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Speciation and Release Kinetics of Zinc in Contaminated Paddy Soils

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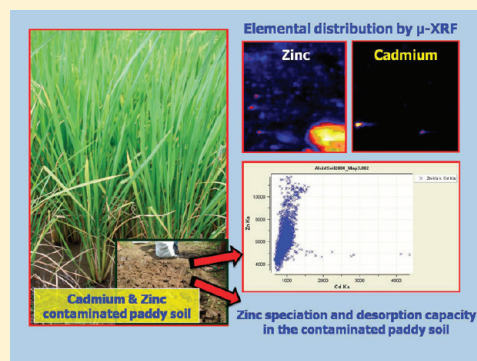
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Supporting Information

ABSTRACT: Zinc is an important nutrient for plants, but it can be toxic at high concentrations. The solubility and speciation of Zn is controlled by many factors, especially soil pH and Eh, which can vary in lowland rice culture. This study determined Zn speciation and release kinetics in Cd–Zn cocontaminated alkaline and acidified paddy soils, under various flooding periods and draining conditions, by employing synchrotron-based techniques and a stirred-flow kinetic method. Results showed almost no change in Zn speciation and release kinetics in the two soils, although the soils were subjected to different flooding periods and draining conditions. The mineral phases in which Zn is immobilized in the soil samples were constrained by linear least squares fitting (LLSF) analyses of bulk X-ray absorption fine structure (XAFS) spectra. Only two main phases were identified by LLSF, i.e., Zn-layered double hydroxides (Zn/Mg-hydrotalcite-like, and ZnAl-LDH) and Zn-phyllsilicates (Zn-kerolite). Under all soil pHs, flooding, and draining conditions, less than 22% of Zn was desorbed from the soil after a two-hour desorption experiment. The information on Zn chemistry obtained in this study will be useful in finding the best strategy to control Cd and Zn bioavailability in the Cd–Zn cocontaminated paddy soils.



INTRODUCTION

Zinc-mining and smelter activities can result in Zn and Cd contamination in environments, including paddy soils.^{1–5} Although Zn is an essential element for plants, it can be toxic at a high level. The degrees of Zn toxicity, bioavailability, and mobility in soils are directly controlled by Zn speciation.⁶ The latter is controlled by many factors, including soil pH and Eh, which can vary in lowland rice culture during the flooding and draining cycles employed. These variations could modify Zn distribution in the paddy soil, and the bioavailability of Zn to rice. Under acidic and oxic conditions, Zn is one of the most soluble and mobile trace metal cations.⁷ Gao⁸ reported that the bioavailability of Zn diminished under aerobic conditions, while Mandal et al.⁹ showed that Zn uptake and accumulation in rice were high under anaerobic conditions, i.e., when the soil was flooded. In the Mae Sot district, located in the northern part of Thailand near Zn mining activities, around 2200 ha of paddy soils have been heavily contaminated by Cd and Zn.^{3,10} The total concentrations of Zn at these contaminated sites can reach 3000 mg/kg, which is twenty times higher than the total Cd concentrations at the same locations.³ New analytical tools that use synchrotron radiation allow scientists to investigate *in situ* Zn speciation in soils, minerals, and sediments.^{2,11–15} However, only one study has addressed the speciation of Zn in paddy soils.¹⁶

Our research aims to characterize Zn desorption from soil components of the contaminated paddy soils in the Mae Sot

district, and identify the phases in which Zn is distributed in the soil. Zinc speciation and release kinetics are investigated, before and after the alkaline soil was acidified to pH 6, spiked with K₂SO₄, and flooded for different periods, using synchrotron based techniques, and a stirred-flow kinetic approach. The information provided in this study will be useful in finding the best strategy to control Cd and Zn mobility as well as their solubility in Cd and Zn cocontaminated paddy soils at the Mae Sot district.

MATERIALS AND METHODS

Study Site and Soil Characterization. The IWMI³ measured Cd and Zn concentrations in several Cd–Zn cocontaminated paddy soils located near a Zn mining area, in the Mae Sot district, Tak province, Thailand. One of these sites studied by the IWMI, which contains more than 3000 and 100 mg/kg of Zn and Cd, respectively, was selected as our study site. Surface samples (0–15 cm) were collected at random locations in this site, within an area of about 10 × 10 m², using a compositing technique.¹⁷ A single composite sample was then used as representative of soil samples collected at this site. The soil was treated by acidification using HNO₃, and addition of

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Table 1. Physicochemical Properties of the Alkaline Paddy Soil

soil	soil pH		OM (%)	total concentration (mg/kg)					before treatment			treated (acidified to pH 6 using HNO ₃ , and spiked with K ₂ SO ₄)		
	water	buffer		Cd	Zn	Cu	Fe	Ca	total sulfur (mg/kg)	total nitrate (mg/kg)	total soluble salts (mmhos/cm)	total sulfur (mg/kg)	total nitrate (mg/kg)	electrical conductivity (EC) (mmhos/cm)
alkaline	7.3	8.1	4.3	142	3050	25	18 328	34 360	282	1.7	0.3	3618	12 300	18

K₂SO₄, to increase the amount of sulfur in the soil and enhance metal release from soil components.^{18,19} This treated soil is referred as acidic soil in this study. The untreated soil is referred to in this study as the alkaline soil. Basic soil physicochemical properties, such as texture, pH, elemental concentrations, and organic matter content, were determined by standard procedures.^{20–23}

Incubation Experiment: Flooding and Draining Conditions. To investigate Zn speciation and release kinetics at environmental conditions relevant to lowland rice culture, we employed different flooding periods and draining conditions to conduct incubation experiments. Two periods of flooding and two draining conditions were selected to mimic the environmental settings found in paddy soils undergoing lowland rice culture. The two periods of flooding were 1 and 30 days, based on the understanding that the chemical properties of paddy soils usually reach apparent equilibrium within 30 days,²⁴ and information obtained from Cd study.²⁵ The draining cycles were carried out to saturation (Sat), i.e., ~75% soil moisture content, and at field capacity (FC), i.e., ~58% soil moisture content. These two moisture contents are relevant to those found in Thai paddy soils during draining periods. The incubation experimental procedures were similar to those previously reported.²⁵ At the end of the flooding period, samples were drained to saturation or field capacity. The soil samples were then immediately mounted on sample holders for XAS analyses or used for desorption experiments. The pH and Eh of the soil suspensions were measured throughout the flooding periods, using pH- and Eh-meters, respectively.

Desorption Experiments. Zinc desorption kinetics were conducted using a stirred-flow technique, with soil samples flooded for different periods and draining conditions. The experimental setup was similar to the one used in Strawn and Sparks.²⁶ Diethylenetriamine pentaacetate (5 mM)—triethanolamine (100 mM)—CaCl₂ (10 mM) (DTPA-TEA-Ca) was used as a desorption agent, at pH 7.3.²⁷ The experiments were run for 120 min at a flow rate of 0.8 mL·min⁻¹, a mixing rate of 500 rpm, and the effluent was collected in 12 tubes, one every 10 min. Each experiment was run in duplicate, and Zn concentrations were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES) to subsequently calculate cumulative Zn desorption percentages.²⁸

Zinc Speciation, and Elemental Distributions by XAS Techniques. *Zinc Standard Preparation.* Zinc standards considered in XAS analyses included Zn-CuCO₃, Zn-hydroxalcalcite, Zn/Mg hydroxalcalcite-like phase, Zn-CuS, Zn-CuCO₃, Zn-hydrous manganese oxide (Zn-HMO), Zn-humic acids, Zn-fulvic acid, Zn-kaolinite, Zn-illite, Zn-vermiculite, Zn-montmorillonite, Zn-kerolite, ZnAl-layered double hydroxide (ZnAl-LDH), Zn-gibbsite, Zn-ferrhydrite, Zn-goethite; willemite (Zn₂SiO₄), hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O), sphalerite (ZnS from XLS Ruby sphalerite, Joplin, MO), smithsonite (ZnCO₃), hydrozincite (Zn₅(CO₃)₂(OH)₆), ZnS, ZnCO₃, ZnO, Zn(SO₄), ZnFeO, and a solution of 1 mM Zn²⁺.

The experimental procedures to prepare Zn-CuCO₃, Zn-hydroxalcalcite, Zn/Mg hydroxalcalcite-like phase, Zn-CuS, Zn-CuCO₃, and Zn sorbed to humic acid are reported in the Supporting Information (SI). The ZnS, ZnCO₃, ZnO, Zn-(SO₄), and ZnFeO were ACS reagent grade. Standards were mixed with 95% boron nitride, and then mounted for XAFS analyses. Willemite, hemimorphite, Zn-kerolite, Zn-LDH, Zn-gibbsite, Zn-ferrhydrite, Zn-goethite, and Zn fulvic acid spectra were synthesized in three previous studies carried out in our laboratory.^{2,11,15,29}

Bulk XAFS Spectroscopy. The Zn standards and soil samples were analyzed by bulk-XAFS at the zinc K-edge (9659 eV), at beamline X-11A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY. This beamline features a monochromator with two Si (111) crystals, with an entrance slit of 0.5 mm. The beam energy was calibrated to the first inflection point of the first derivative of the Zn absorption edge (9659 eV) of a Zn(0) metal foil XANES spectrum. Bulk-XAFS spectra were collected at room temperature, from 150 eV below the absorption edge energy, to *k* values of 12.5 Å⁻¹. At least three scans were collected per sample, to improve the signal-to-noise ratio. Both fluorescence and transmission modes were used to collect spectra, depending on the concentration of the Zn standards. A 6-μm Cu filter was placed between the sample and the detector to reduce elastic scatterings.

Each raw bulk-XAFS spectrum at the Zn-K edge was normalized to obtain the extended X-ray absorption fine structure (EXAFS) function, using SixPack software package.³⁰ The mineral phases in which Zn were present in the soils were identified and quantified with SixPack, using principal component analysis (PCA), target transformation (TT), and linear least-squares fitting (LLSF) procedures. These tools have been used to identify metal speciation in heterogeneous samples.^{31–34} The energy calibrations for LLSF analyses of EXAFS functions of soil and reference samples were set at the same value (9659 eV). The PCA and LLSF were performed using the EXAFS function, which was *k*³ weighted, with *k* values between 2 and 10 Å⁻¹. SPOIL values obtained from TT analysis were used to select principal components for LLSF analysis.

μ-XRF Analyses. Micro X-ray fluorescence analyses were conducted at beamline 13-ID-C (APS), to determine elemental distributions in the contaminated paddy soils. The μ-XRF maps were 200 μm² in size, with a 2 μm step size, and 1 s dwell time. The beam energy was set to 29 000 eV for μ-XRF analyses of Cd, Ca, Cu, Fe, K, Zn, and Mn distributions in the soil samples.

RESULTS AND DISCUSSION

Soil Analysis. Bulk physicochemical properties of the alkaline Thai paddy soil before and after treatment are shown in Table 1. The total concentration of Zn in the soil was 3050 mg/kg, which is nearly 44 times higher than the background Zn concentration found in Thai soils, i.e., 70 mg/kg.³⁵ The amounts of total sulfur and nitrate in the acid soil were 60 and

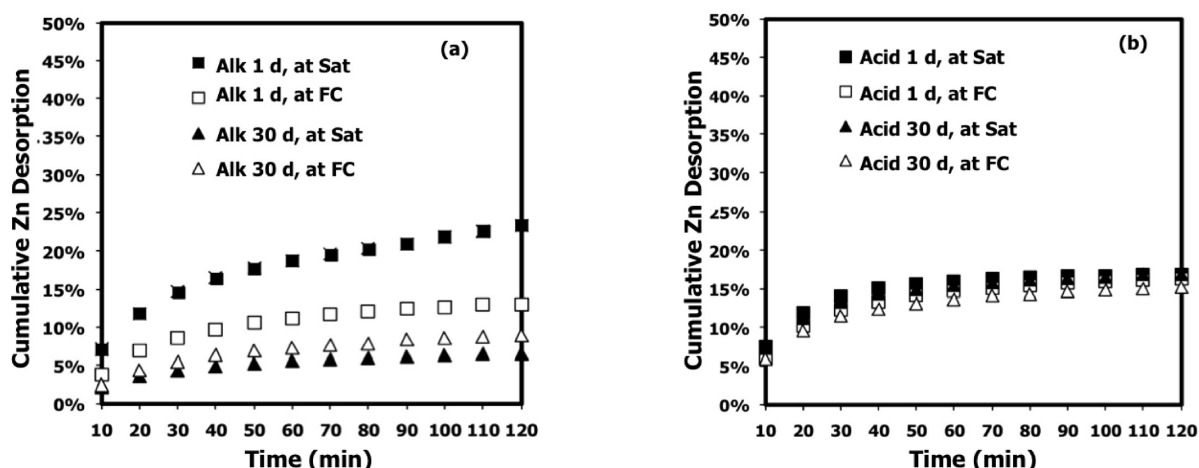


Figure 1. Cumulative Zn desorption (in %) by DTPA-TEA-Ca from (a) the alkaline soil (Alk) and (b) the acidified soil (Acid), after 1 and 30 days (d) of flooding, and draining to saturation (Sat) or field capacity (FC).

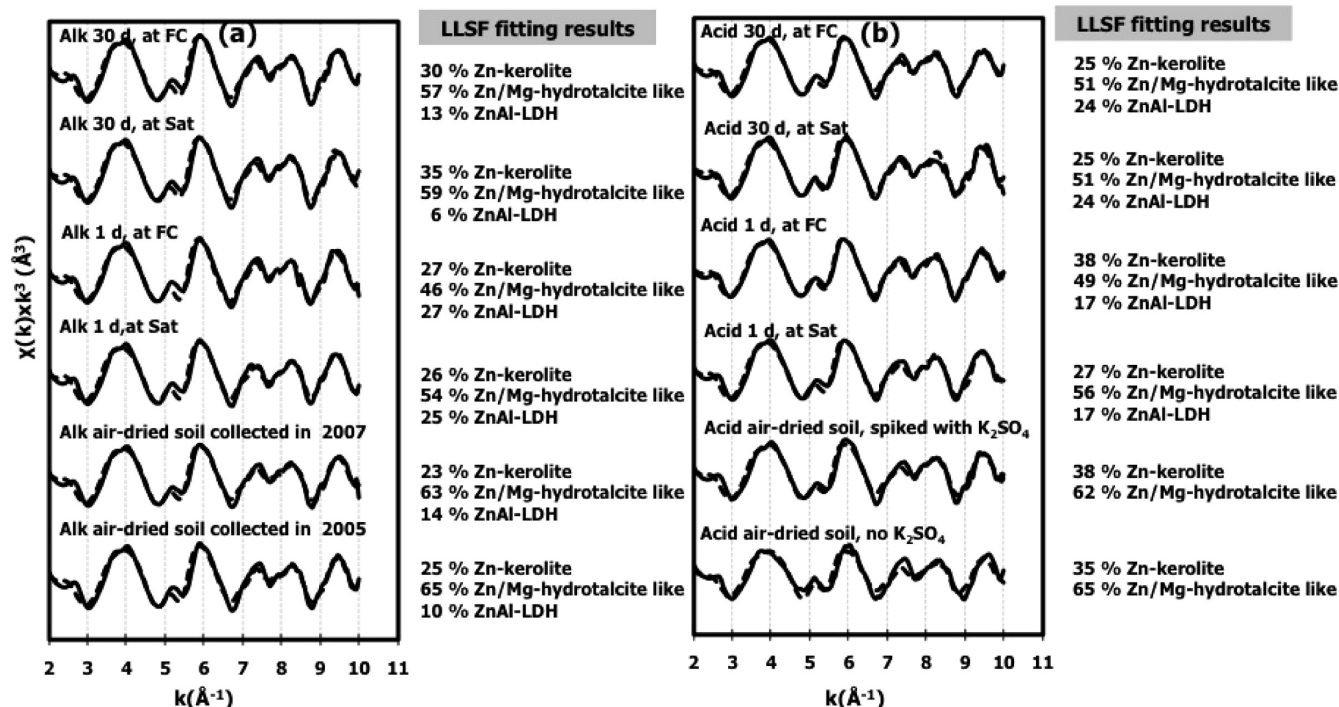


Figure 2. Linear least-squares fitting results for bulk-XAFS spectra of the (a) alkaline soil (Alk) and (b) the acidified (Acid) soil, air-dried or flooded for different periods (d = days), and drained to saturation (Sat) or field capacity (FC). Solid lines represent the k^3 -weighted χ -spectra and the dotted line represents the best fits obtained using linear least-squares fitting.

7200 times higher than in the alkaline soil, respectively. The variations in pH and Eh in the soil suspension during 30 days of flooding of the alkaline and treated soils are shown in SI. In the alkaline soil, after one day of flooding, the soil suspension pH decreased from ~ 8 to ~ 7.5 , and the Eh of the soil suspension decreased dramatically from $\sim +210$ mV to ~ -80 mV, and reached almost -300 mV after 7 days of flooding. Conversely, the soil suspension pH of the acid soil slowly increased from pH 6 to 7 while the soil suspension Eh slowly decreased from $\sim +315$ mV to $\sim +240$ mV. The decrease in soil suspension Eh in paddy soils can occur with increasing flooding period. However, it can be inhibited by several factors, including the type and amount of electron acceptors present in soil solution, i.e., NO_3^- and SO_4^{2-} .^{36–39} The slow decrease in soil suspension Eh in the acid soil could be due to the presence of nitrate in the acid soil

(Table 1). Additionally, the high S concentration and electrical conductivity (Table 1) indicate that sulfate may be present in solution, which could also act as electron acceptor in the acid soil.

Zinc Release Kinetics. After 2 h of desorption, using DTPA-TEA-Ca, the highest amount of Zn was released from the acidic soil spiked with K_2SO_4 , i.e., $\sim 20\%$ of cumulative Zn desorption (SI). For both soil pHs, less than 22% (~ 660 mg/kg) of Zn was desorbed from the soils after flooding for two different periods and draining at Sat or FC (Figure 1). The extent of Zn desorption in these experiments might have been magnified by the continuous mixing and flow rate of the stirred-flow method employed. Therefore, the actual amount of Zn that is potentially bioavailable to plants is likely lower than the ~ 660 mg/kg that was desorbed by DTPA. This hypothesis is

supported by the results from our batch experiments, which desorption protocol was based on Lindsay and Norvell,²⁷ using DTPA as the desorbing agent. These results indicated that at all soil pHs, flooding and draining conditions, less than 200 mg/kg of Zn was desorbed (not reported). During the batch and stirred-flow experiments, the highest release was found in the alkaline soil after 1 day of flooding, which could be partly due to the soil pH and Eh. Reddy and Patrick³⁶ reported that under moderately reduced to reduced condition (+300 to −200 mV) and at pH 7.5, the soluble and extractable Zn can be higher than at lower pH values and similar reduced conditions.³⁷

The release kinetics of Zn reported in this study are dramatically different from those of Cd in the alkaline and acidified soils reported in Khaokaew and Khaokaew et al.^{38,39} The cumulative release percentages of Cd in most soil samples were greater than those of Zn, especially for the treated or acid soil. These results suggest that Zn is more immobilized than Cd in the alkaline paddy soil at Mae Sot. The smaller release percentages of Zn from the paddy soil measured in this study compared to those of Cd reported in Khaokaew³⁹ could be due to a transformation of Zn mineral phases in the soils into more stable secondary phases after long periods of time.^{13,15,40} Two studies^{13,15} reported that ZnAl-LDH phases can form in soils, and greatly reduce Zn mobility. Results from XAFS analyses presented in the next section suggest that, indeed, Zn-LDH phases are present in the soils.

Zinc Speciation and Elemental Distribution. *Bulk-XAFS Analysis.* The extracted EXAFS spectra of the Zn standards, results of the principle component analysis of the bulk-EXAFS soil sample spectra, and SPOIL values of the standard samples obtained from TT analysis are shown in SI. Results from principal component analysis (PCA) showed that in the alkaline soil, the first component contributed up to 82% of the total experimental variance, and the first two components contributed 84% of the total variance in the acidified soil. The SPOIL values of the standard samples obtained from target transformation (TT) analysis are shown in SI. Because the Zn standards had similar SPOIL values, they were individually used for LLSF fitting of each bulk-XAFS spectrum of the soil samples, to determine the LLSF fit's reduced chi square values (R) per soil sample. Results revealed that in air-dried or flooded alkaline and acidified soils, two main Zn phases were found, i.e. Zn-layered double hydroxides (Zn-LDH), and Zn-phyllsilicates (Figure 2). The most dominant Zn-LDH phase found in all soil samples was a Zn/Mg-hydrotalcite-like phase, and the most dominant Zn-phyllsilicate was a Zn-kerolite. Although the soils were flooded for different periods and drained to field capacity or saturation, the nature of the phases in which Zn was distributed in the soils did not vary significantly (Figure 2). Additionally, the same Zn-phases were identified in two soil samples, taken within a two-year interval from the same location in a contaminated soil of Mae Sot. This indicated that the stability of Zn in the soil is very high.

Similarities were observed in the Fourier Transform EXAFS spectra for all soil treatments (SI). This suggests that the local molecular environments of Zn in all soil treatments are similar to each other. The similar Fourier Transform EXAFS spectra for all soil treatments also support our results obtained by LLSF analysis, which indicated that the nature of the phases in which Zn is present in the soil did not change when the soil was flooded, acidified to pH 6, and spiked with K_2SO_4 . Three main shells are present in each spectrum. The first shell, located at ~ 2 Å, is similar to the distances of Zn–O in ZnAl-LDH (2.07

Å), Zn-kaolinite (2.02 to 2.07 Å), and Zn-goethite (2.02 to 2.06 Å).¹⁵ The second shell, at ~ 3 Å, is close to the Zn–Al, Zn–Zn, or Zn–Fe distances found in Zn-kaolinite and ZnAl-LDH (3.06–3.19 Å).^{2,13,15} However, this distance also corresponds to Zn–Zn or Zn–Mg found in phyllosilicates.⁴¹ The third shell, between ~ 3.7 and 4 Å, is similar to the distance of Zn–Fe when Zn is sorbed to iron oxides, or the distance of O backscattering in O–Si shells, as found in Zn-kerolite.^{15,41}

Previous studies have suggested that $Zn_5(OH)_5(CO_3)_2$, $Zn(OH)_2$, and $ZnCO_3$ may be the primary species controlling Zn stability in alkaline soils, at high Zn concentrations.^{42,43} In soils that have a pH between 6 and 8, and very high concentrations of Zn, franklinite and sphalerite can occur.^{2,11,44–46} However, all these minerals are not dominant Zn phases in our soil samples. Franklinite, sphalerite, ZnS , $ZnCO_3$, or $Zn(OH)_2$ used as Zn standards in LLSF analyses of the soil samples did not contribute to the fits. The speciation of Zn in the alkaline and acidified soils determined by bulk-XAFS analysis in this study was different from the speciation of Cd in the same soils reported in Khaokaew and Khaokaew et al.^{38,39} Khaokaew et al.³⁸ showed that calcium carbonates and humic species were the primary phases that retained Cd in the alkaline paddy soil at Mae Sot. Also, the flooding period influenced the release of Cd. Khaokaew³⁹ reported that treating the soil with HNO_3 and K_2SO_4 changed the nature of the mineral phases associated with Cd and enhanced Cd desorption capacity in the paddy soils of Mae Sot. In these soils, the differences of Cd and Zn chemistry could be due to soil conditions, especially pH, ionic radius, affinity of these two metals with clay minerals, and their total concentration in the soil samples. Several studies have shown that Cd^{2+} and Ca^{2+} can substitute for each other in minerals, e.g. phosphate and carbonate minerals, due to the similar ionic radius of these two elements.^{42,47,48} Zinc can incorporate in Al oxyhydroxide phases during aging, which are precursor minerals of LDH phases.^{49,50} This is not the case with Cd, since the ionic radius of Zn^{2+} is smaller than that of Cd^{2+} . The formation of Zn-phyllsilicate clays and Zn-LDH phases in soils, at various pH values, have been reported in several studies.^{6,12,15,16,51–54} The LDH phases have a general structural formula of $[Me^{2+}_{1-x}Me^{3+}_x(OH)_2]^{x+} \cdot (x/n)A^{n-} \cdot mH_2O$, where Me^{2+} and Me^{3+} represent divalent and trivalent cations, respectively; x is equal to the ratio $Me^{3+}/(Me^{2+} + Me^{3+})$ and A^{n-} is the interlayer anionic species, with charge $n-$ neutralizing the excess positive charge.^{51,52} Hydrotalcite, a Mg–Al layered double hydroxide, with a formula of $[Mg_3Al_2(OH)_{16}][CO_3] \cdot 4H_2O$, is one of the most abundant LDH phases occurring in alkaline soils, and the most common hydroxide compound containing aluminum.^{55,56} Juillot et al.⁵² showed that a Zn/Al-hydrotalcite phase was dominant in Pb and Zn smelter-impacted soils. Kerolite is a poorly crystalline, hydrated, nonexpanding, talc-like trioctahedral phyllosilicate, found in various depositional carbonate environments, e.g. basaltic caves and smelter-impacted soils.^{12,58,59} The Zn-bearing kerolite standard used in our study, which has a general formula of $[Si_4(Mg_{3-x}Zn_x)O_{10}(OH)_2 \cdot H_2O]$, was the same standard used in Manceau et al.¹² This mineral phase was found to be dominant in Zn-contaminated soils in an abandoned Zn-smelter site.¹² Therefore, it is possible that Zn-LDH phases, i.e. Zn/Mg hydrotalcite-like and ZnAl-LDH, and Zn-kerolite are formed in the paddy soil at Mae Sot. These phases are more stable than hydrozincite, $Zn(OH)_2$ and $ZnCO_3$,^{11,34,52} and can thus greatly reduce the bioavailability of Zn in soils. This could explain why less than 22% cumulative amount of Zn was

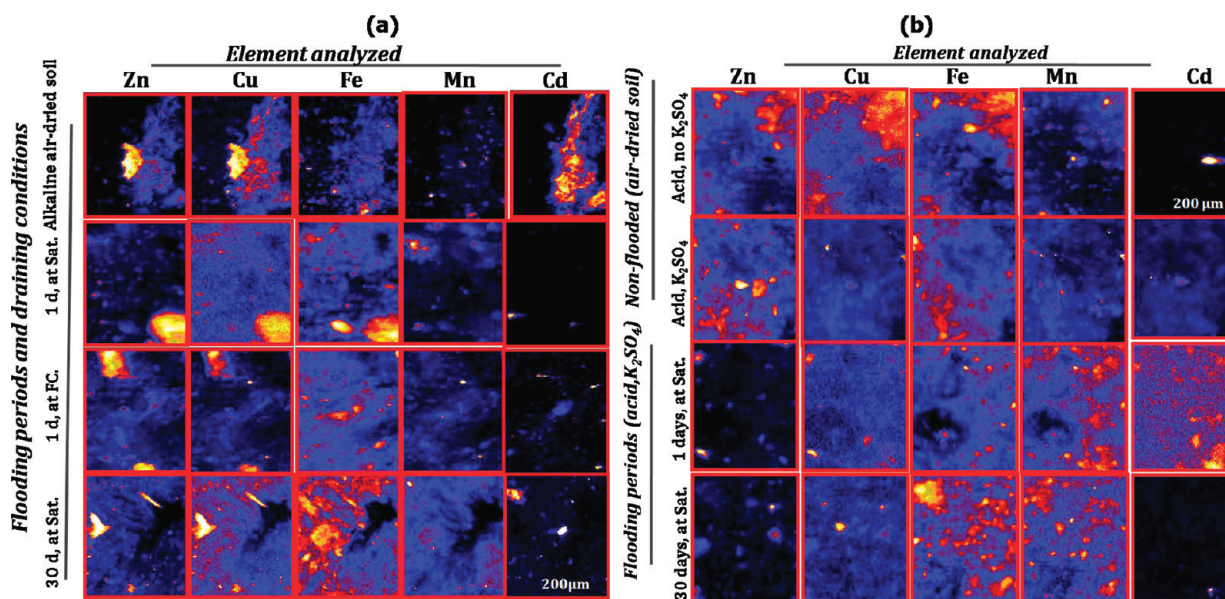


Figure 3. Micro-XRF maps, showing the elemental distribution of zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), and cadmium (Cd) in the (a) alkaline air-dried soil, flooded for 1 and 30 days and drained to saturated (Sat) or field capacity (FC), and (b) in the acidified air-dried soil, not spiked with K_2SO_4 , the acidified air-dried soil spiked with K_2SO_4 , and the acidified soil spiked with K_2SO_4 flooded for 1 and 30 days and drained to saturation. In each map, the brightest color (white) represents the highest count or highest concentration of an element, while the darkest color represents the lowest count or lowest concentration of an element.

desorbed from the soil samples during stirred-flow experiments, even when the soil was acidified to pH 6, spiked with K_2SO_4 , and flooded for different periods (Figure 1).

Micro-XRF Maps. Micro-XRF maps of Zn, Cd, Cu, Fe, and Mn distributions in the alkaline and acidified soils, flooded for different periods, are depicted in multicolor maps (Figure 3). In each map, the brightest color (white) represents the highest count or highest concentration of an element, while the darkest color represents the lowest count or lowest concentration of an element. Our μ -XRF results indicated that Zn was locally distributed with Cu in most samples, and to a minor extent with Fe and Mn (Figure 3). These μ -XRF maps also show that Cd was not distributed with Cu, Fe, and Mn, but rather with Ca, as reported in Khaokaew et al.³⁸ In all samples, no correlation between Cd and Zn could be observed (Figure 3 and SI-8). This agrees with our XAFS results, since those reported in this study indicated that Zn is associated with phyllosilicates and Zn-layered double hydroxides, while LLSF fitting reported in Khaokaew et al.³⁸ showed that Cd is mainly associated with calcium carbonate. Two studies showed that Zn was mainly sorbed to Fe and Mn oxides in the paddy soils of Mae Sot, based on elemental correlation plots of soil fractions obtained from sequential extractions.^{60,61} Although it is likely that Fe and Mn oxides can indeed retain some Zn in the soils, they are not the main phases that immobilize Zn, based on the LLSF and μ -XRF results (Figure 3 and SI-8). Additionally, results from LLSF analyses performed on all soil samples showed that the Zn-standards containing Fe, Mn, and/or Cu (i.e., ZnFeO, Zn-goethite, Zn-ferrihydrite, Zn-hydrous manganese oxide (HMO), Zn-CuS, Zn-CuCO₃, Zn-humic acid, and Zn-fulvic acid), did not significantly contribute to the fits (Figure 2). This suggests that Zn was not mainly sorbed to pure mineral phases of Cu, Mn, and/or Fe. The associations between Zn and Cu, Mn, or Fe observed in μ -XRF maps could be rather due to sorption of these elements to clay minerals, e.g. on the clay surfaces or in their interlayers, or their

incorporation in the clay structures.^{15,16,51,61} Further molecular investigations should be carried out to confirm these hypotheses and better understand Zn chemistry in Cd–Zn cocontaminated paddy soils.

■ ASSOCIATED CONTENT

Supporting Information

Zinc sorption on CuCO₃, hydrotalcite, a Mg-hydrotalcite-like phase, CuS, CuCO₃, humic acid, soil suspension pH and Eh of the alkaline and acidified Thai paddy soils over 30 days of flooding, bulk EXAFS k^3 weighted spectra of Zn reference samples, results of the principle component analysis of the bulk-EXAFS soil sample spectra, and target transformation SPOIL values of selected reference spectra obtained by PCA analysis, the Fourier Transform EXAFS spectra for all soil treatments, and μ -XRF correlation maps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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