interfaces. Subsequently, the long-period x-ray standing wave fluorescent yield (LP-XSW-FY) method has been used to probe the vertical distribution of atoms at a number of different types of interfaces, including electrochemical interfaces (Bedzyk et al., 1986; Abruna et al., 1989); biological membranes (Bedzyk et al., 1988; Bedzyk et al., 1990; Wang et al., 1991; Wang et al., 1992), organic thin films (Bedzyk, 1992), and mineral surfaces coated with microbial biofilms or thin organic films (Templeton et al., 2001; Templeton et al., 2003; Yoon et al., 2005; Levard et al., 2011; Wang et al., 2013; Wang et al., in press-a & in press-b). Excellent reviews of these various applications of LP-XSW-FY spectroscopy are given by Bedzyk and Cheng (2002) and Trainor et al. (2006).

The LP-XSW-FY technique requires a reflecting surface to generate a well-defined intensity field from the superposition of the incident and reflected x-ray beams on the reflective surface in grazing incidence mode under total reflectance conditions (Bedzyk and Cheng, 2002; Trainor et al., 2006). The generated standing wave can excite x-ray fluorescence from the elements present within thin films when the antinodes of the standing waves coincide in position with the elements, and the resulting x-ray fluorescence emission can be detected using an energy

dispersive x-ray detector, from which the vertical distribution of the elements present can be obtained (Bedzyk and Cheng, 2002; Trainor et al., 2006). The LP-XSW-FY technique provides a spatially localized periodic probe with a sub-nanometer scale XSW period that is particularly well suited for studying trace element distributions within thin films or layered samples including microbial biofilm- and organic film-coated single-crystal mineral surfaces (Bedzyk and Cheng, 2002; Trainor et al., 2006). In addition, the energy of incident x-rays can be tuned to simultaneously excite multiple elements present in a thin-film coating on a mineral surface, which provides a new capability for probing the interactions of various elements present in trace concentrations, including competitive sorption effects among multiple metal ions for binding sites within the thin films and on the mineral surfaces.

Templeton and co-workers (Templeton et al., 2001) first applied the LP-XSW-FY approach to investigate *in situ* Pb(II) distributions on a monolayer biofilm (*Burkholderia cepacia*)-coated metal-oxide surfaces and found that the biofilm coatings did not block the reactive sites of the mineral surfaces. In a related study, we applied LP-XSW-FY spectroscopy to probe *in situ* Pb(II) and Zn(II) distributions on a multilayer biofilm (*S. oneidensis* MR-1)-coated metal-oxide surface and found that even thick reactive biofilms do not change the intrinsic reactivity of the underlying mineral surfaces (Wang et al., in press-a). We have also used the LP-XSW-FY method to probe Pb(II) and As(V) (Yoon et al., 2005) and Pb(II) and Zn(II) (Wang et al., 2013) distributions on polyacrylic acid (PAA)-coated single-crystal α -Al₂O₃ and α -Fe₂O₃ substrates, and found that the partitioning of these ions depends on the properties of the PAA film (i.e. carboxylate content) as well as on the intrinsic reactivities of the metal-oxide substrates. In the present study we employed LP-XSW-FY spectroscopy to investigate the partitioning of metal ions at NOM/metal-oxide interfaces using a model soil humic acid.

Reaction kinetics in metal-NOM-mineral systems is another important component of the present study. In the past, modeling/predicting trace metal distributions and speciation was based mainly on data obtained under equilibrium conditions (Buffle et al., 2007; Louis et al., 2009). However, fluctuating physicochemical conditions in natural systems such as rivers, lakes, estuaries, and oceans can lead to systems far from equilibrium (Tipping, 2002; Buffle et al., 2007; Louis et al., 2009). Many past experimental studies of NOM-metal interactions have not taken reaction kinetics into account or they assume fast kinetics so that the system is under equilibrium as a simplification (Tipping, 2002; Van Riemsdijk et al., 2006; Louis et al., 2009).

Predictions of metal speciation in natural systems based on such assumptions should be viewed with caution (Hering and Morel, 1988a; Hering and Morel, 1988b; Tipping, 2002; Buffle et al., 2007; Louis et al., 2009). If reactions are slow, the application of speciation models to natural aquatic systems may result in overestimation of metal toxicity (Hering and Morel, 1988b; Tipping, 2002; Louis et al., 2009). Hering and Morel (1989) showed that the kinetics of trace metal complexation can be considerably lowered in marine environments due to the competitive effect with calcium and magnesium cations (Hering and Morel, 1989). Slow dissociation rates of aqueous Ca–Mg NOM-complexes and competition with other trace elements are the key factors controlling reaction kinetics in such systems (Hering and Morel, 1988b; Hering and Morel, 1989).

In the present study, we chose Elliott Soil Humic Acid (ESHA) as a coating on Al-oxide and Fe-oxide substrates. ESHA is a model soil humic acid that has known physicochemical properties (International Humic Substances Society - IHSS). An ESHA concentration of 10 g/L was chosen as representative of the humic acid concentration in soil waters. At this concentration the ESHA coatings contain substantial amounts of metal ions (~0.0004-0.05%) which were originally present in the native form of ESHA, which allowed us to investigate the partitioning of these trace metal ions between the metal-oxide surfaces and the ESHA coatings as a function of time, without introduction of any additional metals to the system. Solution chemistry conditions, including pH and calcium content, were varied to study their effects on trace metal-ion partitioning in the native ESHA film coatings. Oriented, single-crystal surfaces of α -Al₂O₃ (0001), α -Al₂O₃ (1-102), and α -Fe₂O₃ (0001) were chosen as model metal-oxide surfaces. The use of different crystallographic orientations of single-crystal Fe- and Al-oxides provides information on intrinsic differences in chemical reactivity of different crystallographic surfaces of these common metal oxides (Eng et al., 2000; Trainor et al., 2002; Trainor et al., 2004; Tanwar et al., 2007).

2. MATERIALS AND METHODS

2.1. Crystal preparation

The single-crystal alumina surfaces were highly polished α -Al₂O₃(0001) and α -Al₂O₃(1-102) purchased from Saint-Gobain Crystals & Detectors Co. Single-crystal α -Fe₂O₃(0001)

surfaces were prepared from natural specular hematite from Bahia, Brazil. The hematite crystals were cut into approximately 1 cm² wafers of ~2 mm thickness and polished parallel to a (0001) natural growth surface using a chemical-mechanical polishing (CMP) procedure that produced surfaces of sufficient quality for x-ray reflectivity and LP-XSW-FY measurements in previous studies (Eng et al., 2000; Trainor et al., 2002; Trainor et al., 2004; Yoon et al., 2005; Tanwar et al., 2007; Wang et al., 2013; Wang et al., in press-a & in press-b). The r.m.s. surface roughness is consistently less than 5 Å for these wafers as determined by atomic force microscopy (Veeco Multimode Scanning probe microscope). The polished crystal substrates were carefully cleaned with acetone, then washed in 10^{-3.5} M sodium hydroxide for 20 minutes, and subsequently washed in 10⁻² M nitric acid for an hour. Each chemical washing step was followed by extensive rinses with MilliQ water. The commercial α-Al₂O₃ crystals (1-inch square α-Al₂O₃ (1-102) wafers and 2-inch diameter α-Al₂O₃ (0001) wafers) were also cleaned as described above and then baked at 350°C for 4 hrs to minimize excess carbon on the surfaces. This cleaning procedure was repeated as necessary until impurity metals on the surfaces were undetectable (<0.1%) and organic (adventitious) carbon on the surfaces was less than ~10% as determined by x-ray photoelectron spectroscopy (XPS) (Surface Science S-Probe, monochromatic Al Kα radiation).

2.2. Deposition of ESHA coatings

Elliott Soil Humic Acid (ESHA) was purchased from the International Humic Substance Society (IHSS, 1S102H) and used without further purification. ESHA stock solutions of 10 g/L were prepared by dissolving the ESHA powder into N₂-sparged 0.01M NaNO₃ solution. The solution pH was adjusted to 6.0 and equilibrated overnight using an end-over-end rotator; any deviation from pH 6.0 was adjusted by adding small volumes of 0.01M NaOH or 0.01M HNO₃ solution. Depending on experimental conditions, 2 mM Ca(NO₃)₂ was added to some of the ESHA solutions to test the effect of calcium on metal-ion partitioning. The ESHA solutions were then filtered using 0.2 µm syringe filters. All ESHA solutions were kept in the dark at all times to prevent any photo degradation. Each clean metal-oxide substrate was placed inside a Petri dish. A 200-µl aliquot of ESHA solution was then pipetted onto each crystal surface and equilibrated for the desired reaction time ranging from 3 hours to 7 days. A wet KimwipeTM was kept inside the closed Petri dish to reduce evaporation. After reaction, the samples were carefully

transferred to the stage of the spin-coater and then spin-coated to dryness onto the metal-oxide surfaces at 1300 rpm for 40 seconds using a Headway Research, Inc., EC101DT spinner.

The trace metal contents of ESHA solutions were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Because of the interference of the high organic carbon content with the metal analyses, ESHA solutions were diluted from 10 g/L to 0.5 g/L to obtain acceptable data from ICP-AES. Carbon K-edge near edge x-ray absorption fine structure (NEXAFS) spectroscopy data were collected at the scanning transmission x-ray microscopy (STXM) end station of beam line 11.0.2.2 at the Advanced Light Source (Lawrence Berkeley National Laboratory). Sample preparation for the STXM measurements consisted of placing 2- μ l droplets of freshly prepared 0.1g/L ESHA solutions on 100 nm-thick Si₃N₄ membranes, and allowing them to air dry in a clean hood. Energy calibration was done initially using the peak at 294.96 eV of gaseous CO₂ for the C K-edge. Normalization and background correction of the C K-edge NEXAFS spectra were performed by dividing each spectrum by a second spectrum from a C-free location on the same sample. The aXis2000 software package was used for image and spectral processing (Hitchcock, 2000). ICP-AES and STXM analyses were also performed for Suwannee River Humic Acid (SRHA) and Suwannee River Fulvic Acid (SRFA) using the same procedure for comparison.

2.3. LP-XSW-FY measurements and data analysis

LP-XSW-FY measurements were performed at the GSECARS sector on undulator beamline 13-ID-C at the Advanced Photon Source (APS) using a general-purpose Kappa diffractometer. X-rays were monochromatized using a liquid N₂-cooled Si(111) monochromator and were focused using Rh-coated double-focusing mirrors. The x-ray beam was collimated to 1.0 mm vertical and 20 μ m horizontal. Samples were mounted in a TeflonTM sample cell covered with a polypropylene film, and the space over the sample was purged by dry helium gas during the experiments. The x-ray incidence angle was scanned between 0.0 and 0.5° in 0.002° steps for the x-ray reflectivity measurements while the incident (I_0) and reflected (I_1) x-rays were monitored through N₂-filled gas ionization chambers. The fluorescence yield of various trace metal ions was collected using an incident x-ray beam energy of 14 keV. Fluorescence spectra were acquired using a 4-element silicon drift detector (SII NanoTechnology, Vortex-ME4) coupled to digital x-ray processor electronics (X-ray Instrumentation Associates, xMAP). The detector array was

located in the horizontal plane and 90° to the incident beam in order to suppress the charge scattering background from the sample. Each of the four detector elements was fit with a collimator so that it could only detect the x-ray foot print at the center of the sample and thus block scatter and fluorescence x-rays from background being collected by the detector. The fluorescence yield spectrum from each of the four detector elements was averaged and corrected for deadtime. The total area of each fluorescence peak was fit using a Gaussian line shape on a linear background. Repetitive scans of LP-XSW-FY and reflectivity profiles with the x-ray beam centered at different positions on various samples showed identical profiles. This observation suggests that x-ray beam exposure of the ESHA-coated mineral surfaces did not cause changes in the metal-ion distribution during the LP-XSW-FY measurements. However, in order to avoid undetectable changes that might be caused by the x-ray beam, the initial alignment was performed at one position, and each subsequent LP-XSW-FY profile was then collected at a fresh spot (at least 1 mm away from the initial alignment position) after quick realignment to reduce beam exposure.

LP-XSW-FY fitting analysis was done using the procedure described in previous studies (Kitts et al., 2009; Levard et al., 2011; Wang et al., 2013; Wang et al., in press-a & in press-b). The specular x-ray reflectivity was fit using a routine based on Parratt's recursion formula (Parratt, 1954), and was then modeled to obtain the thickness, density, and roughness of the film layer(s) with least-squares fitting. The resulting fit parameters were used to calculate the LP-XSW-FY field intensity modulation. The distribution of the fluorescing species was then obtained by combining the distribution function with the electric field intensity modulation. A two-box model was used in this study, which divides the interface into two regions: one near the substrate surface with a thickness of 5 Å and another extending from 5 Å to the top of the ESHA coatings. Attenuation of the emitted fluorescence intensity is accounted for in the LP-XSW-FY calculations. A least-squares routine was used to fit the parameters for the distribution model, from which the element partitioning profiles were obtained. The fitting was performed using custom-made LP-XSW-FY codes in the Igor program (Igor Pro, WaveMetrics, Lake Oswego, Oregon).

3. RESULTS

3.1. Properties and metal-ion contents of ESHA coatings

ESHA contains much higher nitrogen, phosphorous, total amino acid, and total sugar contents compared with the other types of NOMs provided by IHSS (see Table A1). The high nitrogen content is consistent with the high amount of amino acid for ESHA, indicating a high content of N-containing functional groups. The high sugar content of ESHA allows it to form a relatively smooth and uniform film on the metal-oxide surfaces. Fig. 1 shows STXM-based C K-edge NEXAFS spectra for ESHA as compared to SRFA and SRHA. The spectrum of the ESHA sample shows an intense, broadened peak at ~285.0 eV, indicating abundant unsaturated carbon moieties including aromatic, aliphatic, and alicyclic carbon groups. This observation is consistent with the NMR data provided by IHSS, which show a higher content of aromatic (50 ppm) relative to carboxyl groups (18 ppm) in ESHA as compared with other humic substances such as SRHA and SRFA (IHSS). The spectral features at 286.6 eV and 288.6 eV marked by dashed lines indicate the presence of phenolic and carboxylic functional groups, respectively.

LP-XSW-FY has been shown to be a suitable surface characterization technique that can detect elements at trace concentrations (nM to mM) (Yoon et al., 2005; Kitts et al., 2009; Levard et al., 2011). Fig. 2 presents a typical fluorescent-yield spectrum collected for ESHA coatings at an incidence angle of 0.1 degree and an incident x-ray beam energy of 14 keV. Our ESHA sample, as received from IHSS, contains more than 15 different detectable elements, including Pb, Zn, Cu, Cl, S, Se, Br, Ca, K, Fe, Ni, and P (LP-XSW-FY spectra of these elements are presented in Fig. A1). Table 1 lists the concentration of Zn, Cu, Fe, K, and Pb in several humic substances analyzed by ICP-AES, as well as a comparison of the Zn/Cu ratios obtained from ICP-AES analyses with those obtained using the LP-XSW-FY technique. Because of the interference between signals from organics and metal ions, ICP-AES analyses of metal ions at low concentrations are limited to NOM solutions with organic concentrations of 0.5 g/L or lower. The two measurements show good agreement for the Zn/Cu ratio derived from these two methods considering that ICP-AES measurements required a 20x dilution and LP-XSW-FY modeling includes a number of corrections for x-ray attenuation. Three different types of humic substances contain different amounts of elements possibly due to the large compositional differences of the sources of these model compounds. Notably, Fe is present in a significant

amount in all three NOM samples examined (Table 1). Based on ICP-AES and LP-XSW-FY analysis, some elements such as Fe, K, S, and P in the ESHA films had concentrations higher than 0.05% by weight. The amount of Cu ions (0.0226% based on ICP-AES) in ESHA coatings is about 3 times greater than that of Zn (0.009% based on ICP-AES), whereas Pb (~0.0004% based on LP-XSW-FY) is present in trace amounts. The content of selected metal ions in ESHA coatings is in the order Fe (0.0812% ICP-AES) > Cu (0.0226%) > Zn (0.009%) > Pb (~0.0004%) based on LP-XSW-FY analysis.

3.2. Metal-ion partitioning between ESHA coatings and α -Al₂O₃ (1-102) single-crystal substrates as a function of time, calcium content, and pH

Similar to polyacrylic acid (PAA) (Yoon et al., 2005; Wang et al., 2013) and biofilm-coated α -Al₂O₃ (1-102) surfaces (Templeton et al., 2001; Wang et al., in press-a & in press-b), the critical angle of the α -Al₂O₃ (1-102) substrate in the x-ray reflectivity profile is 0.165 ± 0.010 degrees at 14 keV incident x-ray energy as shown in Fig. 3. LP-XSW-FY profiles for Pb(II) partitioning as a function of time between ESHA coatings and the α -Al₂O₃ (1-102) substrate are shown in Fig. 4 (10 g/L ESHA, pH = 6.0 ± 0.05 , 0.01M NaNO₃, [Ca(II)] = 2 mM). Table 2 lists the thickness and roughness of ESHA coatings, and LP-XSW-FY fitting results for Pb(II), Cu(II), and Zn(II) partitioning at the surface for the various samples examined. The thicknesses of the ESHA coatings on the α -Al₂O₃ (1-102) surfaces vary from ~250 to ~450 Å, depending on experimental conditions, with roughness ranging from ~8 to ~24 Å. Note that there are large differences of ESHA film thickness for samples reacted for different lengths of time. There are some uncontrolled factors such as humidity and temperature variations in the lab during spin-coating experiments that could contribute to the observed differences in film thickness for humic-acid coated α -Al₂O₃ (1-102) surfaces for the kinetic experiments (0-7 days). Because the humic acid prepared before spin coating was in the aqueous phase, water does not evaporate as quickly as the solvents commonly used during the spin-coating process. Although there is a vent above the spin coater to control ventilation, it is good to control the evaporation of common solvents during the spin-coating process; however, it was not good enough to control the rate of water evaporation for our experiments because we observe differences in film thickness of the same type of sample prepared under the same spin-coating conditions but performed at different times when humidity and temperature vary in the lab. As a result, there are differences in film

thickness for the different kinetic experiments (0-7 days) for humic-acid coated α -Al₂O₃ (1-102) surfaces. Because we are focusing on probing metal partitioning, based on the percentage of metal ions in the films and on the metal-oxide surfaces, film thickness is normalized in all samples and should not affect the metal partitioning data.

Pb(II) LP-XSW-FY profiles (Fig. 4) show two characteristic FY maxima, one at $\sim 0.125^\circ \pm 0.010$ (the critical angle of the ESHA) and one at $0.165^\circ \pm 0.010$ (the critical angle of the α -Al₂O₃ (1-102) surface). The exact peak positions and peak shapes for these two FY maxima vary with each particular sample due to differences in the ESHA film properties as shown in Table 2. Simulations of the x-ray reflectivity and LP-XSW-FY profiles as a function of metal distribution, film thickness, and film roughness clearly demonstrate that these profiles are very sensitive to the metal distribution (Fig. A2), film thickness (Fig. A3), and film roughness (Fig. A4). The relative intensities of the two maxima in LP-XSW-FY profiles shown in Fig. 4 correlate with the metal-ion distributions in the ESHA coatings and on the α -Al₂O₃ (1-102) surfaces. For samples with short-time equilibration (< 24 hours), the lower angle peak ($\sim 0.125^\circ$) in the LP-XSW-FY profile exhibits a much greater intensity than the higher angle peak ($\sim 0.165^\circ$), which suggests that Pb(II) is mainly sorbed in the ESHA coatings. An increase of the second FY maximum close to the critical angle of α -Al₂O₃ (1-102) surfaces was observed as the reaction time increased, indicating that more Pb(II) ions partitioned onto the Al₂O₃ (1-102) surfaces. Fitting the LP-XSW-FY profiles using the two-box model allows extraction of quantitative information on the partitioning of Pb(II) between ESHA coatings and the metal-oxide surfaces. The percentage of Pb(II) onto the α -Al₂O₃ (1-102) surfaces for each reaction time is presented in Table 2. As the reaction time increased, the percentage of Pb(II) ions on the α -Al₂O₃ (1-102) surfaces increased from 11.4% after 3 hours to 57.4% after 7 days (for system with 2 mM Ca(II) added).

In general, the LP-XSW-FY data and model fits agree well except in a few cases. Duplicates on two samples showed that the standard deviations of the metal partitioning data are less than 5%. The misfits between data and fits are generally attributed to the non-ideality of the samples and system error such as slight misalignments in the x-ray reflectivity and sample background scattering. We tried our best during data collection for good alignment and choose the optimal setting for FY collection to obtain the best data quality. However, occasionally there are still small shifts (± 0.010 degree) in alignment due to non-ideality of the samples, which cause deviations of the critical angle of the underlying metal-oxide surfaces from the theoretical values.

This difference could be the reason for the misfit of data and the model fit for sample Pb_7d for ESHA coated α -Al₂O₃ (1-102) surface (pH = 6, 2 mM Ca(II), and 7 days of reaction time) shown in Fig. 4.

Fig. 5 shows the LP-XSW-FY profiles for Cu(II) ions at ESHA-coated α -Al₂O₃ (1-102) surfaces as a function of reaction time. Unlike Pb(II) ions, the FY profiles for Cu(II) ions show maxima at $\sim 0.125^\circ$ consistently as reaction time increased, suggesting that ESHA coatings dominated the sorption of Cu(II). LP-XSW-FY model fitting results show that more than 99% of Cu(II) ions are associated with ESHA coatings regardless of the reaction time (Table 2). Similar results were found for Zn(II) partitioning (see Fig. A5 and Table 2). ESHA coatings dominated Zn sorption (> 99%) at all reaction times tested. It is likely that some Cu(II) and Zn(II) ions partitioned onto the α -Al₂O₃ (1-102) surfaces; however, due to the high concentrations of Cu(II) and Zn(II) ions in the ESHA coatings, the two-box model is insensitive and the amounts of both ions present at α -Al₂O₃ (1-102) surfaces are not resolvable. Similarly, LP-XSW-FY fitting for the other ions present in the systems shows that more than 99% of S, Ca, Cl, Se, Br, and Ni ions are present in the ESHA coatings, and do not show the time-dependent partitioning behavior observed for Pb(II) ions.

Cu(II), Zn(II), and Pb(II) partitioning between ESHA coatings and the α -Al₂O₃ (1-102) substrates in the system without the addition of calcium were measured (see Fig. A6) and the metal-ion partitioning results are also presented in Table 2. Fig. 6 shows the influence of Ca(II) ions on Pb(II) and Cu(II) partitioning as a function of reaction time. Similar to the system with added Ca(II), the partitioning of Pb(II) to the α -Al₂O₃ (1-102) surfaces increased as reaction time increased, suggesting that Pb(II) was increasingly mobilized to the reactive α -Al₂O₃ (1-102) surfaces. The kinetic data for both systems with and without the addition of Ca(II) can be divided into four regions: (1) time 0 to 3 hours; (2) 3 hours to 24 hours; (3) 24 hours to 72 hours; and (4) 72 hours to 7 days. An initial rapid increase in the percentage of Pb(II) partitioned onto the α -Al₂O₃ (1-102) surfaces (0 to 3 hours) was observed followed by a slower increase (3 hours to 24 hours), then subsequently another significant increase (24 hours to 72 hours) and then a leveling off from 72 hours to 7 days. From the initial reaction to about 48 hrs, the addition of 2 mM Ca(II) ions to the system did not cause much difference in Pb(II) partitioning to the α -Al₂O₃ (1-102) surfaces considering the standard deviations associated with the partitioning data (< 5%). However, for longer reaction times (from 48 hours to 7 days), we observed a slightly higher

Pb(II) partitioning to the α -Al₂O₃ (1-102) surfaces in the presence of 2 mM Ca(II) relative to the system without added Ca(II).

ESHA film thickness, roughness, and the percentage of Pb(II), Cu(II), and Zn(II) ions in the ESHA coatings and on the metal-oxide surfaces as a function of pH are reported in Table 3. As the pH was increased from 4.0 to 9.0, the reflectivity profiles changed significantly, which indicates that the properties of the ESHA film changed (see Fig. A7). Note that the samples for these experiments as a function of the pH were prepared at the same time and under the same experimental conditions; therefore, film properties can be directly compared for this system. At pH 4.0 and 9.0, the ESHA coatings were much rougher (~45 and ~24 Å rms roughness, respectively) compared with the coatings formed at pH 6.0 (~10 Å rms roughness). As pH increased from 4.0 to 9.0, Pb(II) partitioning to the α -Al₂O₃ (1-102) surfaces increased from ~4% to ~55% as shown in the LP-XSW-FY fitting results (Table 3). In contrast, no changes in Cu(II) and Zn(II) partitioning to the α -Al₂O₃ (1-102) surfaces were observed, i.e. more than 99% of Cu(II) and Zn(II) ions remain in the ESHA coatings as pH increased from 4.0 to 9.0.

3.3. Metal-ion partitioning between ESHA coatings and α -Al₂O₃ (0001) and α -Fe₂O₃ (0001) single-crystal surfaces

Short time (3 hours) and long time (72 hours) samples were collected for ESHA-coated α -Al₂O₃ (0001) and α -Fe₂O₃ (0001) single-crystal surfaces. X-ray reflectivity curves collected for the ESHA-coated α -Al₂O₃ (0001) surfaces (see Fig. 3 and Fig. A8) are similar to those for ESHA-coated α -Al₂O₃ (1-102) surfaces, with a critical angle of 0.165 ± 0.010 degree at 14 keV incident x-ray energy. ESHA coatings formed on α -Al₂O₃ (0001) surfaces are generally thinner (200-270 Å) than ESHA coatings formed on α -Al₂O₃ (1-102) surfaces (Table 3). Unlike the α -Al₂O₃ (1-102) surface, Cu(II), Zn(II), and Pb(II) present in the ESHA coatings on the α -Al₂O₃ (0001) surface do not show time-dependent partitioning from the coatings to the surface (Table 3). More than 99% of the Pb(II), Cu(II), Zn(II), Ni(II), S, Fe, P, Se, Cl, and Br ions remained in the ESHA coatings even after 72 hours of reaction. This finding is consistent with the fact that α -Al₂O₃(0001) is a relatively inert surface, as shown in our previous studies (Liu et al., 1998; Templeton et al., 2001; Yoon et al., 2005; Wang et al., 2013). Note that the fits for the LP-XSW-FY data and model fits are not as good as for the metal-ESHA- α -Al₂O₃ (1-102) system described

in Section 3.2, especially in the high-angle region. This is likely due to the thinner films formed on α -Al₂O₃ (0001) surfaces, which are more subject to higher edge-scattering background.

Reflectivity profiles collected for ESHA-coated α -Fe₂O₃ (0001) surfaces (see Fig. 3 and Fig. A9) show that the critical angle of the substrate is $0.185^\circ \pm 0.010$ at 14 keV incident x-ray energy. ESHA coatings formed on α -Fe₂O₃ (0001) surfaces are generally thicker (349 Å after 3 hours of reaction to 542 Å after 72 hours of reaction) than those formed on the α -Al₂O₃ (0001) and α -Al₂O₃ (1-102) surfaces (Table 3). Significant amounts of Pb(II) ions quickly redistributed to the α -Fe₂O₃ (0001) surface after 3 hours (74.1%) and increasingly partitioned to the surface after 72 hours of reaction (91.7%) (see Table 3 and Fig. A5). These changes indicate that the α -Fe₂O₃ (0001) surface is much more reactive to Pb(II) compared with the α -Al₂O₃ (1-102) surface. In contrast to Pb(II), both Cu(II) and Zn(II) ions showed almost no partitioning from the ESHA coatings to the α -Al₂O₃ (0001) and (1-102) surfaces with respect to reaction time (> 99% of the ions were in the ESHA coatings). However, even Cu(II) ions showed a slight partitioning (2.4%) to the α -Fe₂O₃ (0001) surface after 3 hours of reaction and continuously increased to 6.4% after 72 hours even though Cu(II) ions have much higher concentrations in the ESHA coatings compared with that of Pb(II) ions. Similarly, 3.7% of Zn(II) ions partitioned to the α -Fe₂O₃ (0001) surface after 3 hours and 7.7% of Zn(II) ions partitioned to the α -Fe₂O₃ (0001) surface after 72 hours. Note that the misfits in the high-angle region for the two samples shown in Fig. A8 are also likely due to the edge effects because the α -Fe₂O₃ (0001) crystals are much thicker (1mm) than alumina crystals (330 μ m), which are more subject to high edge-scattering background resulting in the misfits.

Table 3 compares the partitioning of Pb(II), Cu(II), and Zn(II) ions between ESHA coatings and the three mineral surfaces: α -Al₂O₃ (0001), α -Al₂O₃ (1-102), and α -Fe₂O₃ (0001). For the inert α -Al₂O₃ (0001) surfaces, the ESHA coatings were the dominant sinks for all three metal ions regardless of reaction time. For the α -Al₂O₃ (1-102) surfaces, only Pb(II) ions showed significant partitioning to the surface after 3 hours, and the surfaces dominated Pb(II) sorption after 7 days for the system with added calcium. For the α -Fe₂O₃ (0001) surfaces, all three metal ions migrated toward the surface after 3 hours, and the partitioning continued to increase after 72 hours of exposure time. Therefore, the α -Fe₂O₃ (0001) surface is the most reactive surface toward these metal ions, followed by the α -Al₂O₃ (1-102) and α -Al₂O₃ (0001) surfaces.

4. DISCUSSION

4.1. Understanding metal-ion partitioning behavior between ESHA coatings and α -Al₂O₃ (1-102) single-crystal substrates at as a function of time

The increases of Pb(II) partitioning to α -Al₂O₃ (1-102) with increasing reaction time in systems with and without added Ca(II) demonstrate the kinetic aspects of metal-ion partitioning and sorption at ESHA coatings and underlying α -Al₂O₃ (1-102) substrates. At least two reaction steps are hypothesized in order to explain the reaction kinetics. First, metal ions in the ESHA coatings must dissociate from the metal-humic complex, and then the free metal ions can react with the α -Al₂O₃ (1-102) surfaces as indicated by the following reactions (Hering and Morel, 1988b; Hering and Morel, 1989; Tipping, 2002):

where Me represents the metal ions, Me-A is the metal ion-humic complex, M-OH represents the Al- or Fe-(oxy)hydroxide surfaces, and Me-O-M is the metal complex with Al- or Fe-(oxy)hydroxides. The decomplexation/dissociation reaction of metal ions from humic acid is described in reaction 1. Dissociation of monodentate complexes is a hydrolysis reaction involving displacement of the organic ligand by H₂O (Tipping, 2002). Complexation of metal ions with a mineral surface is described in reaction 2. Redistribution of metal ions from ESHA coatings to the underlying mineral surfaces would be expected if metal ions have a higher affinity for the alumina or hematite surface as described by the two simplified reactions. Reaction 2 can occur on a time scale of seconds, and is generally fast compared to reaction 1 (Tipping, 2002; Buffle et al., 2007). Therefore, reaction 1 is likely to be the rate-limiting step, especially for strong metal-humic complexes because the rate of dissociation is inversely related to the stability of the complex. The more stable the M-A complex, the slower reaction 1 will be (Tipping, 2002).

The composition of NOM is very important in metal-ion sequestration because composition is directly related to the different types of reactive sites in the NOM and their metal binding properties. Competitive effects between different metal ions binding to a variety of reactive sites

in humic substances have been studied extensively employing several models such as the Non-Ideal Competitive Adsorption (NICA)-Donnan model and Models V and VI (Tipping, 1993; Benedetti et al., 1995; Kinniburgh et al., 1999; Tipping, 2002; Koopal et al., 2005). Most models describing metal-humic acid interactions often use at least three types of binding sites: type A (monodentate site ML type), type B (bidentate site ML₂ type), and type C (tridentate/multidentate, and strong reactive N and S-containing groups) (Benedetti et al., 1995; Kinniburgh et al., 1999; Tipping, 2002; Koopal et al., 2005). Similarly, on the α -Al₂O₃ (1-102) surface, the presence of strong and weak binding sites is also expected (Templeton et al., 2001; Yoon et al., 2005). Thus mobilization of metal ions such as Pb(II) from ESHA coatings to the metal-oxide surfaces may involve multiple reaction steps depending on site densities and binding affinities of the various sites in the ESHA films and on the α -Al₂O₃ (1-102) surfaces, the conformation of the humic molecules, and the physical accessibility of various reactive sites on the surface to metal ions.

The abundant weak binding sites of humic substances are divided into weaker carboxylic binding sites (type A sites) and stronger phenolic (type B sites), which have been extensively studied by experiments as well as modeling (Alberts and Filip, 1998; Tipping, 2002). Certain metal ions such as Al(III) and Pb(II) were found to preferentially bind to phenolic groups, whereas Ca(II), Mg(II), Cd(II), and Fe(II) preferentially bind to carboxylic groups. Others cations such as Cu(II), Zn(II), Ni(II), and Fe(III) tend to bind to both phenolic and carboxylic groups (Rey-Castro et al., 2009).

Strongly binding but less abundant sites, such as N- and S-containing functional groups (Type C sites), in humic substances are also important for metal-ion sorption. Cu, Zn, and Hg are expected to bind preferentially to very strong reactive sites such as N- or S-containing functional groups, and the binding affinities for these sites can vary significantly depending on different sources of humic materials with different N- and S-containing groups and N and S contents (Tipping, 2002). Frenkel et al. (2000) found that Cu binds predominantly to N-containing groups at low metal loadings and pH 4.0, whereas binding to the carboxylic groups dominates at higher metal loadings. Alberts and Filip (1998) concluded that N-containing groups play a more important role than O-containing functional groups for Cu(II) binding in humic acid.

Although Pb(II) generally has a strong affinity for various functional groups present on bacterial and mineral surfaces (Bargar et al., 1997; Templeton et al., 2001; Bargar et al., 2004;

Ha et al., 2010), the partitioning of Pb(II) from the ESHA coatings to the underlying mineral surface found in the present study suggests that Pb(II) is not as strongly associated with ESHA coatings as Cu(II) and Zn(II). Cu(II) is expected to bind more strongly to functional groups in NOM than Pb(II) due to the affinity of Cu(II) for strong N-containing functional groups in humic acid. Tipping (2002) predicted a “crossover” for Cu(II) and Pb(II) binding in humic acid using Model VI, based on the reasoning that Pb(II) ions have a higher affinity than Cu(II) for the abundant weakly binding sites, but a lower affinity for the more rare strongly binding sites.

The difference in metal-ion partitioning behavior observed for Cu(II), Zn(II), and Pb(II) in the present study may be due to the presence of strong binding sites such as N-containing groups in the ESHA coatings. ESHA has considerably higher N content and total amino acids than other IHSS humic acids, as mentioned in section 3.1 (see Table A1). Because the metal ions considered in this study are naturally present in ESHA, they are expected to bind to the strong binding sites of ESHA. Comparison of the Cu(II) and Zn(II) ion concentrations in the ESHA coatings (0.0226% and 0.009%, respectively) with the N concentration in ESHA (4.14%), suggests that these ions bind mostly to N-containing groups in ESHA coatings, and thus should be stable and immobile in the ESHA. We found no evidence that Pb(II) has a strong affinity for N-containing groups; instead, it binds most likely to phenolic groups in humic acid (Rey-Castro et al., 2009). Titration studies have shown that the pK_a values for carboxylic groups and phenolic groups in ESHA are 4.36 and 9.8 (IHSS), respectively, which fall in the general range of pK_a values for these two types of functional groups. However, the phenolic content of ESHA is quite low compared to the other types of NOMs from IHSS (see Table A1), and the concentration of carboxylic groups is much higher than that of phenolic groups in ESHA (see Table A1), indicating that phenolic groups are not the dominant functional groups in ESHA (IHSS). Thus, it is likely that Pb(II) binds weakly to ESHA. As a result, Pb(II) ions are likely to bind to the strong reactive sites on the underlying α -Al₂O₃ (1-102) surfaces. Therefore, Pb(II) is more labile than Cu(II) and Zn(II) under the experimental conditions used here. The weaker binding of Pb(II) by ESHA can also be linked to the low Pb content (~0.0004%) of the ESHA coatings in its native state.

N- and S-containing groups such as amine and thiol groups in NOM are considered very strong binding sites due to their high affinities for soft metals such as Cu and Hg with log *K* values > 20 (Tipping, 2002). However, knowledge of metal binding with the strong binding sites

in humic substances is quite limited due to the low concentration of these sites and the lack of suitable analytical techniques for detecting metal speciation at very low metal loadings (Tipping, 2002; Louis et al., 2009). LP-XSW-FY has been shown to be a suitable surface characterization technique that can detect elements at trace concentrations (Yoon et al., 2005; Kitts et al., 2009; Levard et al., 2011). The excellent detection limits of the LP-XSW-FY method used in this study allowed us to probe metal concentrations in the nM range. This, together with the ability to simultaneously collect fluorescence yield from the different elements present in ESHA, opens the possibility of studying metal-ion binding to strong binding sites of NOM as well as competition among the metal ions for the same binding sites in ESHA coatings and the metal-oxide substrates.

Another possible mechanism to explain the observed metal partitioning behavior at ESHA coated metal-oxide surfaces does not require the two reaction steps proposed above. Due to the concentration gradient of metal-humic complexes across the ESHA film to the metal-oxide substrates, the redistribution of metal ions from ESHA films to metal-oxide surfaces could be simply the diffusion/migration or reorganization of the entire metal-humic complexes closer to metal-oxide surfaces, which does not require the breaking of metal-humic ligand bonds (reaction 1) and subsequently forming the metal-surface complexes (reaction 2). If the speciation of metal complexes at the interface could be probed using the grazing-incidence x-ray absorption fine structure (GI-XAFS) technique, we could differentiate between the two possible mechanisms in our system. However, due to the low concentration of metal-complexes at the interface, our GI-XAFS measurement could not resolve the speciation of metals.

In this study, we focused primarily on three model single-crystal metal-oxide surfaces, which serve as simplified surrogates of the complex metal-NOM-mineral systems found in nature. Clearly, small solid particles with high surface areas and disordered surface structures, particularly nanoparticles, are more realistic solids in real metal-organic matter-mineral-water systems; however, LP-XSW-FY spectroscopy methods as well as x-ray reflectivity and surface scattering methods have not yet been successfully applied to these more realistic systems. In the mean time, the insights about metal-ion partitioning at the nm scale gained from the reductionist approach used here on simplified single-crystal systems are valuable. It is also important to point out that reaction kinetics of the metal-oxide surfaces could also play a key role in metal-ion transfer, especially for poorly crystallized mineral phases because of their strong interaction with

organic matter and metal ions. In this case, both organic film and the highly reactive metal-oxide surfaces could compete strongly for metal-ion adsorption and could significantly change metal-ion partitioning behavior.

4.2. The effect of calcium ions on metal-ion partitioning between ESHA coatings and α - Al_2O_3 (1-102) single-crystal substrates

Because of the abundance of Ca(II) in natural waters, competition between Ca(II) and other metal ions for the different binding sites of humic substances and mineral surfaces can be significant (Hering and Morel, 1988a; Hering and Morel, 1988b; Hering and Morel, 1989). For example, Hering and Morel (1988b) found that the kinetics of metal complexation with humic acid can be lowered significantly due to the competition of abundant Ca(II) and Mg(II) with other cations for humic acid binding sites in marine environments. They suggested that the slow dissociation rate of Ca/Mg-NOM-complexes coupled with these competitive effects are the key factors controlling trace metal reaction kinetics (Hering and Morel, 1988b).

Calcium ions can affect metal ion/humic acid interactions in a number of ways. They can (1) provide charge neutralization of the abundant negatively charged functional groups in humic macromolecules; (2) bind to humic acid at non-specific sites (electrostatic attraction) and weakly complex with the carboxylic groups in humic acids, and thus act as a potential major competitor to other metal ions for sorption sites in NOM; (3) increase the ionic strength of the solution more effectively than monovalent ions such as Na and K; and (4) cause bridging between humic molecules, resulting in conformational changes that could lead to physical hindrance of metal binding (Hering and Morel, 1988b; Hering and Morel, 1989; Tipping, 2002). The effect of Ca(II) ions on metal-humic binding is an intricate interplay of these factors. Therefore, it is important to consider the kinetics of metal ion-humic acid complexation/dissociation perturbed by the addition of cations such as Ca(II).

The slightly enhanced partitioning of Pb(II) ions to Al_2O_3 (1-102) surfaces with 2 mM calcium added at longer reaction time indicates that Ca(II) ions compete with Pb(II) for binding sites in ESHA coatings, i.e. large amounts of introduced Ca(II) ions replaced weakly bound Pb(II) in the ESHA and increased the amount of Pb(II) redistributed to the α - Al_2O_3 (1-102) surface. Competitive sorption effects of Ca(II) on Cu(II) and Cd(II) binding by humic acid have been studied by Kinniburgh et al. (1999). Ca(II) was reported to compete much more effectively

with Cd(II) for the low affinity sites (carboxylic groups) than with Cu(II) for high affinity sites (phenolic and N- or S-containing groups) (Kinniburgh et al., 1999). The effect of Ca(II) on Cd(II) binding was found to be significant, but almost no effect of Ca(II) was observed for Cu(II) binding to humic acids (Tipping, 2002).

On the other hand, increasing Ca(II) concentration increased the solution ionic strength, which promotes ion pairing and electrostatic shielding and decreases metal binding in humic substances. Although ionic strength does not play a major role in controlling inner-sphere complexation reactions, it becomes an important parameter for metal-ion sorption on highly negatively charged humic molecules, especially for weaker binding sites. Metal-ion binding to humic acids has been shown to decrease with increasing ionic strength (Fitch et al., 1986; Zachara et al., 1994). The NICA-Donnan model predicts that the effect of ionic strength is more pronounced for Pb(II) than Cu(II) (Tipping, 2002). In our case, Pb(II) binding by ESHA is weakened by competition with Ca(II) and increasing ionic strength; therefore, more Pb(II) is redistributed to the α -Al₂O₃ (1-102) surfaces compared to the systems without added Ca(II).

In addition, Ca(II) has been found to increase the aggregation of humic macromolecules, and increase the adsorption of humic acids to iron-oxide surfaces (Tipping, 2002). In our study, the film-air roughness was always higher in all the samples with 2 mM Ca(II) added compared to the systems without Ca (Table 2). This finding is likely due to the fact that addition of Ca(II) ions causes more aggregation of the macromolecules in the ESHA coatings. The well-known bridging effect of Ca(II) on humic acid can cause steric interference or physical hindrance, resulting in Pb(II) ions being released from humic acid, which could help explain why the effect of Ca(II) competition with Pb(II) binding by humic acid in our study was not obvious during the initial 24 hours of reaction.

4.3. The effect of pH on metal-ion partitioning between ESHA coatings and α -Al₂O₃ (1-102) single-crystal substrates

The differences in roughness of ESHA coatings for samples reacted at different pH values suggest that the ESHA macromolecules in the coatings may have undergone conformational changes as pH changed. Such changes in the conformation of fulvic acid in solution have been previously observed using transmission x-ray microscopy (Myneni et al., 1999). Solution chemistry, including pH and ionic strength, has a profound influence on the size and

conformation of NOM molecules causing its structural complexity (Myneni et al., 1999). At pH 4.0, both carboxylic ($pK_a = 4.3$) and phenolic ($pK_a = 9.8$) functional groups are protonated and thus ESHA has a relatively low negative charge. In this case, ESHA macromolecules tend to aggregate due to their low electrostatic repulsive interactions (Tipping, 2002). Aggregate formation could lead to the high roughness observed for the ESHA coatings at pH 4.0. However, ESHA macromolecules can still be easily attached to α - Al_2O_3 (1-102) surfaces because this surface has a positive charge at pH 4.0. The pH_{PZC} of α - Al_2O_3 (1-102) single-crystal surfaces was found to be 5.1 (Wang et al., in press-c). At pH 9.0, most of the functional groups of ESHA are deprotonated and have significant negative charges, thus molecules tend to be more linear, flexible chains instead of coils (Myneni et al., 1999), and fewer aggregates will be formed in the ESHA coatings as compared with pH values of 4.0 and 6.0. On the other hand, the (1-102) surface of α - Al_2O_3 has a negative charge at pH 9.0, and the attachment of the ESHA coatings is expected to be more difficult at this pH value as compared with pH 4.0 and 6.0. Based on the above reasoning, the ESHA film formed at pH 6.0 should have the lowest roughness compared with the ESHA films formed at pH 4.0 and 9.0.

Similar to the observed changes in film roughness discussed above, the increased partitioning of Pb(II) to the α - Al_2O_3 (1-102) surface at higher pH can also be attributed to changes of the electrostatic interactions of both the ESHA coatings and the α - Al_2O_3 (1-102) surface. At pH 4.0, the surface of α - Al_2O_3 (1-102) has a positive charge compared to ESHA, and therefore positively charged Pb(II) ions have a higher affinity for the negatively charged ESHA, resulting in ~96% of the Pb(II) being associated with the ESHA coatings, as shown in Table 3. On the other hand, the charge of the α - Al_2O_3 (1-102) surface tends to be more negative and has a more attractive interaction with Pb(II) cations as pH increases; thus sorption of Pb(II) ions on the α - Al_2O_3 (1-102) surface becomes more favorable.

4.4. The effect of ESHA coatings on the reactivities of α - Al_2O_3 (0001), α - Al_2O_3 (1-102), and α - Fe_2O_3 (0001) single-crystal substrates

Results for Pb(II), Zn(II), and Cu(II) partitioning at three ESHA-coated single-crystal substrates have shown that the reactivities of these substrates are in the order: α - Fe_2O_3 (0001) > α - Al_2O_3 (1-102) > α - Al_2O_3 (0001) (see Section 3.3). Past studies have shown that the mode of binding and mechanism of formation of metal-ion sorption complexes formed on at metal-

oxide/water interfaces are strongly dependent on the orientation, composition, and structure of the surfaces (Bargar et al., 1996; Bargar et al., 1997; Trainor et al., 2000; Trainor et al., 2001; Bargar et al., 2004). For example, Pb(II) sorption complexes formed on alumina surfaces are sensitive to the crystallographic orientation and sorption density: Pb(II) forms primarily outer-sphere complexes on α -Al₂O₃ (0001) surfaces (Bargar et al., 1996), but it forms a variety of inner-sphere complexes (mononuclear at low sorption to multinuclear at high sorption density) on α -Al₂O₃ (1-102) surfaces (Bargar et al., 1997; Bargar et al., 2004). In contrast, Pb(II) forms dominantly inner-sphere complexes on both the (0001) and (1-102) surfaces of α -Fe₂O₃ (Bargar et al., 2004). Templeton et al. (2001) showed that the site densities of the strong binding sites on the α -Fe₂O₃ (0001) surfaces are about 2.5 times higher than those on the α -Al₂O₃ (1-102) surfaces and α -Al₂O₃ (0001) surfaces, and Pb(II) binding affinities to the strong binding sites on α -Fe₂O₃ (0001) are about 4.5 times and 20 times higher than those on α -Al₂O₃ (1-102) surfaces and α -Al₂O₃ (0001) surfaces, respectively (Templeton et al., 2001). In a DFT study of Pb(II) sorption on α -Fe₂O₃ (0001) and α -Al₂O₃ (0001) surfaces, Mason et al. (2009) found that the adsorption energy of Pb(II) is four times greater on the former surface. As a result, Pb(II) is quickly mobilized from the ESHA coatings to the more reactive α -Fe₂O₃ (0001) surfaces as compared to α -Al₂O₃ (1-102) and α -Al₂O₃ (0001) surfaces. Even Cu(II) and Zn(II) ions partitioned more to reactive α -Fe₂O₃ (0001) surfaces at longer reaction times (72 hours), whereas they remained in the ESHA films for α -Al₂O₃ (1-102) and α -Al₂O₃ (0001) surfaces.

A general trend in reactivity exists among the three model surfaces with respect to reactivity with metal ions: α -Fe₂O₃ (0001) > α -Al₂O₃ (1-102) > α -Al₂O₃ (0001), as shown in various metal-ion sorption studies on clean uncoated surfaces as well as on biofilm- and PAA-coated surfaces (Liu et al., 1998; Templeton et al., 2001; Yoon et al., 2005; Wang et al., 2013; Wang et al., in press-a & in press-b). The reactivity of surfaces with respect to metal-ion sorption observed in this study is consistent with this general trend. Thus, we conclude that the intrinsic order of reactivity of the metal-oxide surface is preserved even with 200-500 Å thick, dense ESHA coatings, suggesting that the ESHA coatings do not block reactive sites on the metal-oxide surfaces. However, they do slow down the rate of reaction of metal ions with the metal oxide surfaces they coat due to a diffusion/reaction mechanism (Wang et al., in press-a).

In addition, the ESHA film thicknesses vary significantly with respect to three single-crystal metal-oxide surfaces under the same experimental conditions as shown in Table 3 (ESHA = 10

g/L, 0.01 M NaNO₃, pH = 6.0 ± 0.05, 2 mM Ca(II) added, 72 hours of reaction): α-Fe₂O₃ (0001) > α-Al₂O₃ (1-102) > α-Al₂O₃ (0001). Such a trend can be explained by the difference of pH_{PZC} of three different crystals. The pH_{PZC} values of α-Al₂O₃ (0001), α-Al₂O₃ (1-102), and α-Fe₂O₃ (0001) single-crystal surfaces were found to be 4.5, 5.1, and 6.5, respectively (Wang et al., in press-c). At near neutral pH 6, α-Fe₂O₃ (0001) single-crystal surfaces exhibit positive charges compared to negatively charged humic acid molecules, and therefore, a thicker coating is expected. This is in contrast to α-Al₂O₃ (0001) and α-Al₂O₃ (1-102) single-crystal surfaces, because both surfaces would be negatively charged at pH 6, where more repulsive interactions would occur between these two single-crystal surfaces and humic acid molecules. Furthermore, the α-Al₂O₃ (0001) single-crystal surface is more negatively charged compared to α-Al₂O₃ (1-102) due to its lower pH_{pzc}, and therefore, the thinnest coating would be expected on this surface.

5. CONCLUSIONS

Partitioning of Cu(II), Zn(II), and Pb(II) ions between ESHA coatings and oriented, hydrated single-crystal Al- and Fe-oxide substrates was studied using the LP-XSW-FY technique as a function of reaction time (0 to 7 days), pH (4 to 9), and calcium content. More than 15 different naturally present elements were detected in the ESHA coatings, some of which had concentrations higher than 0.05% by weight (Fe, K, S, and P). The concentrations of Cu(II), Zn(II), and Pb(II) in the ESHA coatings were much lower (0.0226%, 0.009%, and ~0.0004%, respectively). Unlike Cu(II) and Zn(II) ions, Pb(II) ions partitioned strongly from the ESHA coatings to reactive sites on the α-Al₂O₃ (1-102) and α-Fe₂O₃ (0001) surfaces, suggesting weak binding of Pb(II) to ESHA functional groups as compared to Cu(II) and Zn(II) ions, which are likely associated with strong N-containing sites in ESHA coatings. Adding calcium to the ESHA/α-Al₂O₃(1-102) system slightly increased Pb(II) partitioning to the α-Al₂O₃ (1-102) surfaces at longer reaction time, possibly due to the competitive binding effects of calcium. The partitioning of Pb(II) to the α-Al₂O₃(1-102) surfaces was also found to increase with increasing pH due to enhanced electrostatic attraction resulting from the increasing negative charge of these surfaces. The intrinsic order of reactivity of the three metal-oxide surfaces was found to be α-Fe₂O₃ (0001) > α-Al₂O₃ (1-102) > α-Al₂O₃ (0001) in the presence of ESHA coatings. This order

of reactivity is the same as that of the uncoated surfaces with respect to metal-ion adsorption. In addition, the thickness and roughness of humic acid films vary significantly with the pH and Ca content/ionic strength of humic acid as well as the types of underlying metal-oxide surfaces under the same experimental conditions. The LP-XSW-FY technique is a promising analytical tool for probing strong binding sites of NOMs as well as for studying competitive effects of different metal ions at complex environmental interfaces. This study provides new insights into the binding affinity, reaction mechanisms, and reaction kinetics of Pb(II), Cu(II), and Zn(II) with common soil organic matter and common Fe- and Al-oxide surfaces. Our results shed new light on the potential bioavailability of these metal contaminants in soils and natural aquatic systems containing humic materials and common metal oxides.

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Table 1. ICP-AES analysis results for metal concentrations in 0.5 g/L NOM solutions and comparison of Zn/Cu ratios determined by ICP-AES and LP-XSW-FY analysis.

Type of NOM	Zn (ppb)	Cu (ppb)	Fe (ppb)	K (ppb)	Phosphorus (ppb)	ICP-AES (Zn/Cu)	LP-XSW-FY (Zn/Cu)
SRFA	51	8	159	174	24	6.35	6.02
SRHA	114	9	530	214	41	12.53	13.11
ESHA	45	113	406	816	567	0.388	0.324

Table 2. Results from x-ray reflectivity and LP-XSW-FY analyses of the partitioning of Pb(II), Cu(II), and Zn(II) between ESHA coatings and α -Al₂O₃(1-102) surfaces (pH = 6.0 $\pm$ 0.05, ESHA concentration = 10 g/L, 0.01M NaNO₃).

Time (hours)	Added [Ca(II)]	Film thickness (Å)	Film-air interface roughness (Å)	Pb% on the surface	Cu% on the surface	Zn% on the surface
0	2 mM	267	17.4	4.0	< 1	< 1
3	2 mM	334	16.3	11.4	< 1	< 1
12	2 mM	281	11.2	13.2	< 1	< 1
24	2 mM	392	23.7	21.5	< 1	< 1
48	2 mM	422	20.9	40.0	< 1	< 1
72	2 mM	345	23.1	58.3	< 1	< 1
168	2 mM	323	12.4	57.4	< 1	< 1
0	-	416	8.2	< 1	< 1	< 1
3	-	323	8.4	13.6	< 1	< 1
12	-	387	9.0	16.2	< 1	< 1
24	-	303	7.7	20.1	< 1	< 1
48	-	360	9.1	33.9	< 1	< 1
72	-	326	9.9	39.8	< 1	< 1
168	-	453	12.0	46.1	< 1	< 1

Table 3. Results from x-ray reflectivity and LP-XSW-FY analyses of the partitioning of Pb(II), Cu(II), and Zn(II) between ESHA coatings and α -Al₂O₃(1-102), α -Al₂O₃(0001), and α -Fe₂O₃(0001) surfaces (ESHA concentration = 10 g/L, 0.01M NaNO₃).

Substrate	Time (hours)	pH	Added [Ca(II)]	Film thickness (Å)	Film-air interface roughness (Å)	Pb% on the surface	Zn% on the surface	Cu% on the surface
<i>The effects of metal-oxide surface</i>								
α -Al ₂ O ₃ (0001)	3	6.0 ± 0.05	2 mM	200	8.8	< 1	< 1	< 1
α -Al ₂ O ₃ (1-102)	3	6.0 ± 0.05	2 mM	334	16.3	11.4	< 1	< 1
α -Fe ₂ O ₃ (0001)	3	6.0 ± 0.05	2 mM	349	13.4	74.1	3.7	2.4
α -Al ₂ O ₃ (0001)	72	6.0 ± 0.05	2 mM	271	18.5	< 1	< 1	< 1
α -Al ₂ O ₃ (1-102)	72	6.0 ± 0.05	2 mM	345	23.1	58.3	< 1	< 1
α -Fe ₂ O ₃ (0001)	72	6.0 ± 0.05	2 mM	542	15.2	91.7	7.7	6.4
<i>The effects of pH</i>								
α -Al ₂ O ₃ (1-102)	72	9.0 ± 0.10	-	295	24.7	54.3	< 1	< 1
α -Al ₂ O ₃ (1-102)	72	6.0 ± 0.05	-	326	9.9	39.8	< 1	< 1
α -Al ₂ O ₃ (1-102)	72	4.0 ± 0.05	-	305	44.7	3.8	< 1	< 1

Fig. 1 STXM-based C K-edge NEXAFS spectra for dry humic substances. Features marked by dashed lines indicate (i) unsaturated carbon moieties including aromatic, aliphatic, and alicyclic carbon groups (285.0 eV), (ii) phenolic (286.6 eV), and (iii) carboxylic/peptidic (288.6 eV) functional groups.

Fig. 2 LP-XSW-FY-generated x-ray fluorescence spectra of the ESHA film (ESHA concentration = 10 g/L, 0.01M NaNO₃, pH = 6.0, reaction time = 3 hours, 2 mM Ca(II), at incidence angle 0.1°).

Fig. 3 X-ray reflectivity profiles for ESHA-coated metal-oxide surfaces (ESHA = 10 g/L, 0.01 M NaNO₃, pH = 6.0, 2 mM Ca(II), reaction time = 3 hours): ALR is α -Al₂O₃(1-102), ALC is α -Al₂O₃(0001), and FEC is α -Fe₂O₃(0001). Open symbols represent the collected x-ray reflectivity data at different metal-oxide surfaces; solid blue lines represent the corresponding x-ray reflectivity model fits.

Fig. 4 LP-XSW-FY spectra for Pb(II) distributions at ESHA-coated α - Al_2O_3 (1-102) surfaces as a function of reaction time (ESHA = 10 g/L, 0.01 M NaNO_3 , 2 mM Ca(II) , $\text{pH} = 6.0 \pm 0.05$). Open symbols represent the collected LP-XSW-FY data at different reaction times; solid grey lines represent the corresponding LP-XSW-FY model fits.

Fig. 5 LP-XSW-FY spectra for Cu(II) distributions at the ESHA-coated α -Al₂O₃ (1-102) surfaces as a function of reaction time (ESHA = 10 g/L, 0.01 M NaNO₃, 2 mM Ca(II), pH = 6.0 $\pm$ 0.05). Open symbols represent the collected LP-XSW-FY data at different reaction times; solid grey lines represent the corresponding LP-XSW-FY model fits.

Fig. 6 The effect of calcium on Pb(II) and Cu(II) distributions at ESHA-coated α -Al₂O₃ (1-102) surfaces as a function of reaction time.