1 **2017-3-13**

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3 **Macroscopic and Microscopic Investigation of Adsorption and Precipitation of**
4 **Zn on γ -alumina in the Absence and Presence of As**

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Abstract

Contaminants zinc (Zn) and arsenate (As) often coexist in soils. However, little is known concerning the impacts of coexisting As on Zn adsorption and precipitation on soil minerals. In the present study, adsorption and precipitation of Zn on γ -alumina in the absence and presence of arsenate was investigated employing batch experiments and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. Results indicated that Zn formed edge-sharing tetrahedral surface complexes at pH 5.5 and Zn-Al LDH-like (layered double hydroxide) precipitates at pH 7.0 on the surface of γ -alumina. The presence of arsenate significantly enhanced Zn sorption densities, and remarkably changed its bonding environment. At pH 5.5, SR-XRD (Synchrotron Radiation-based X-ray Diffraction) and EXAFS showed that koettigite-like precipitate were formed in the cosorption of Zn and As on γ -alumina regardless of the addition sequence of As and Zn. At pH 7.0, when Zn was preequilibrated with γ -alumina prior to the As introduction, mixed Zn-Al LDH-like and amorphous adamite-like precipitates formed. However, when Zn and As were added simultaneously, only amorphous adamite-like precipitate was observed. Zn inner-sphere complexes and surface ternary complexes γ -alumina-As-Zn were the main outcome when As was preequilibrated firstly. Zn-arsenate precipitates could significantly decrease the concentration of Zn in aqueous solution and decrease the bioavailability and mobilization of Zn in soils.

Keywords: Zinc; arsenate; adsorption; surface precipitation; layered double

40 hydroxide; EXAFS;

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Introduction

Adsorption and precipitation at soil/water interfaces are among the most important chemical processes controlling mobilization and sequestration of metal(loid)s in soils (Sparks, 1999). The determination of metal speciation in soils is crucial to developing a thorough understanding of soil processes controlling metal transport, biomineralization and soil formation processes (Churakov and Dähn, 2012; Ginder-Vogel and Sparks, 2010; Ha et al., 2009; Stietiya et al., 2011).

Zinc (Zn) is a key element to plant growth and human health. It is an essential element for the normal activity of DNA polymerase and protein synthesis, and plays a vital role in the healthy development of many life forms (Fraga, 2005; Mengel et al., 2001). Excessive amounts of Zn, however, can be toxic, especially to aquatic biota (Oliver, 1997). Most agriculture soils contain Zn in a range of 10 to 300 mg kg⁻¹, depending on their parent materials (Chen, 2005). However, fast industrialization has led to Zn contamination in soils in many areas, with the Zn concentration up to thousands mg kg⁻¹ (Juillot et al., 2003; Liu et al., 2005; Wang et al., 2006).

Sorption of Zn on hydrous metal oxides, clays, organic matter and soils is well documented (He et al., 2011; Liang et al., 2007; Tang et al., 2009; Trivedi et al., 2001; Trivedi et al., 2004; Yang et al., 2009). Zn can react with soil and metal oxides to form outer- and inner-sphere complexes. Waychunas et al. (2002) found Zn reacted with ferrihydrite to form inner-sphere complexes, while Trivedi et al. (2001) observed outer-sphere complex formation on hydrous ferric oxide. Outer-sphere adsorption complexes are weakly bound to mineral surfaces and hence more readily

exchangeable with other competing ions than more strongly bound inner-sphere adsorption complexes (Sparks, 1999).

In addition to inner- and outer-sphere complex formation, Zn has also been observed to form solid precipitate phases upon reaction with various mineral surfaces, especially at high pHs (Ford and Sparks, 2000; Lee et al., 2004; Schlegel and Manceau, 2006). Ha et al. (2009) suggested Zn could form polynuclear surface complexes at low Zn(II) sorption densities on hematite nanoparticles with a local coordination structure similar to that of a Zn(OH)₂(am) precipitate, while at high surface loadings, Zn(II) formed a precipitate resembling Zn(OH)₂(am) and perhaps a mixed-metal hydrotalcite-like coprecipitate. Ford and Sparks (2000) observed the formation of a Zn–Al layered double hydroxide (LDH) surface precipitate when pyrophyllite was reacted with Zn at pH 7.5. Lee et al. (2004) found Zn formed a polynuclear complex on montmorillonite when samples were reacted up to 11 days and a mixed metal Zn-Si precipitate such as a Zn phyllosilicate-like precipitate when samples were reacted more than 20 days. Trainor et al. (2000) observed Zn precipitate formation on the surface of α -Al₂O₃ as a hydrotalcite-like phase. It was suggested that dissolved Al from the sorbent phase was incorporated into the precipitate structure. Regardless of the sorption mechanism, there is evidence that formed precipitate phases may serve to stabilize Zn in soil environments, making it less mobile and bioavailable.

Multiple pollutants usually exist in the same environment, requiring understanding their complex interactions to predict their environmental fate (Vijver et

al., 2010). Zn and As commonly concur in many contaminated soils (Helmhart et al., 2012; Li et al., 2011; Liu et al., 2005). It is likely that the co-existence affects their respective adsorption and precipitation behavior on mineral surfaces in co-contaminated soils and sediments. However, little has been conducted on the formation and stability of such precipitates (Grafe et al., 2004; Grafe and Sparks, 2005).

Gräfe and Sparks (2005), examining co-sorption kinetics of Zn and As, suggested that depending on the solid–solution ratio of goethite, Zn and As(V) formed precipitates similar to koettigite, koritnigite and adamite in addition to surface-adsorbed species. The formation of a solid phase that contains environmentally critical elements, that has low solubility, and that increases in stability over time is favorable from an environmental remediation standpoint. Reaction processes/mechanisms and factors that contribute and inhibit the formation of such solid phases should be understood well to make appropriate decisions for contaminated sites.

It is well documented that zinc can form mixed Zn-Al hydroxide surface precipitates on soil clays, which is an important mechanism for Zn sequestration in natural environments (Ford and Sparks, 2000; Lee et al., 2004; Schlegel and Manceau, 2006; Sparks, 1999; Trainor et al., 2000). And also Zn can form Zn–arsenate phases in the presence of arsenate (Grafe et al., 2004; Grafe and Sparks, 2005; Sadiq, 1997). There is some research on cosorption of Zn and arsenate on oxides and soils especially Fe oxides (Grafe et al., 2004; Grafe and Sparks, 2005; Liang et al., 2007),

but little or no research has been conducted on co-sorption of Zn and arsenic on Al-bearing minerals that are major solid phases in soils. In this study, we examined co-sorption of As(V) and Zn on γ -alumina surfaces under environmentally relevant pH conditions (5.5 and 7.0) using macroscopic batch experiments and molecular scale XAS techniques. Our study indicated formation of Zn-Al-LDH and Zn-As precipitate phases on alumina surfaces.

Materials and methods

Materials Aluminum oxide (Aluminum Oxide C, Degussa), identified by powder X-ray diffraction as γ -Al₂O₃ (γ -alumina), was used as the adsorbent. The γ -alumina powder exhibited a BET specific surface area of 136 m² g⁻¹ and a pH_{PZC} of 9.1. Comprehensive characterizations on this material can be found in our previous research (Arai and Sparks, 2001; Li et al., 2012). All chemicals used in these experiments were of reagent grade. All glassware was acid washed prior to contact with the reagents. All solutions were prepared with double-deionized water.

A homogeneously precipitated zinc-arsenate (Zn-As precipitate) reference phase was prepared by reacting 25 mM Zn(NO₃)₂ with 25 mM Na₂HAsO₄ at pH 7.0 in 0.01 M NaNO₃ solution. The suspension was mixed on a reciprocal shaker at 150 rpm for 24 h. During the equilibration, the precipitate suspension was maintained at pH 7.0 by adding 1 M NaOH. After the equilibration, the solid was centrifuged and washed with double-deionized water until the electric conductivity of the supernatant was close to that of deionized water. The solid was then freeze-dried prior to EXAFS analysis.

Sorption Isotherms Sorption isotherms of Zn in the absence and the presence of As

on γ -alumina were conducted under ambient conditions using a batch technique. A 0.10 g aliquot of dry γ -alumina powder was added to 15 mL of 0.01 M NaNO_3 solution at pH 5.5 or 7.0. The pH was buffered using 10 mM MES or MOPS, respectively. Previous studies showed that MES and MOPS do not interfere with transition metal sorption to mineral surfaces (Li et al., 2012). Then the suspension was added with 5 mL 0.01 M NaNO_3 solution containing various concentration of $\text{Zn}(\text{NO}_3)_2$ of (0, 2.5, 5, 10, 15, 20, and 25 mM). A Zn speciation diagram (Figure S1) indicates Zn^{2+} (aq) is the dominant species under the experimental conditions used in this study. Subsequently, 5.0 mL of 0.01 M NaNO_3 solution, containing 0, 5, 10 or 25 mM As as NaH_2AsO_4 , were added. The suspension pH was adjusted to 5.5 and 7.0 with 0.01 mol L^{-1} HNO_3 or NaOH . A final volume was 25 mL, resulting in $\text{Zn}(\text{II})$ concentrations of 0, 0.5, 1, 2, 3, 4 or 5 mM and As concentrations of 0, 1, 2, or 5 mM. The suspensions were continuously shaken at 25 ± 1 °C for 24 h that was sufficient for the reactions to reach pseudo equilibrium (Figure S2). The suspensions were then centrifuged at 9,000 g for 10 min, and the supernatant solutions were filtered through 0.45- μm filter membranes. The solution pHs at equilibrium were recorded before the solution was acidified to pH 1 -2 by adding one or two drops of concentrated HNO_3 . The concentration of Zn and As in the filtrate was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The amount of Zn adsorbed was calculated from the difference in concentrations between the initial and equilibrium solutions. The experiments were performed in duplicates.

Sorption of Zn on γ -alumina with Different Sequence of Additions. Ternary systems involving all three components (Zn/As/ γ -alumina) were studied using well-defined component sequence of additions. In all cases, two components were

allowed to equilibrate at pH 5.5 or 7.0 for 24 h prior to the addition of the third component. The sequences of additions were: (1) Zn-alumina-As: A 0.10 g aliquot of dry γ -alumina powder was added to a 50-ml centrifuge tube containing 15 mL 0.01 M NaNO_3 solution and 5 ml 25 mM Zn. The pH of the solution was adjusted to 5.5 or 7.0 with 0.1 M HNO_3 and 0.1M NaOH . The suspensions were pre-equilibrated for 24 h before the addition of 5 ml 25 mM As. After As was added, the mixtures were equilibrated again for another 24 h. During this period, the solution pH was kept at 5.5 or 7.0. The final concentrations of both Zn and As in the suspensions were 5 mM. (2) As-alumina-Zn: γ -alumina, and arsenic were pre-equilibrated for 24 h before the addition of zinc solution; and (3) Zn-As-alumina: γ -alumina, zinc solution and arsenic were added into the test tube at the same time and the mixtures were equilibrated for 48 h. For all above experiments, after 48 h of equilibration, 1 ml of suspension was withdrawn for the measurement of the zeta potential, and the rest of the suspension was centrifuged and filtered for measurement of concentration of Zn in the supernatant. The solid samples were washed with deionized water to remove the residual Zn ion on the surface of γ -alumina, and then freeze-dried for EXAFS analysis.

Desorption of Zn on the Surface of γ -alumina in the Absence and the Presence of As. Immediately following the adsorption experiment of Zn, the centrifuged residues were weighed to calculate the amount of occluded solution (to take the metal dissolved in this solution into account when calculating the desorption of Zn) and were then re-suspended in 25 ml of 0.10 M $\text{Ca}(\text{NO}_3)_2$ and equilibrated at 25°C for another 24 h before centrifugation of the suspension and filtration of the supernatant. The concentrations of Zn in the supernatant were measured as described above, and the desorbed Zn were calculated and expressed as a

percentage of previously adsorbed Zn.

X-ray Absorption Fine Structure Spectroscopy and Synchrotron-based X-ray

Diffraction EXAFS data were collected from the sorption samples in fluorescence mode using a Lytle detector at beamline BL14W at the Shanghai Synchrotron Radiation Facility (SSRF). The beamline was equipped with a Si(111) crystal monochromator. The Lytle detector was positioned 90° to the beam. Each sample was mounted in a thin plastic sample holder covered with Kapton tape and placed at 45° to the incident beam. The EXAFS spectrum of a Zn metal foil ($E_0 = 9659$ eV) was simultaneously collected with each sample as the internal reference for energy calibration. The data were background-subtracted, normalized, and k^3 -weighted prior to the Fourier transformation. EXAFS data deduction and fitting were performed with the program SIXPACK (Webb, 2005). Multiple raw spectra were averaged after energy calibration using the Zn foil. After background removal and normalization, the obtained $\chi(k)$ function was k^3 weighted prior to Fourier transformation. Shell-by-shell fitting was conducted in R-space. The amplitude reduction factor, S_0^2 , was fixed to 0.956 which was determined from the spectra fitting of a $\text{Zn}(\text{NO}_3)_2$ solution (25 mM, pH 1.0).

Micro synchrotron-based X-ray diffraction (SR-XRD) data were collected from the references and the samples using a CCD detector at BL15U at SSRF. The exposure time ranged from 0.5 s to 20 s. The sample-to-detector distance was calibrated with a CeO_2 powder standard. The 2-D images were integrated to produce 1-D intensity versus 2θ curves. The data processing was conducted using the Fit2D program (Hammersley, 1998). The XRD pattern of the kapton tape was subtracted from those of the samples and references for background removal before peak analysis.

Results and Discussions

Sorption isotherms of Zn on γ -alumina Sorption isotherms of Zn on γ -alumina with and without arsenate at pH 5.5 and 7.0 are shown in Fig. 1. The quantity of Zn adsorbed on γ -alumina increased with increasing Zn concentration in the equilibrium solution. The adsorption quantity of Zn on γ -alumina at pH 7.0 was much higher than at pH 5.5. Little sorption of Zn occurred in the pH 5.5 suspensions. The adsorption data over a range of Zn concentrations was described well using the Freundlich equation ($Q_s = K_f C_e^{1/n}$), where Q_s is the amount of Zn adsorbed ($\mu\text{mol m}^{-2}$ of γ -alumina), C_e is the equilibrium concentration of Zn (mM), and K_f and n are the constants that give estimates of the adsorptive capacity and intensity, respectively. Adsorption isotherms of Zn on γ -alumina fit the Freundlich equation with high correlation coefficients (r^2 are 0.78 and 0.97 at pH 5.5 and 7.0, respectively.). As shown in Table S1. The K_f of Zn at pH 7.0 is 10.4 times higher than that at pH 5.5. At pH 5.5, the surface of alumina is positively charged, which will repel Zn ions, resulting in a low surface saturation. At pH 7.0, the negative charge increases, which will increase the electrostatic attraction, resulting in higher surface saturation (Liang et al., 2007). At pH 7.0, Zn can form Zn-Al-LDH precipitates also resulting in higher surface saturation (Ford and Sparks, 2000).

When arsenate was present in the solution, Zn adsorption on γ -alumina significantly increased, especially at pH 5.5. Surface saturation of Zn on γ -alumina increased by 244%, 796% and 4132% at pH 5.5 and 35%, 112%, 666% at pH 7.0 in the presence of 1, 2, and 5 mM arsenate, respectively. Gräfe et al. (2004) found

similar results when studying the co-sorption of Zn and As on the surface of goethite. Zinc sorption on goethite increased by 800% at pH 4 and 1300% at pH 7 in the presence of arsenate. Liang et al. (2007) found that the presence of arsenate led to an increase in both adsorption and desorption of Zn(II) in variable charge soils. They suggested that the enhanced Zn(II) adsorption by arsenate was mainly due to an increase in negative surface charge of the soils induced by the specific adsorption of arsenate. The increase in electrostatically adsorbed Zn(II) was responsible for the increase in the desorption of Zn(II).

Adsorption of Zn on γ -alumina in the presence of arsenate with different additive sequences. In order to explore the mechanism of the effect of arsenate on the sorption of Zn on γ -alumina, adsorption of Zn on γ -alumina in the presence of arsenate with different sequences of additions were conducted (Fig. 2), at an initial concentration of 5 mM of Zn. The surface density of Zn on γ -alumina was 0.396 and 8.73 $\mu\text{mol m}^{-2}$ at pH 5.5 and 7.0, respectively. The presence of arsenate markedly increased the surface density of Zn on γ -alumina, especially at pH 5.5, which increased by 1466%. At pH 7.0, the sequence of addition of Zn and As has little influence on the sorption of Zn on γ -alumina, while the sequence significantly affected the sorption of Zn on γ -alumina at pH 5.5. The surface density of Zn on γ -alumina followed the order of Zn- γ -alumina-As > Zn-As- γ -alumina > As- γ -alumina-Zn. In addition, there is no significant difference between the sequence of As- γ -alumina-Zn and Zn-As- γ -alumina.

The zeta potential of γ -alumina after equilibration with Zn and As were

measured, as shown in Fig.3. The zeta potential of γ -alumina at pH 5.5 is more positive than at pH 7.0, which partly explains the lower surface density of Zn at pH 5.5. The presence of arsenate markedly decreased the zeta potential of γ -alumina resulting in a higher surface density of Zn when arsenate was added. The formation of inner-sphere bidentate binuclear complexes for the oxyanion of As(V) at the γ -alumina surface (Zhu and Elzinga, 2015). On the contrary, the presence of Zn increased the zeta potential of γ -alumina. When Zn and As were both present, the results were significantly different from the binary system. In the ternary system, when Zn was preequilibrated with γ -alumina, the lowest zeta potential was at pH 7.0, resulted from the formation of Zn-Al-LDH precipitates. The zeta potential of γ -alumina followed the sequence: Zn- γ -alumina-As > As- γ -alumina-Zn > Zn-As- γ -alumina. The sequence of zeta potential is different from the sequence of surface densities of Zn on γ -alumina. This further confirmed the chemisorption of Zn on γ -alumina because the chemisorption of the metal was not totally dependent on the zeta potential of the absorbent.

Synchrotron Radiation-Based Powder X-ray Diffraction. SR-XRD was used to analyze the crystalline structure of the cosorption and coprecipitate samples (Fig. 4). Adsorption of Zn on surface of γ -alumina did not change the patterns of γ -alumina at pH 5.5 significantly, but some specific peaks (2θ at 10.5° , 14.98° and 15.26°) were produced at pH 7.0, which are consistent with the characteristic peaks of Zn-Al LDH. The d-spacing of the peak at $\sim 10.5^\circ$ is 0.38 nm, which could be indexed to the (006) reflection of Zn-Al LDH (Liu et al., 2007). This confirmed that the crystalline Zn-Al

LDH precipitate formed at higher pH. Also, it is consistent with the increasing coordination number of the Zn–Zn/Al shell in the EXAFS spectra (discussing in the following section). It was also discovered by using high-resolution transmission electron microscopy (HR-TEM). Li et al. found that some crystalline and nano size Zn-Al LDH was formed at pH 7.5 on the surface of γ -alumina (Li et al., 2012). It can be seen that the presence of arsenic significantly changes the XRD patterns, especially at pH 5.5. At pH 5.5 no matter what sequence of addition is, there are always some new peak formed such as 2 θ at 10.11°, 12.3°, 13.2°, 17.1° and 19.0°, and these peaks were assigned to the crystalline structure of koettigite ($\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$). Just as described below, the presence of As significantly change the local structure of Zn on the surface of γ -alumina. A crystalline koettigite-like precipitate was formed on the alumina surface. But at pH 7.0, we did not find the peaks of precipitate containing Zn and As, the structure similar to koettigite, in the XRD patterns of Zn sorption samples in the presence of arsenate. The possible reasons are 1) that an amorphous precipitate may have formed; 2) that no precipitate formed. We found the Zn-Al LDH peaks in the Zn preequilibrated sample, this is consistent with the EXAFS spectra, when Zn was preequilibrated first, the crystalline Zn-Al LDH also formed. However, Zn-Al LDH peaks disappeared in the sorption samples with the simultaneous addition of Zn and As or As preequilibrated first. The addition of oxyanion inhibited the formation of Me(II)-Al(III) layered double hydroxides (LDHs) (Boyle-Wight et al., 2002; Zhu and Elzinga, 2015). And one of the possible mechanism is that the oxyanion such as arsenate could complexed on the surface of γ -alumina to decrease the dissolution of

Al; and the other is that the oxyanions compete with the precipitation of Zn-Al LDH (Zhu and Elzinga, 2015).

Zinc K-edge EXAFS Spectroscopy The EXAFS spectra of Zn-containing reference compounds and samples are presented in Figure 5 A and B. The reference compounds included 25 mM $\text{Zn}(\text{NO}_3)_2(\text{aq})$ solution (pH 1.0), Zn-Al layered double hydroxide (Zn-Al LDH), a Zn-arsenate precipitate (Zn-As Pre) and adamite mineral ($\text{Zn}_2(\text{AsO}_4)(\text{OH})$). Fitting of the $\text{Zn}(\text{NO}_3)_2$ solution spectrum indicated that Zn was coordinated with six oxygen atoms at an inter-atomic distance of 2.08 Å (Table S2), in good agreement with previous studies (Ha et al., 2009; Lee et al., 2004; Trainor et al., 2000). For Zn-Al LDH, EXAFS analysis indicated that the first shell Zn-O distance was 2.08 Å with 6.3 oxygen atoms, and that the second shell had Zn-Al and Zn-Zn distances of 3.12 Å and 3.12 Å, respectively with a coordination number of 6.0 and 8.6. The first shell of the Zn-As precipitate was fitted with two Zn-O scattering paths, showing a Zn coordination with 2.7 O atoms at 1.99 Å and 1.4 O atoms at 2.12 Å. In the second shell, Zn was coordinated to 3.5 As atoms at 3.40 Å and 1.50 Zn atoms at 3.67 Å. These structural parameters indicate formation of koettigite, a Zn-As compound (Grafe et al., 2004). However, the bonding environment of koettigite consisted of 10 O atoms at 2.12 Å and 2 O atoms at 2.03 Å. The synthesized Zn-As precipitate contained not only koettigite-like mineral but also other minerals. In adamite, two Zn-O scattering paths were fitted in the first shell, in which Zn was coordinated with 4.8 O atoms at 2.05 Å and with 2.1 O atoms at 2.23 Å. As Grafe et al. (2004) fitted, in the second shell, Zn was coordinated with 3.3 Zn atoms at 3.10 Å, 5.0

As atoms at 3.26 Å and 2.8 Zn atoms at 3.47 Å. Two types of Zn-O scattering paths were fitted in Zn-As precipitate and adamite. One is shorter ($R_{\text{Zn-O}}=2.0$ Å), designated Zn-O (1); the other is longer ($R_{\text{Zn-O}}=2.2$ Å), designated Zn-O (2). However, the ratio of two types of Zn-O scattering paths is different. The ratio of Zn-O (2) is larger in the Zn-As precipitate or koettigite-like precipitate than that in adamite.

Zn Sorption in the Absence of Arsenate. In comparison with the spectrum of $\text{Zn}(\text{NO}_3)_2$, a significant shift of the spectra to higher wavenumbers ($\text{\AA}^{-1}$) was apparent for Zn at pH 5.5 from 3.65 to 4.05 $\text{\AA}^{-1}$, suggesting a different coordination sphere around Zn in this sample. This gives a small shift of the first major peak to lower $R + \Delta R$ (Å) from 1.6 to 1.5 Å in the RSFs suggesting that the Zn-O bond distance decreased. As shown in Table S2, the Zn-O bond distance decreased from 2.08 to 1.94 Å. The coordination number of the O atom also changed from 6.0 to 4.6. Zn was in a 4-fold coordination environment at pH 5.5. Fitting of the second-shell feature yielded Al at 2.74 Å ($R + \Delta R$). Fitting results showed that Zn was coordinated to 0.6 Al atoms at 2.94 Å. The observed Zn–Al distance suggested that Zn formed tetrahedral complexes on γ -alumina, sharing edges with AlO_6 octahedral, consistent with Trainor et al. (2000). It means that the bidentate mononuclear surface complex was mainly formed in the system with only Zn sorption on γ -alumina at pH 5.5.

For the Zn sorption sample in the absence of arsenate at pH 7.0, there are two distinct peaks representing the first and second coordination shells of the zinc atom. Oxygen atoms were at 1.6 Å ($R+\Delta R$), and the second peak is at 2.7 Å in the RSFs. Fitting results of the first shell show that Zn was coordinated with 7.4 O atoms, and

the Zn-O bond distances were 2.05 Å. The best fits of the second shell of the EXAFS spectra were obtained by including both Zn-Zn and Zn-Al backscattering paths. Zn-Al and Zn-Zn distances were 3.09 Å and 3.10 Å with coordination numbers of 3.1 and 4.7, respectively. The Zn-Zn bond distance (3.10 Å) of the sorption samples compared well to Zn-Al LDH phases (3.09 Å) (Lee et al., 2004). The fitting results of Zn-Zn and Zn-Al scatterings and their contribution to the second shell indicate there was formation of mixed metal precipitates, consistent with the fitting results of Zn-Al LDH. In addition, the characteristic peaks (2θ 10.5°) of Zn-Al LDH were observed in the Zn sorption sample in the absence of arsenate at pH 7.0. Therefore, this newly formed precipitate could be a Zn-Al LDH.

Zn Sorption in the Presence of Arsenate. The presence of arsenate significantly increased the surface density of Zn. At pH 5.5, when Zn was pre-equilibrated first, the EXAFS fitting showed that in the first shell Zn was coordinated to 3.44 O and 1.62 O atoms at 2.07 Å and 2.22 Å, respectively, and in the second shell Zn was coordinated to 0.5 As atoms at 3.32 Å and 0.1 Zn atoms at 3.82 Å. Similarities were observed in the $\chi(k)$ spectra and RSFs of spectra for As preequilibrated first and added simultaneously. When As was preequilibrated first, the first shell was also fitted with two Zn-O scattering paths showing a Zn coordination with 2.9 O atoms at 2.01 Å and 1.9 O atoms at 2.18 Å. In the second shell, Zn was coordinated to 0.6 As atoms at 3.33 Å and 0.6 Zn atoms at 3.83 Å. When Zn and As were added simultaneously, the first shell was fitted with two Zn-O scattering paths showing a Zn coordination with 3.1 O atoms at 2.01 Å and 2.1 O atoms at 2.19 Å. In the second shell, Zn was coordinated to

1.2 As atoms at 3.37 Å and 1.2 Zn atoms at 3.71 Å. The coordination environments of Zn and As cosorption samples consisting of Zn-O (1), Zn-O (2), Zn-As and Zn-Zn were observed, similar to those of synthesized Zn-As precipitate. As SR-XRD analyzed, the characteristics peaks of koettigite were observed in the Zn sorption samples in the presence of arsenate at pH 5.5, no matter what the addition sequence of arsenate and zinc is. Gräfe et al. (2004) found that Zn was coordinated to 1.9 As atoms at 3.38 Å and 1.5 Zn atoms at 3.66 Å in a synthesized Zn-As precipitate, which are in agreement with the coordination environment of koettigite. It suggested therefore that a koettigite-like precipitate had been formed on the alumina surface of Zn sorption samples in the presence of arsenate at pH 5.5.

At pH 7.0, when Zn was preequilibrated first, special features appear in the higher k range at 7.2 Å^{-1} , similar to that of a Zn-Al LDH. This is consistent with the presence of heavy back-scattering atoms in the local coordination environment of retained Zn. Nonlinear least-squares of the first shell showed Zn coordination with 5.5 O atoms at 2.01 Å and 1.9 O atoms at 2.20 Å. The fitting results are in agreement with that of adamite, especially the ratio of Zn-O (1) and Zn-O (2). The best fits of the second shell of the EXAFS spectra were obtained by including both Zn-Zn and Zn-Al or Zn-As backscattering paths. Zinc was coordinated to 1.4 Al atoms at 3.07 Å, 1.1 Zn atoms at 3.05 Å, 0.7 As atoms at 3.32 Å and 0.4 Zn atoms at 3.69 Å. The fitting results of Zn-Zn, Zn-Al, Zn-As, and the long distance of Zn-Zn scattering contribution to the second shell indicated there was formation of mixed coprecipitates. The peaks in the SR-XRD pattern of sample with Zn preequilibrated were indexed to the

reflection of Zn-Al LDH. These newly formed coprecipitates could be a mixture of Zn-Al LDH-like and amorphous adamite-like precipitates.

When As was preequilibrated first, the first shell was fitted with two Zn-O scattering paths showing Zn coordination with 4.4 O atoms at 1.98 Å and 1.0 O atoms at 2.16 Å. In the second shell, Zn was coordinated to 0.8 Al atoms at 3.07 Å and 0.5 As atoms at 3.28 Å. The absence of Zn-Zn contributions in the spectrum suggested the formation of precipitate containing Zn did not occurred in this system. In the system of the coexistence of As(V) and Zn, the surface ternary complex might be formed, including γ -alumina-As-Zn with As as bridge and γ -alumina-Zn-As with Zn as bridge. In consideration of As(V) preequilibrated, the surface ternary complex γ -alumina-As-Zn might formed. In this case, only Zn-O and Zn-As paths would be fitted by shell-by-shell fitting of EXAFS analysis. However, Zn was also coordinated by 0.8 Al atoms at 3.07 Å, showing that it is likely to generate inner-sphere complexes on the surface of γ -alumina. Above all, both Zn inner-sphere complexes and surface ternary complexes γ -alumina-As-Zn coexisted in the system with As preequilibrated first at pH 7.0. When Zn and As were added simultaneously, in the first shell, Zn was coordinated with 3.5 O atoms at 1.98 Å and 0.8 O atoms at 2.15 Å, which is in agreement with that of adamite. In the second shell, Zn was coordinated to 1.9 As atoms at 3.26 and 0.8 Zn atoms at 3.68 Å. The fit results suggested therefore that an amorphous adamite-like precipitate might formed on the alumina surface when As and Zn were added simultaneously at pH 7.0.

Desorption of Zn from alumina in the absence and the presence of As. Desorption

is an important process that controls the bioavailability of metals in soils. In order to further discuss the sorption mechanism of Zn on γ -alumina, the desorption of Zn from γ -alumina were conducted immediately after the sorption experiments. More detailed information was shown in Fig. S3. Only 1.37% of sorbed Zn was released into the desorption solution at pH 5.5 in the absence of As, which further confirmed the EXAFS results that Zn sorption on γ -alumina, resulted in inner-sphere surface complexes or chemisorption was formed at pH 5.5. Meanwhile, the desorption of Zn was also very low at pH 7.0. Zn can be precipitated to form Zn-Al LDH at pH 7.0, which is stable and very difficult to dissolve into the desorption solution.

The presence of As significantly increased the sorption of Zn on γ -alumina, but the desorption is also higher. As shown in Fig. S3, 10-14% and 3-10% of sorbed Zn were released into solution at pH 5.5 and 7.0 in the presence of As. The desorption rate of Zn was lower at pH 7.0 than that at pH 5.5. The addition sequence markedly influenced the desorption of Zn in the following order: As- γ -alumina-Zn > Zn-As- γ -alumina > Zn- γ -alumina-As, which is contrary to the sorption order. When Zn was preequilibrated with γ -alumina first, Zn could form an inner-sphere surface complex and Zn-Al-LDH precipitate, the remaining Zn in the equilibrated solution could precipitate with As after the addition of As. Only 3% of sorbed Zn was released when Zn was preequilibrated with γ -alumina first at pH 7.0. As discussed above, when Zn was preequilibrated with alumina, the mixed Zn-Al LDH-like and adamite-like precipitate could form at pH 7.0, while only amorphous adamite-like or koettigite-like precipitate could form with other addition sequences. Zn-Al LDH is

much more stable than adamite-like or koettigite-like precipitate, resulting in the lowest desorption rate. When As was pre-equilibrated with γ -alumina, Zn sorption could substitute on sites where As was specifically adsorbed, and As could act as a bridge between the mineral and Zn. Such a complex is not stable, resulting in a high desorption rate.

Conclusion Zinc and arsenate are common pollutants in soils, and they often occur in soils simultaneously. In our study, adsorption and precipitation of Zn on alumina was investigated from the macroscopic to the microscopic scale using batch experiments and EXAFS techniques, respectively. Zn can form inner-sphere complexes on the surface of alumina, which is more stable than those of outer-sphere complexes. At pH 7.0, Zn can form a Zn-Al LDH-like precipitate. The presence of arsenate significantly enhanced the surface density of Zn at two pHs (5.5 and 7.0). Different sequences of addition markedly change the bonding environments. At pH 5.5, when Zn and As was co-sorbed on alumina, Zn formed a koettigite-like precipitate. At pH 7.0, when Zn was pre-equilibrated with alumina, a mixed Zn-Al LDH-like and amorphous adamite-like precipitate formed. When Zn and As were added simultaneously, an amorphous adamite-like precipitate formed. Zn-arsenate precipitates could significantly decrease the concentration of Zn in aqueous solution and decrease the bioavailability and mobilization of Zn in soils. Our results may therefore be useful in devising remediation strategies for site contaminated with multiple metals. Due to the weak backscatters of phosphate, it is very difficult to detect by the EXAFS technique. Arsenate and phosphate are in the same group, have the same chemical characteristics.

Our results are also the supplementary information to explore the molecular mechanisms of the effect of phosphate on the adsorption and precipitation of Zn in soils. However, additional kinetics research is needed to describe Zn-As interaction on alumina and the factors controlling the cosorption reactions.

Acknowledgements

This research was supported by the National Key Research and Development Program of China (2016YFD0800403, 2016YFD0800407), and National Natural Science Foundation of China (Grants No. 41422105) and Youth Innovation Promotion Association CAS (Grants No. 2011226). It was also funded by the National Science Foundation (NSF) through the Delaware EPSCoR program (Grants No. EPS0814251). The authors would like to thank the Shanghai Synchrotron Radiation Facility for use of the synchrotron radiation facilities.

Supporting Information

Speciation diagram of 5 mM Zn as a function of pH in solution at 298K (Figure S1), Zn sorption kinetics (Figure S2), desorption of Zn on γ -Al₂O₃ (Fig S3), Freundlich sorption model coefficients for Zn sorption isotherms on γ -Al₂O₃ in the absence and presence of As at pH 5.5 and 7.0 (Table S1) and Structural parameters from EXAFS analyses of Zn sorbed samples and some references samples (Table S2)

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Fig. 1. Adsorption isotherms of Zn on Al_2O_3 in the absence and the presence of As at pH 5.5 and pH 7.0 in 10 mM NaNO_3 solution at 25°C)

Fig. 2. Adsorption of Zn on Al₂O₃ in the presence of As with different adding sequence. (Background electrolyte solution is 10 mmol L⁻¹ NaNO₃, temperature is 25°C)

Fig. 3. Zeta potential of alumina

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590 Fig. 4. SR-XRD patterns of cosorption and coprecipitation sample and the reference

591 samples (alumina, Zn-Al LDH, Adamite and Koettigite, which were calculated based

592 on Al_2O_3 (PDF # 10-0425), Zaccagnaites $\text{Zn}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 12\text{H}_2\text{O}$ (PDF# 54-0720),593 Adamite $\text{Zn}_2(\text{AsO}_4)(\text{OH})$ (PDF # 39-1354), Koettigite $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (PDF #

594 33-1467)). The wavelength of the X-ray beams is 0.06906 nm.

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598 Fig. 5 A. Raw (x) and fitted (line) k^3 -weighted χ -function EXAFS spectrum of Zn

599 contained reference compounds and sorption samples; B. Raw (x) and fitted (line)

600 k^3 -weighted corresponding Fourier transforms of Zn containing reference compounds

601 and sorption samples.