Speciation and Release Kinetics of Cadmium in an Alkaline Paddy Soil under Various Flooding Periods and Draining Conditions

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S *Supporting Information*

ABSTRACT: This study determined Cd speciation and release kinetics in a Cd−Zn cocontaminated alkaline paddy soil, under various flooding periods and draining conditions, by employing synchrotron-based techniques, and a stirred-flow kinetic method. Results revealed that varying flooding periods and draining conditions affected Cd speciation and its release kinetics. Linear least-squares fitting (LLSF) of bulk X-ray absorption fine structure (XAFS) spectra of the air-dried, and the 1 day-flooded soil samples, showed that at least 50% of Cd was bound to humic acid. Cadmium carbonates were found as the major species at most flooding periods, while a small amount of cadmium sulfide was found after the soils were flooded for longer periods. Under all flooding and draining conditions, at least 14 mg/kg Cd was desorbed from the soil after a 2-hour desorption experiment. The results obtained by micro X-ray fluorescence (μ-XRF) spectroscopy showed that Cd was less associated with Zn than Ca, in most soil samples. Therefore, it is more likely that Cd and Ca will be present in the same mineral phases rather than Cd and Zn, although the source of these two latter elements may originate from the same surrounding Zn mines in the Mae Sot district.
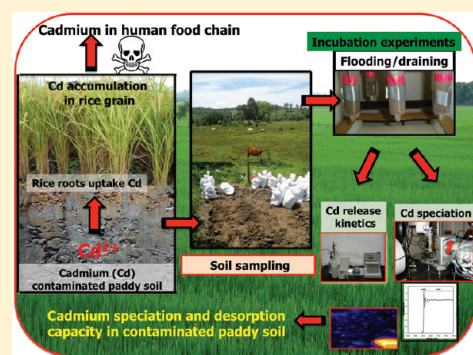
INTRODUCTION

Cadmium is toxic to humans, animals, and plants. Humans can be exposed to this metal via the consumption of Cd-contaminated foods, particularly rice grain.[1−3] Although some soils can naturally contain Cd, the main sources of this metal, when present at high concentrations in soils, often originate from anthropogenic activities such as zinc mining and smelting operations.[3−5] The International Water Management Institute (IWMI) reported in 2003 that Zn-mining activities in the Mae Sot district, in the Northern part of Thailand, have resulted in Cd contamination of irrigation water, paddy soils, and rice grain. Villagers in this district risk developing severe chronic health issues from Cd exposure via contaminated soils and crops.[2,6,7] Cadmium contamination in paddy soils has been reported in several countries, including China, Japan, Bangladesh, Thailand, and Korea.[2,8−11] A number of in-situ and ex-situ remediation methods have been employed to minimize Cd bioavailability.[10,12−16] However, applying these remediation methods at the field scale is intricate and often expensive. To optimize their effectiveness, understanding metal speciation in contaminated soils is needed.

In lowland rice culture, paddy soil undergoes a flooding and draining cycle (i.e., anaerobic and aerobic conditions), which can modify the biological and chemical properties of the soil, especially pH and Eh. These modifications of soil properties may affect Cd speciation present in the Cd-contaminated paddy soils. This research was aimed to investigate Cd speciation and release kinetics in a Cd−Zn cocontaminated alkaline paddy soil, subjected to various flooding periods and draining conditions. Synchrotron-based X-ray absorption spectroscopy (XAS) techniques were employed to determine Cd speciation, distribution, and association with other elements in the soil. A stirred-flow technique was used to measure Cd release kinetics. Results reported in this study will be useful in choosing the best strategy to remediate Cd in paddy soils, especially at the Mae Sot district.

MATERIALS AND METHODS

Study Site and Soil Characterization. The IWMI[2] measured Cd 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 100 mg/kg of Cd, 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 m^2, using a compositing technique.[17] A single composite sample was then used for incubation experiments and basic physicochemical analyses. Basic soil physicochemical properties, such as texture, pH, elemental concentrations, and organic matter content, were determined by standard procedures.[18−21]

Table 1. Physicochemical Properties of the Soil Used in This Study

particle size (%)			soil pH		O.M. (%)	total concentration (mg/kg)							
sand	silt	clay	water (1:1)	buffer (Adam−Evans)		Cd	Zn	Fe	Ca	Cu	Mn	Mg	S
12	49	39	7.3	8.1	4.3	142	3050	18,328	34,360	25	878	5793	281

total soluble salts	0.3 mmhos/cm
nitrate	1.7 mg/kg
clay mineralogy	kaolinite > illite

Incubation Experiment: Flooding and Draining Conditions. To investigate Cd speciation and release kinetics at environmental conditions relevant to lowland rice culture, we employed different flooding periods and draining conditions to conduct incubation experiments. Four periods of flooding and two draining conditions were selected to mimic the environmental settings found in paddy soils undergoing lowland rice culture. The four periods of flooding were 1, 7, 30, and 150 days, based on the understanding that the chemical properties of paddy soils usually reach apparent equilibrium within 30 days,[22] and the longest period of flooding in lowland rice does not exceed 150 days. 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 are provided in the Supporting Information (SI). At the end of the flooding period, samples were drained to saturation or to 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 a pH- and Eh-meter, respectively.

Desorption Experiments. Cd desorption kinetics were conducted using a stirred-flow technique, with soil samples flooded for different periods and draining conditions. The experimental set up was similar to the one used in ref 23. Diethylenetriamine pentaacetate (5 mM)−triethanolamine (100 mM)−$CaCl_2$ (10 mM) (DTPA-TEA-Ca) was used as a desorption agent, at pH 7.3.[24] The experiments were run for 120 min at a flow rate of 0.8 mL·min^{-1}, mixing rate at 500 rpm, and the effluent was collected in 12 tubes, one every 10 min. Each experiment was run in duplicate, and Cd concentrations were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES) to subsequently calculate cumulative Cd desorption percentages.[25]

Cadmium Speciation, and Elemental Distributions by XAS Techniques. *Cd Standard Preparations.* Cadmium standards considered for XAS analyses included some Cd phases, i.e., $CdCO_3$, CdS, $Cd(OH)_2$, $Cd(NO_3)_2$, $CdSO_4$, and Cd sorbed to some mineral phases, i.e., Cd-ferrihydrite, Cd-goethite, Cd-gibbsite, Cd-humic acids, Cd-montmorillonite, Cd-kaolinite, Cd-$CaCO_3$, and Cd-illite.

The experimental procedures for Cd sorbed to $CaCO_3$, ferrihydrite, goethite, clay minerals, and humic acids are reported in SI.

Solid compounds of CdS, $Cd(OH)_2$, $Cd(NO_3)_2$, $Cd(SO_4)$, and $CdCO_3$, ACS reagent grade, were also mounted on sample holders for XAFS analyses after mixing each of them with 95% boron nitride.

Bulk XAFS Spectroscopy. The Cd standards and soil samples were analyzed by bulk-XAFS at the cadmium K-edge (26711 eV), at beamline 10-ID, Advanced Photon Source (APS), Chicago, IL,

and at beamlines Bio 7-3 and 11-2, Stanford Synchrotron Radiation Laboratory (SSRL), Stanford University, CA. The energy was calibrated from the first inflection point of the first derivative of a Cd metal foil X-ray absorption near edge structure (XANES) spectrum (K-edge, 26711 eV). Each XAFS spectrum was collected with an energy range from 150 eV below the Cd absorption edge, to k values of 12 Å^{-1} above the absorption edge, in either fluorescence or transmission modes.

Each raw bulk-XAFS spectrum of Cd−K edge was normalized to obtain the extended X-ray absorption fine structure (EXAFS) function, using Athena version 8.0.054 and the SixPack software package.[26,27] The mineral phases in which Cd 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. The energy calibrations for LLSF analyses of EXAFS functions of soil and reference samples were set at the same value (26711 eV). The PCA and LLSF were performed using the EXAFS function, which was k^3 weighted, with k values between 2 and 8.5 Å^{-1}. SPOIL values obtained from TT analysis were used to select principal components for LLSF analysis.

Sulfur XANES analyses on the air-dried soil sample and sulfur standards (CdS, $CdSO_4$, and Cd-humic acids) were performed at beamline X15B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY. The samples were placed in a small hutch box filled with He and equipped with a Ge fluorescence detector. Elemental S was used to calibrate the Si(111) monochromotor, and the adsorption edge was set to 2472 eV. The energy range of the incident X-ray beam was from 2380 to 2550 eV with step size of 0.2 eV. Each raw spectrum of S K-edge was normalized using Athena version 8.0.054 and the SixPack software package.[26,27] The shape of the XANES spectrum of the air-died soil sample was then compared to those of the sulfur reference samples.

μ-XRF and μ-XANES Analyses. Micro X-ray fluorescence and μ-XANES analyses were conducted at beamline 13-ID-C (APS), to determine elemental distributions and Cd speciation in the contaminated paddy soils. The μ-XRF maps were 200 μm^2 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. Micro XANES spectra were then collected, from about −100 eV below to about 200 eV above the Cd−K edge, at local regions observed in μ-XRF maps where Cd was relatively highly concentrated. Three scans were taken per location to maximize the signal-to-noise ratio.

■ RESULTS AND DISCUSSION

Soil Analysis. Bulk physicochemical properties of the alkaline Thai paddy soil are shown in Table 1. The total concentration of Cd in the soil was 142 mg/kg, which is nearly 1000 times higher
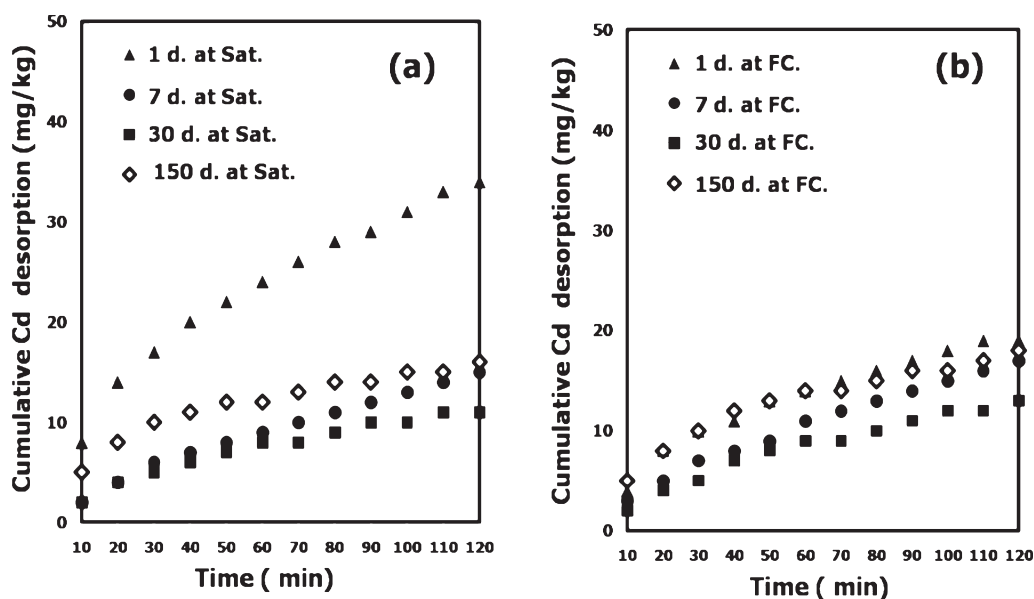
Figure 1. Cumulative Cd desorption (mg/kg) by DTPA-TEA-Ca, after 1, 7, 30, and 150 days of flooding and draining to (a) saturation (Sat), and (b) field capacity (FC).

than the background Cd concentration found in Thai soils, i.e., 0.15 mg/kg.[28] Soil organic matter content was 4.3%, and the total Zn and S concentrations were 3,050 and 282 mg/kg, respectively. Kaolinite was the dominant clay mineral in the soil. The variations in pH and Eh in the soil suspension during 30 days of flooding are shown in SI. The high soil pH is due to application of limestone to the fields by farmers to reduce adverse effects of excessive soil Cd and Zn on soybean and rice yields.

Cadmium Release Kinetics. Desorption experiment results showed that a small amount of Cd was released, although the soils were subjected to various flooding periods and draining conditions. The cumulative amount of Cd released during 2 h, in most treatments, was about 14 mg/kg, or 10%, calculated using the equation reported by ref 25, which gives the expression of the cumulative desorption of an element using a stirred-flow technique. Small variations in the amounts of Cd released from the samples drained to the saturated point or field capacity were observed when the period of flooding was varied (Figure 1). Varying the flooding period seemed to affect Cd release from the soils only to a minor extent, and varying draining conditions had an even lesser effect on Cd desorption. These results support those reported in ref 29, which showed that Cd sorption to soil components was not significantly affected by soil moisture content.

Cadmium Speciation and Elemental Distribution. *Bulk XAFS Analysis.* The extracted XAFS spectra of Cd standards are shown in Figure 2a. 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 PCA showed that three components contributed ~81% of the total experimental variance. The standards that gave excellent and good SPOIL values were selected to perform LLSF analyses. Linear least-squares fitting was performed with the set of three standards that provided the best fit for each bulk-XAFS spectrum of the soil samples. The LLSF fitting results revealed that Cd speciation varied when the soil was subjected to different flooding periods and draining conditions (Figure 2b). For the air-dried soil and the soil flooded for one day, Cd-humic acid 1 standard contributed up to 50% of the fit. After the soil was flooded for 7 days, the contribution

of Cd-humic acid 1 in the fit was no longer noticeable, and Cd carbonate species, i.e., Cd-CaCO$_3$ and CdCO$_3$, became the most dominant. These two standards also dominated the fit for the soil flooded for 30 and 150 days, and a small amount of CdS also contributed to the fit. The standard representing Cd bound to kaolinite contributed at least 22% of the fit for all spectra shown in Figure 2b of the soils flooded for different periods. Results from our study show that Cd is associated with several mineral phases during flooding periods in the paddy soils, including carbonates, kaolinite, ferrihydrite, humic acid, and CdS. This differs from previous studies, which suggested from macroscopic observations that Cd is mainly present as CdS in paddy soils during flooding periods.[5,12,13,30] Studies have shown that humic acids enhance Cd sorption to hematite, goethite, or kaolinite.[31−33] Humic acids can directly bind metals via their functional groups, and sorb to oxides and clay minerals, allowing the formation of ternary surface complexes.[32,34] Cadmium bound to humic acids is not stable, especially at lower pH values.[35,36] Some amount of Cd bound to humic acids could be released to solution during our flooding experiments, which could be partly due to a slight decrease in pH and a dramatic decrease in Eh during the flooding period (SI). The amount of Cd released from humic substances could bind to other adsorbents, such as carbonate minerals and kaolinite;[37,38] the latter is the most dominant clay mineral in the paddy soils used in this study. The LLSF showed that the Cd-kaolinite, Cd-CaCO$_3$, and CdCO$_3$ standards contributed significantly to the fits for the soils flooded for long periods of time. One earlier study has shown that at pH above 6, Cd can bind on the edge sites of kaolinite as inner-sphere complexes,[39] and carbonate minerals are important sorbents for metals in alkaline soils.[40,41] Cadmium and calcium can compete for adsorption sites on calcite, since Cd^{2+} and Ca^{2+} have similar hydrated ionic radii.[40,42−45] Therefore, a mix of (Cd,Ca)CO$_3$ precipitates can occur at calcite surfaces.[46] Studies have shown that mononuclear Cd^{2+} can chemisorb to the calcite surface at low Cd concentrations, and/or precipitate, to form CdCO$_3$, at high Cd^{2+} loadings.[42,47] The formation of Cd carbonates, Cd-kaolinite, and CdS species in the alkaline paddy soil used in this study could limit
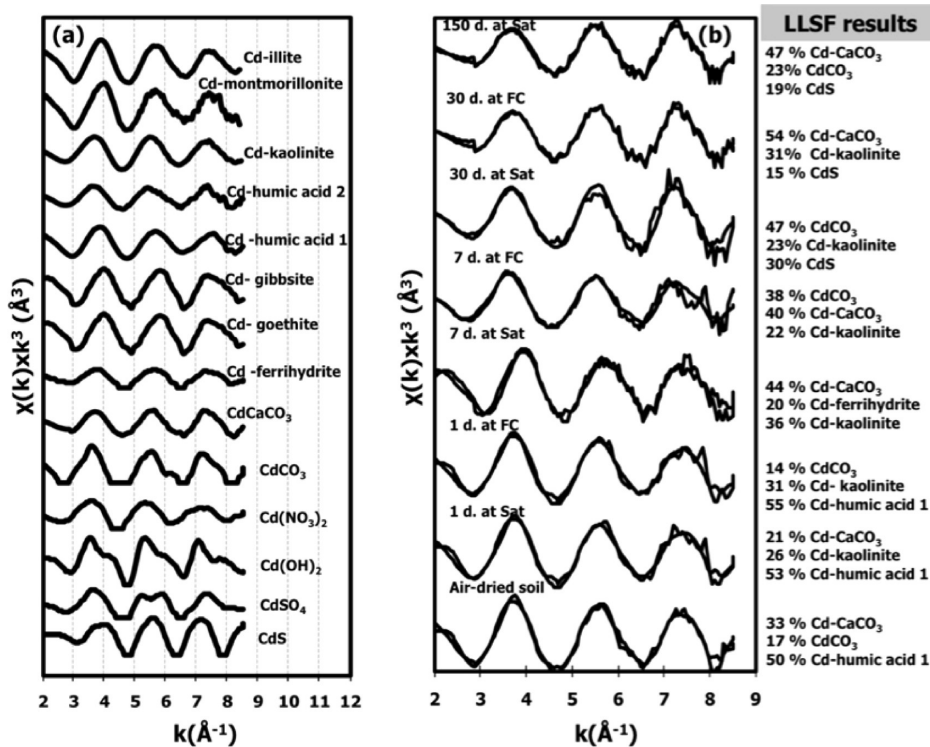
Figure 2. (a) Bulk EXAFS k^3 weighted spectra of Cd reference samples, and (b) linear least-squares fitting results for bulk-XAFS spectra of the alkali air-dried Thai paddy soil under various flooding periods and draining conditions. Solid lines represent the k^3 weighted χ-spectra and the dotted line represents the best fits obtained using linear least-squares fitting.
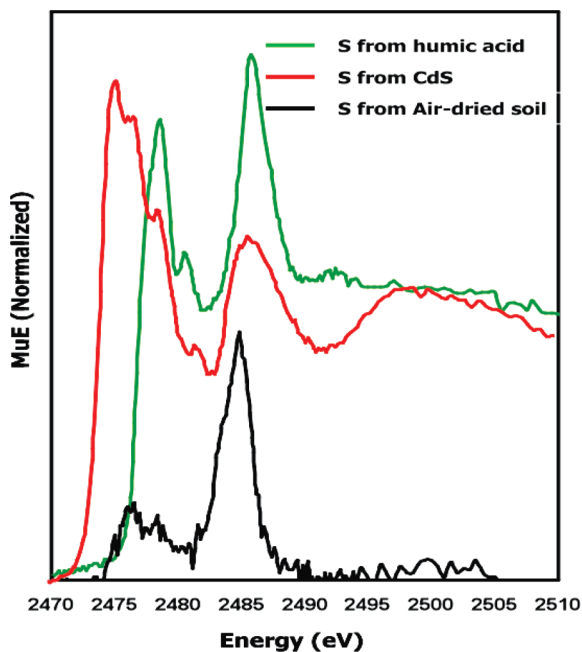

Figure 3. Bulk XANES of sulfur-K edge spectrum of the air-dried soil, compared to bulk XANES spectra of CdS and Cd-humic acid 1 standards.

the release of Cd from the soil. This could explain a small release of Cd found in our study (Figure 1).

The results reported in our study show that Cd bound to ferrihydrite was only noticeable in the LLSF fit for the soil flooded

for 7 days and drained to field capacity, and gave a relative small contribution to the fit (20%). Therefore, although Fe-oxides may contain Cd in our soil sample, they are not the principal Cd sorbents in the alkaline paddy soil analyzed in this study. A previous study found high correlation between the spatial distribution of Cd and Fe in 79 contaminated soil samples from Mae Sot, and concluded that Cd was mostly sorbed to Fe-oxides, based on elemental atomic ratio plot extractograms obtained from continuous-flow desorption experiments, using different extracting reagents in the influent solution.[48] However, no direct microscopic evidence, probing Cd in situ in the soil, was reported in this study. Using extracting reagents to determine the compartmentalization of one element in a soil is often inaccurate because reabsorption and redistribution of the element can occur, which can over- or underestimate the elemental concentration.[49,50] Additionally, extraction procedures only determine the pools in which an element is present in the soil, e.g., the exchangeable, acid soluble, reducible, and oxidizable phases,[49] but do not identify the mineral phases in which the element is present.

A bulk XANES spectrum taken at the S K-edge for the air-dried soil sample featured multi white lines, indicating that S in the soil is present in multiple oxidation states,[51,52] and is similar to the bulk XANES spectrum of the organic sulfur standard (Figure 3). The multiple oxidation states of S in the bulk XANES spectrum of the organic sulfur standard (Figure 3) are observed since sulfur in soil organic matter can exhibit several oxidation states.[51,53] Additionally, the white line position in the XANES spectrum of the air-dried soil is almost at the same energy value as the one found in the XANES spectrum of organic sulfur ($\sim$1 eV different). This shift could be due to a lower S oxidation state in the soil sample than in the organic sample standard.[51] Most of

soil sulfur is present in an organic form, although it can be also present in an inorganic form, to a minor extent.[52,54] Sulfur sorption to organic matter typically occurs in both temperate and tropical soils.[52] Based on S-XANES results shown in Figure 3, organic sulfur is the most dominant S species in the air-dried soil. Our results are supported by those reported in ref 51, which showed that S was distributed mainly with humic acid in the soil samples. Therefore, organic sulfur (e.g., monosulfide and disulfide from humic acid[55]), can occur in the paddy soils of Mae Sot district, and could potentially bind to Cd in the soil.[56]

Micro-XRF and μ-XANES Analyses. Micro-XRF maps of Cd, Ca, Zn, and Fe distributions in the air-dried soil and the soils flooded for different periods are shown in Figure 4a. The brightest color in these maps represents the highest count or highest concentration of an element, while the darkest color represents the lowest count or lowest concentration of an element. These maps show that Cd is distributed both in regions where Cd is diffuse in the soils and in regions where Cd is locally concentrated (hot spots). Cadmium present in the air-dried soil seems to be associated with Zn and Fe at regions where these elements are diffuse, but not in Cd hotspot regions (Figure 4a). After the soil was flooded for different periods, Cd became less diffuse in the soil and seems to concentrate more locally. The locations of these Cd hot spots are not similar to the Zn and Fe hot spots observed in the μ-XRF maps of the flooded soils. However, the locations of some Cd hot spots are similar to those of Ca hot spots observed in the μ-XRF maps of the soils flooded for 7 and 30 days (Figure 4a). Micro-XANES spectra taken at the Cd K-edge were collected at two Cd hot spots in the μ-XRF map of the soil flooded for 30 days and drained to saturation (Figure 4a and b). One notices that the shapes of these two XANES spectra are different from each other, suggesting that Cd is present in different mineral phases at these two locations, which are separated by only a few hundred micrometers in the
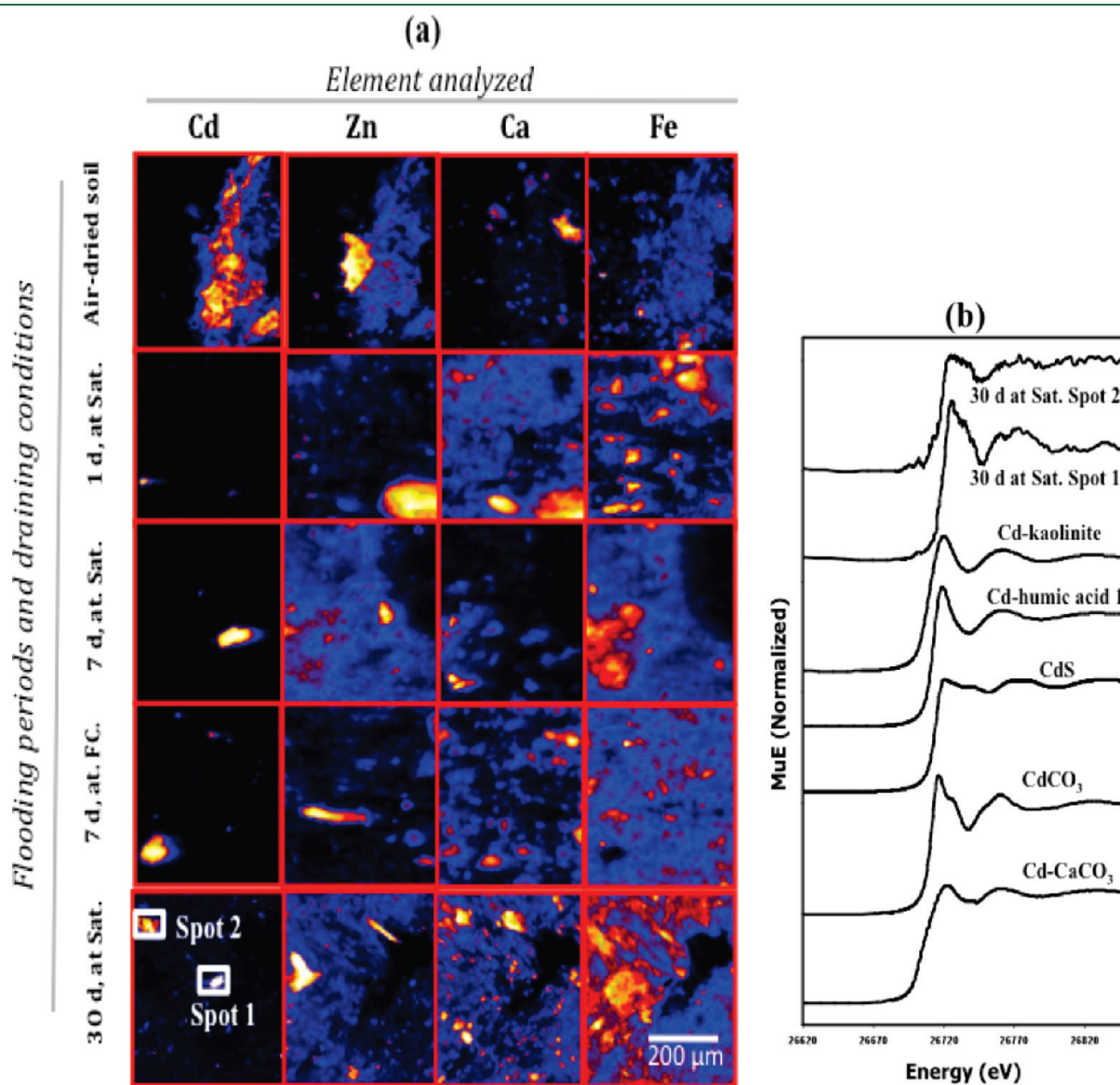

Figure 4. (a) Elemental distributions of cadmium (Cd), zinc (Zn), calcium (Ca), and iron (Fe) in air-dried soil, in the soil flooded for different flooding periods and draining conditions using μ-XRF mapping; and (b) μ-XANES spectra, at the Cd—K-edge, of Cd-CdCO$_3$, CdCO$_3$, CdS, Cd-humic acid 1, and Cd-kaolinite standards, and μ-XANES spectra taken at spots 1 and 2.

μ-XRF map. The shapes of these two μ-XANES spectra were compared with those of CdCO$_3$, Cd-CaCO$_3$, CdS, and Cd-kaolinite XANES spectra, i.e., the four Cd phases that were identified by LLSF analysis for the soil flooded for 30 days (Figure 2b). The shape of the μ-XANES spectrum taken at the first location (spot 1) is similar to those for Cd-CaCO$_3$ and CdS XANES spectra, while the shape of the μ-XANES spectrum taken at the second location (spot 2) is similar to the CdCO$_3$ and Cd-kaolinite XANES spectra. These results support our LLSF results, which showed that Cd can be distributed in several phases in the contaminated paddy soils taken from Mae Sot. Additionally, our results suggest that Fe phases are not important Cd scavengers, which differs from earlier reported results.[48,57] These two latter studies indicated that Cd was mainly sorbed to Fe oxide minerals in the contaminated soils of Mae Sot. However, no direct microscopic evidence, probing Cd in situ in the soil, was reported in these two studies.

Based on LLSF, XRF-mapping, and micro-XANES, several phases containing Cd, under different flooding periods and draining conditions, were found in the Cd−Zn cocontaminated alkaline paddy soil from the Mae Sot district. Under most flooding and draining conditions, at least 14 mg/kg was desorbed from the alkaline Thai paddy soil using DTPA-TEA-Ca, after 2 h of stirred-flow experiments. This amount of Cd that can be potentially desorbed poses a threat to humans.[2,3,10,12,30,58,59] This study demonstrates the urgent need for remediation actions to minimize Cd risks from the contaminated paddy soils in Mae Sot.

ASSOCIATED CONTENT

⑤ Supporting Information. Cadmium sorption on CaCO$_3$, ferrihydrite, goethite, gibbsite, humic acids, and clay minerals, soil suspension pH and Eh of the alkaline Thai paddy soil over 30 days of flooding, 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. This material is available free of charge via the Internet at http://pubs.acs.org.

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