Water incubation-induced fluctuating release of heavy metals in two smelter-contaminated soils

Bin Yang[1,2], Yunzhe Cao[2], Jie Ren[3], Mei Wang[1,2], Huilong Luo[1,2], Fasheng Li[1,2,*]

1. College of Water Science, Beijing Normal University, Beijing 100875, China., E-mail: qingyamu@126.com
2. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
3. School of Ecology and Environment, Inner Mongolia University, Hohhot 010021, China

ARTICLE INFO

ABSTRACT

The soil moisture regime can affect the release of heavy metals in soil. In the previous studies, slightly polluted soils or artificially contaminated soil samples were considered to investigate the effect of soil moisture. We used highly smelter-contaminated and aged soils to study the release of typical heavy metals (Cu, Zn, Cd and Pb) induced by water incubation in batch experiments with characterization via speciation and X-ray diffraction analyses (XRD). The results show that the leachable concentrations of the heavy metals increased slightly in the first 30 days, decreased drastically between 30 and 90 days, and immobilized relatively constant thereafter. The fluctuation was ascribed to the changes of soil Eh and pH, the reductive dissolution of crystalline iron oxides, the formation of new amorphous iron oxides, the absorption of dissolved organic matter and the precipitation of metal sulfide. Speciation analysis indicated that a proportion of the soil heavy metals was transformed from an exchangeable fraction to a less labile fraction after water incubation. And the presence of a lead iron oxide phase and the peak increasing of zinc sulfide were observed via XRD analyses. Finally, water incubation restrained the release of heavy metals after 180 days of incubation, and reduced the leachability of Cu, Zn, Cd and Pb by as much as 1.61%–7.21% for soil A and 0.43%–3.36% for soil B, respectively. The study findings have implications for the formulation of risk control and management strategies for heavy metals in smelter-contaminated soils.

Introduction

Smelting activities worldwide have resulted in the release of large amounts of heavy metals that pose a threat to human health owing to their toxicological effects (Vespa et al., 2010; Girault et al., 2016). Most of heavy metals, such as Cu, Zn, Cd and Pb, are known to be highly toxic or carcinogenic (Qu et al., 2018; Mohamed et al., 2017). For example, Cu causes liver and kidney disease (Gaetke and Chow, 2003); Zn promotes oxygen absorption's decreasing and increasing of heart rate (Plum et al., 2010); while chronic exposure to Cd and Pb can induce various cancers (Williams et al., 2009; Li et al., 2014). Although large-scale smelting activities in the past several decades have significantly contributed to modernization in China, the

* Corresponding author. E-mail: lifs@craes.org.cn. (Fasheng Li).

resulted heavy metal contamination of soils has become a serious problem (Zhao et al., 2015).

Toxicity of heavy metals mainly depends on their release, which is a function of physicochemical properties and environmental conditions (Wu et al., 2006). The soil moisture regime, one of soil properties which was most likely to change in field conditions, plays a key role in controlling the release of heavy metals and therefore influences their potential risk in contaminated soils. It can impact pH, redox potential (Eh), organic matter and iron oxide species of soil, and consequently, may influence the redistribution of heavy metals and further affect their release (Zheng and Zhang, 2011). Han and Banin (1997, 1999) and Han et al. (2002) reported on the transformations and redistributions of heavy metals in arid-zone soils under different moisture regimes. Kashem and Singh (2001) observed greater reductions in Cd, Ni and Zn solubility in flooded soil. Mukwaturi and Lin (2015) found that Zn was initially released, accompanied by the reductive dissolution of iron compounds, and then re-immobilized under water inundation conditions. Widely adopted water management practices in paddy soils, such as flooding and drainage, have been used to restrain the release of Cd and As (Arao et al., 2009; Dittmar et al., 2010; Hu et al., 2015; Khaokaew et al., 2011; Wan et al., 2018). These studies have shown that the release of soil heavy metals can be influenced by changing the soil moisture regime and therefore the leaching risk of heavy metals can be controlled.

Most of the previous studies have mainly focused on slightly contaminated soils and soils artificially contaminated by spiking with fresh heavy metals (Zheng and Zhang, 2011; Han and Banin, 1997, 1999; Han et al., 2002; Kashem and Singh, 2001; Mukwaturi and Lin, 2015; Arao et al., 2009). In fact, there is a significant difference between these soils and the real industrially contaminated soils. And very few studies have concerned the effect of moisture regimes on the release of heavy metals in highly contaminated and aged soils. To achieve this goal, batch experiments of water incubation were carried out by incubating the soils with different moisture regimes in a curing chamber. The aim of the present study was to investigate the release of Cu, Zn, Cd and Pb induced by water incubation in two highly contaminated and aged soils. Speciation and X-ray diffraction analyses were carried out to identify the mechanism. The information obtained from this study will contribute to the development of appropriate strategies to assess and manage the risk of heavy metals in contaminated soils.

1. Materials and methods

1.1. Soil collection and soil properties

Two typical smelter-contaminated soil samples (denoted soils A and B) were collected from a depth of 0–15 cm. Soil A was collected from an abandoned lead and zinc smelting site with nearly 20 years of production history in Baiyin, Gansu province, northwest China (36°33′17″N and 104°12′45″E). Soil B was collected from an iron and steel smelting site

Table 1 – Selected physicochemical characteristics of soil samples.

Parameter	Soil A	Soil B	Permissible limits
Clay [a] (%)	2.98	3.54	/ [i]
pH [b]	6.36	8.60	/
OM [c] (%)	5.74	4.19	/
CEC [d] (cmol/kg)	23.88	36.35	/
Fe_{DCB} [e] (g/kg)	21.36	33.76	/
Fe_{AOX} [f] (g/kg)	8.26	9.83	/
Fe_C [g] (g/kg)	13.10	23.93	/
Cu [h] (mg/kg)	1608.25	656.25	400.00
Zn [h] (mg/kg)	15325.24	19846.67	500.00
Cd [h] (mg/kg)	321.81	512.13	1.00
Pb [h] (mg/kg)	9528.75	3781.67	500.00

[a] Percentage clay with a particle size less than 2 μm.
[b] Aqueous soil pH measured at a ratio of 1:2.5 (W/V) H_2O.
[c] Soil organic matter determined via loss on ignition (550°C, Kennou et al., 2015).
[d] Cation exchange capacity determined via extraction with CH_3COONH_4 (pH 7, Kennou et al., 2015).
[e] Free iron oxides, dithionite-citrate-bicarbonate–extractable iron oxides.
[f] Amorphous iron oxides, ammonium oxalate–extractable iron oxides.
[g] Crystalline iron oxides, $Fe_C = Fe_{DCB} - Fe_{AOX}$.
[h] Chinese environmental quality standard for soils (Grade III: pH > 6.5; GB15618-1995).
[i] No standards.

with nearly 58 years of production history located in Guangzhou, Guangdong province, southeast China (23°04′51″N and 113°15′17″E).

The soil samples were air dried, ground, passed through a 2-mm nylon sieve, and mixed thoroughly to yield homogenized samples for further analyses and incubation experiments. The two smelter-contaminated soils differed in their physicochemical characteristics (Table 1). Soil A had lower pH, clay content, and cation exchange capacity (CEC), but higher organic matter (OM). Soil B had much higher concentrations of different iron oxide species. Total concentrations of heavy metals varied greatly between soil A and B, but both were highly contaminated with multi-heavy metals according to the Chinese Environmental Quality Standard for Soils (GB 15618-1995).

1.2. Experiment of water incubation

Batch experiments were carried out in triplicates to investigate the release of heavy metals induced by water incubation. A 500-g soil sample (dry weight equivalent) was placed in a polypropylene box and pre-weighed deionized water was added to achieve water/soil ratios (W/W) of 0 (CK), 0.2, 0.3, 0.4, 0.5 and >1 (flooding treatment). The polypropylene box was then sealed and placed in a curing chamber at room temperature (25°C) (Appendix A Fig. S1). Prior to the experiment, a preliminary experiment was conducted and to ensure the wet soil in the polypropylene box was well mixed and the box was well sealed. For the flooding treatment, a 3-cm layer of standing water over the samples was always maintained.

1.3. Soil sampling and analysis

During the water incubation period, in situ measurements of the redox potential (Eh) were carried out at 5, 10, 20, 30, 60, 90, 120, 150, and 180 days according to the procedure described by Han and Banin (1997). The 20-g wet sample was withdrawn from each box using an EasyDraw syringe and the sample was only mixed in a local area to guarantee homogeneity of the samples (Appendix A Fig. S2). A portion of the sample was used to determine the moisture regime by oven drying at 105°C, the rest of the wet sample was used for chemical analysis with data presented on a dry weight basis. Soil pH was measured in a 1:2.5 (W/V) soil/water suspension using a digital pH meter (pHs-3C, Shanghai Weiye Instrument Company, China) (NY/T 1121.6-2006). Dissolved organic carbon (DOC) was measured in a settling 1:10 suspension of soil in 0.01 mol/L $CaCl_2$ after filtration through a 0.45-μm filter (Pan et al., 2014). Free iron oxides were estimated using the dithionite–citrate–bicarbonate (DCB) method, while amorphous iron oxides were extracted from bulk soil samples with 0.2 mol/L ammonium oxalate (pH 3) according to Mehra and Jackson (1960). Crystalline iron oxides were calculated by subtracting the concentration of amorphous iron oxides from the concentration of free iron oxides. Concentrations of Fe^{2+} in soils were determined using a UV-Visible spectrophotometer (λ: 510 nm), and Fe^{3+} was calculated by subtracting the concentration of Fe^{2+} from the total Fe concentration (Kim and Hyun, 2015).

Total concentrations of Cu, Zn, Cd and Pb in soil samples were determined via inductively coupled plasma–mass spectrometry (ICP-MS 7500, Agilent, USA), following digestion with HNO_3–HF–$HClO_4$ (3:3:1, V/V/V) in a polyvinyl-fluoride crucible (Bi et al., 2018). Leaching tests were applied to assess the release of heavy metals, which were performed according to method HJ/T300-2007 of the Ministry of Environmental Protection of China; and the procedure is summarized in the Appendix A Supplementary Data. Speciation analysis of heavy metals was performed according to the sequential extraction scheme proposed by the European Community Bureau of Reference (BCR scheme), which releases metals in four operationally defined geochemical fractions: an acid-soluble fraction (AS), a reducible fraction (RD), an oxidizable fraction (OD), and a residual fraction (RS) (Shaheen et al., 2017; Ure et al., 1993). The BCR procedure is outlined in Appendix A Table S1.

The mineralogical composition of the original and water-treated soils was performed at Tsinghua University, with a D8 ADVANCE instrument (Bruker AXS, Germany), using CuK alpha as the radiation source. Data were collected between 10° and 90° in 2θ with a step size of 0.02° and a count time of 3 sec/step. The X-ray diffraction patterns were evaluated using Jade 6.0 software (Materials Data, Inc., Livermore, California, USA) with ICDD and ICSD databases. Water-treated soil samples for XRD analysis were vacuum freeze-dried, ground, passed through a 200-mesh sieve, and thoroughly homogenized.

1.4. Quality control

Polypropylene boxes used in the experiments were washed with 5% (V/V) nitric acid for 24 hr, and then rinsed three times with deionized water before use. In situ Eh measurements were performed by carefully inserting the probe to a depth of 2 cm below the soil surface in each pot; the distance between the Pt electrode and the Ag/AgCl reference electrode was always kept at 2 cm. All subsamples were used for analysis on a dry weight equivalent basis. All reagents used for analyses in this study were of analytical grade or better, which were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and all solutions were prepared with doubly deionized water (Millipore Milli-Q 18.2 MΩ cm; Merck, Germany). For heavy metal analyses, duplicate samples, blanks and internal standards were measured for quality control. The reliability of the BCR procedure was determined by comparing the sum of fractions with the total metal concentration for each soil sample. The sum of fractions and the total concentration ranged from 92.2% to 109.3% (Appendix A Table S2).

2. Results and discussion

2.1. Fluctuated leachate concentrations of heavy metals induced by water incubation

According to method HJ/T300-2007, the leachate concentrations of Cu, Zn, Cd and Pb in soils A and B under different soil moisture regimes are shown in Fig. 1. The leachate concentrations of heavy metals increased slightly in the first 30 days, which was consistent with the results reported by Mukwaturi and Lin (2015). Pan et al. (2016) also found that the total dissolved trace metal concentrations increased first in the flooding treatment. The increase in heavy metal leachate concentrations could be attributed to the reductive dissolution of oxides (Davranche and Bollinger, 2000a, 2000b). Under reductive conditions, soil oxides were dissolved and heavy metals that trapped in oxide structures or absorbed at the oxide surfaces were desorpted, which can release heavy metals from the soil matrix to the aqueous phase. Hence the reductive dissolution of oxides induced by increasing soil moisture regimes led to the increases of heavy metal leachate levels, implying a higher potential risk at the initial stage.

Then leachate levels of heavy metals decreased drastically between 30 and 90 days, and remained relatively constant thereafter. As shown in Fig. 1, the decreases in leachate concentrations of Cu, Zn, Cd and Pb were much greater after flooding treatment than after the other treatments. For soil A, the leachate levels of Cu, Zn, Cd and Pb with water/soil ratio of 0.2 (W/V) decreased slightly from 8.04, 319.50, 12.69 and 55.83 mg/L to 7.83, 309.92, 12.56 and 52.04 mg/L, respectively, while the corresponding levels of Cu, Zn, Cd and Pb with flooding treatment decreased significantly to 6.53, 282.66, 11.53 and 48.16 mg/L, respectively. Similar variation pattern of Cu, Zn, Cd and Pb which decreased with the increasing content of soil moisture were observed in soil B. Additionally, it seems that the reduction of heavy metal concentrations in the leachates were much higher in slightly polluted soil. Kashem and Singh (2001) found that the leaching contents of Cd and Zn decreased by 90% and 91%, respectively, which might be due to the stronger changes in soil pH and Eh.
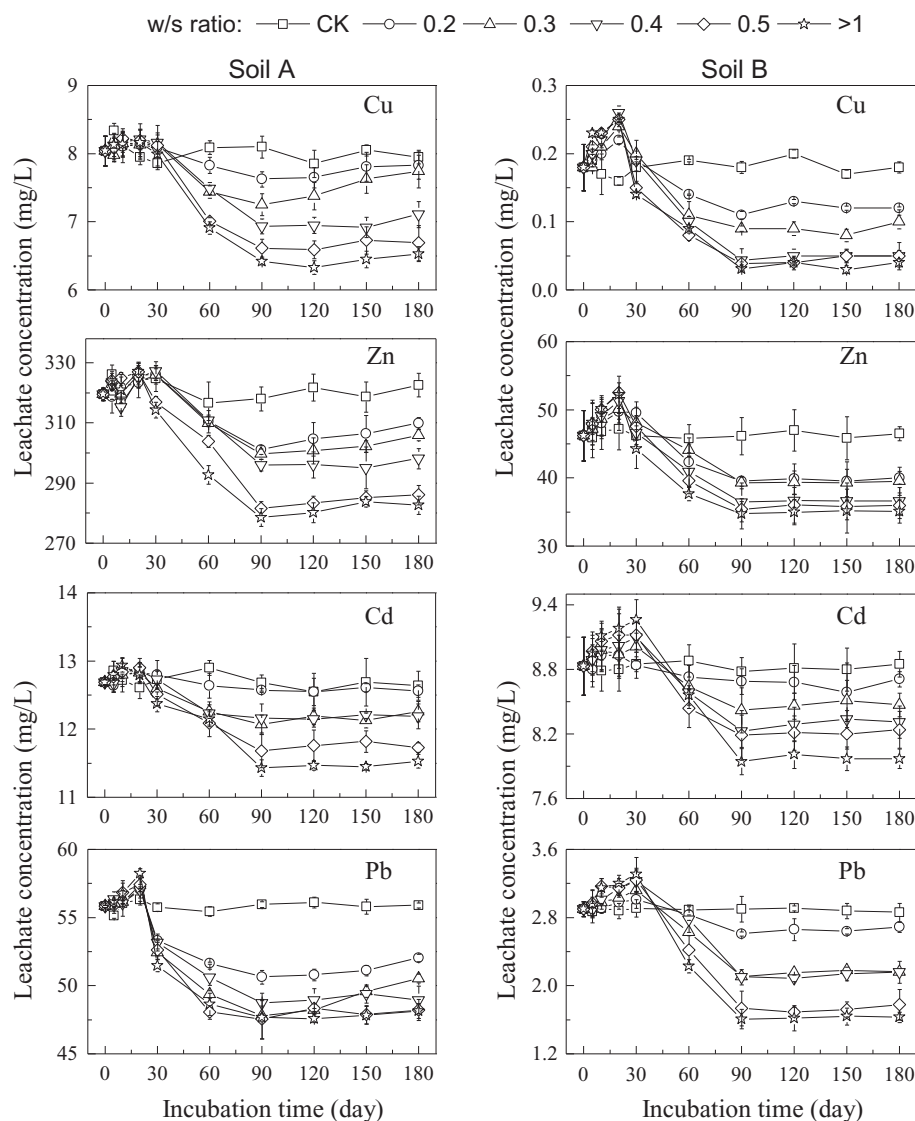
Fig. 1 – Leachate concentrations of heavy metals in soil A (left) and soil B (right) under different soil moisture regimes as a function of incubation time. Error bars represent the standard deviation ($n = 3$). CK, air-dried soil; 0.2, 0.3, 0.4 and 0.5, preweighed deionized water was added to 500 g of soil at water/soil ratios (w/s ratio) of 0.2, 0.3, 0.4 and 0.5 (W/V), respectively; >1, flooding conditions.

The decreases of heavy metal leachate levels during water incubation were the consequence of the absorption and chemical precipitation (Pan et al., 2016). There are three possible explanations for the decreases of heavy metal leachate levels caused by water incubation. First, transformation of iron oxides species from crystalline phase to amorphous phase under lower Eh resulted in much more absorption of heavy metals and reduced the heavy metal leaching concentrations (Davranche and Bollinger, 2000a). Specifically, nearly formed amorphous iron oxides would gradually evolve to more crystalline and stable structures that could also immobilize heavy metals (Lee and Baik, 2009). Second, the decreases could be attributed to reabsorption of dissolved organic matter produced via degradation of organic matter, which acted as a complexing agent between soil matrix and heavy metals and blinded heavy metals in insoluble species (Kashem and Singh, 2001; Li et al., 2013). Third, SO_4^{2-} that present in oxidized phase was reduced to S^{2-} accompanied by a decrease of Eh. Then, the S^{2-} combined with heavy metals to form metal sulfides, which was considered as a stable phase (Wan et al., 2018). Therefore, the subsequent adsorption and precipitation processes resulted in the decreases of leachable heavy metals. In our study, there is a remarkable fact that the potential risks of heavy metals in the initial mobilization stage cannot be ignored and some control strategies should be formulated to prevent the risk. Moreover, decreased leachate concentrations of soil heavy metals were observed after 180-day water incubation, indicating that the immobilization of heavy metals occurred.

As the total and leachate concentrations of heavy metals varied widely in the tested soils, the leachability of heavy metals was used to assess the difference in immobilization between soils A and B. After water incubation, the leachability of Cu, Zn, Cd and Pb decreased by 1.88%, 4.81%, 7.21% and 1.61% in acid soil A, and by 0.43%, 1.12%, 3.36% and 0.67% in alkaline soil B, respectively. These results indicate that the immobilization of heavy metals induced by water incubation was greater in acid soil A than in alkaline soil B. Meanwhile, it appears that Cd and Zn were prone to immobilization via water incubation, which was attributable to the higher mobility of Cd and Zn.

2.2. Changes in soil Eh and pH during water incubation

Numerous studies have shown that the soil moisture regime plays an important role in controlling Eh and pH, with consequent effects on displacement of soil gas, microbial respiration, and reduction processes (Schroll et al., 2006; Kögel-Knabner et al., 2010; Mcbride, 1994). The variations in soil Eh and pH during 180-day incubation are shown in Fig. 2. The soil Eh decreased drastically during the first few days and increased slightly thereafter, which might be because of depletion of O_2 and accumulation of reducing substances. In our study, the minimum Eh values observed were –116 mV after 30 days for soil A and –55 mV after 90 days for soil B. However, the variations of Eh were much stronger in slightly contaminated soil and a maximum negative value of 439 mV was observed by Kashem and Singh (2001), which could be due to the vigorous microbial activity. Additionally, the decrease in soil Eh initiated reduction processes, leading to the release of heavy metals, as confirmed by increases in the leachate concentrations of heavy metals in the initial stage of water incubation (Mukwaturi and Lin, 2015; Pan et al., 2016). Further reduction of SO_4^{2-} can lead to the formation of poorly soluble metal sulfides (Khaokaew et al., 2011; Fang et al., 2016), which would be effectively immobilized. Redox reactions can mobilize or immobilize metals depending on the particular metal species and microenvironments. And the changes in leachate concentrations of heavy metals during water incubation were partly caused by these reduction processes.

The soil pH tended to be neutral on addition of water, especially for the flooding treatment (Fig. 3). The pH of soil A increased from 6.36 to 6.97 on flooding treatment because of H^+ consumption during reduction processes (Pan et al., 2016). Conversely, the pH of soil B decreased because of accumulation of CO_2 produced via respiration by aerobic bacteria, a finding supported by Mcbride (1994). The maximum change in pH in our study was an increase of 0.61 units, which is smaller than the increase of 2.4 units reported by Kashem and Singh (2001). The reason for this difference could be ascribed to the higher concentrations of heavy metals, which would have a toxic effect on soil microflora, slowing down the rate of reduction processes (Han and Banin, 1997). A slight change in pH was observed for leached solutions, demonstrating that the pH of soil varied for different moisture regimes (Appendix A Fig. S3).
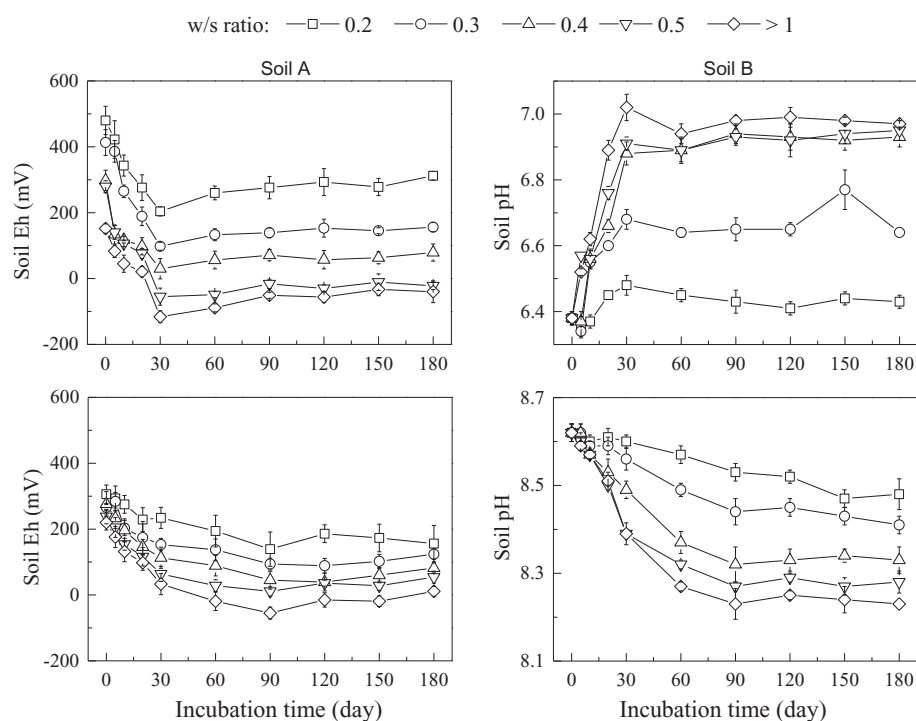

Fig. 2 – Changes in soil Eh and pH of soil A (left) and soil B (right) under different soil moisture regimes as a function of incubation time. Error bars represent the standard deviation (*n* = 3).
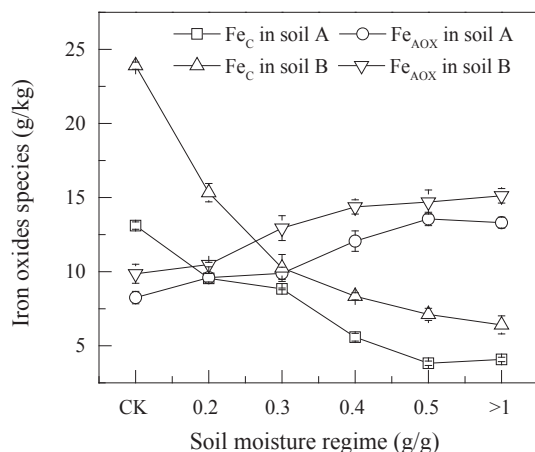
Fig. 3 – Transformation of iron oxide species in soils A and B under different soil moisture regimes after 180 days of water incubation. Fe$_C$, crystalline iron oxides; Fe$_{AOX}$, amorphous iron oxides. Error bars represent the standard deviation (n = 3).

For soil A, the pH increased on addition of water, resulting in an increase in the negative charge on soil constituents, especially hydroxyl ions, and a corresponding decrease in the leachability of heavy metals because of adsorption and precipitation. Conversely, the decrease in pH for soil B might result in the increased release of heavy metals. However, no increase in heavy metal leachability was observed, possibly because of the decreased Eh and the formation of amorphous iron oxides.

2.3. Transformation of iron oxides after water incubation

Another mechanism underlying the fluctuation of heavy metal leachate levels could be the transformation of iron oxide species. It is well recognized that amorphous iron oxides, which have a large surface area/volume ratio, have greater adsorption capacity than more crystalline forms (Zhang et al., 2016). As shown in Fig. 3, the concentration of crystalline iron oxides significantly decreased and that of amorphous iron oxides increased during water incubation. For soil A subjected to flooding treatment, the crystalline iron oxide content decreased from 13.11 to 4.08 g/kg, while the amorphous iron oxide content increased from 8.25 to 13.31 g/kg after 180 days. For soil B, the crystalline iron oxide content decreased by 17.58 g/kg and the amorphous iron oxide content increased by 5.26 g/kg. The higher the amorphous iron oxide content, the greater is the adsorption capacity for heavy metals. Consequently, heavy metals in the smelter-contaminated soils were absorbed as a less liable phase the heavy metal leachability decreased, especially after flooding treatment.

Davranche and Bollinger (2000a) investigated the effect of reductive dissolution on the solubilization of heavy metals for spiked iron hydroxides and found that the risk of solubilization is greater for Pb than for Cd under reductive conditions. Such releases of heavy metals were observed in the first few

30 days of incubation in our study, especially for Zn and Pb, which was due to the reductive dissolution of iron oxides. As the incubation time progressed, leaching of heavy metals significantly decreased with increasing soil moisture, which could be attributable to reimmobilization of heavy metals via the formation of new amorphous iron oxides. Zheng and Zhang (2011) found that more stable soil heavy metals might be related to higher concentrations of amorphous iron oxides. Kashem and Singh (2001) reported that adsorption of Cd and Zn on iron oxyhydroxides was one of the major mechanism responsible for the decrease in solubility under submerged conditions.

Greater reductive dissolution of crystalline iron oxides in soil B have led to greater release of heavy metals. As a result, the decrease in heavy metal leachability was smaller for soil B than for soil A. The decrease in crystalline iron oxides was 1.82 and 3.28 times greater than the increase in amorphous iron oxides for soil A and soil B, respectively. This indicates that the adsorption of heavy metals was much greater on newly formed amorphous iron oxides than on pre-existing crystalline iron oxides. Furthermore, newly formed amorphous iron oxides would gradually evolve to more crystalline and stable structures that could also immobilize heavy metals (Lee and Baik, 2009). In addition, not all of the reduced crystalline iron oxides were converted to amorphous iron oxides. Elevated concentrations of Fe^{3+} and Fe^{2+} in both soil A and soil B were observed (Appendix A Fig. S4).

2.4. Redistribution of heavy metal fractions

Results for heavy metal fractions in soils with different soil moisture regimes before and after incubation are shown in Fig. 4. The relatively high proportion of heavy metals in the AS fraction suggests that they are readily mobile in smelter-contaminated soils, especially Cd in soil A. On addition of water, the concentrations of all four heavy metals decreased in the AS fraction and increased in the RD and OD fractions. This indicates that heavy metals in both soil A and soil B were redistributed from the exchangeable fraction into more stable fractions.

For soil A, the Cd concentration in the AS fraction decreased by up to 13.26%, in agreement with the decrease in heavy metal leachability. Smaller decreases were observed for soil B. However, there was a distinct difference in artificially contaminated soil samples as described by Zheng and Zhang (2011). The proportions of exchangeable Cu, Pb and Cd after flooding decreased by more than 32%, 46% and 26%, respectively, which were particularly noticeable for spiked heavy metals. Han and Banin (1997) also observed that metals were transferred from AS fraction into the more stable fractions (82% for Cd, 40%–85% for Zn and 30% for Cu), which were more stronger than our results. The difference between soil A and B could be attributed to the lower solubility of heavy metals at higher pH, leading to their adsorption or precipitation (Davranche and Bollinger, 2000b). According to the BCR scheme, the AS fraction is readily mobile and is very prone to leaching. The decrease in heavy metal concentration in the AS fraction induced by water incubation was the major reason for reduction of heavy metals in our study.

Reducing conditions induced by water incubation can lead to reductive dissolution of iron oxides and the formation of new amorphous iron oxides (Zheng and Zhang, 2011). Two opposing processes could be involved: the release of heavy metals bound to or adsorbed on the initial iron oxides, and reimmobilization of heavy metals on newly formed amorphous iron oxides. After water incubation, the proportion of heavy metals in the RD fraction increased to varying degrees, suggesting that heavy metals were re-adsorbed onto newly formed iron oxides. Transformed amorphous iron oxides would provide more sites for adsorption and immobilization of heavy metals. The increases in the proportion of heavy metals in the RD fraction were greater in soil A, which is related to the smaller decreases in crystalline iron oxides.

The proportion of heavy metals in the OD fraction increased after water incubation. Pan et al. (2014) found that DOC concentrations increased gradually as organic matter degraded during flooding. However, the DOC concentrations in our soil samples decreased after water incubation (Appendix A Fig. S5), possibly because of readsorption of DOC. Readsorbed DOC would act as a chelating agent and provide a greater reactive surface area for binding and immobilizing heavy metals, and a consequent increase in the proportion of heavy metals in the OD fraction. The increases in heavy metal content in the OD fraction might also be partly due to the presence of S^{2-} on reduction of SO_4^{2-}, which might have led to precipitation of trace metals in the form of poorly soluble minerals (Khaokaew et al., 2012; Fulda et al., 2013).
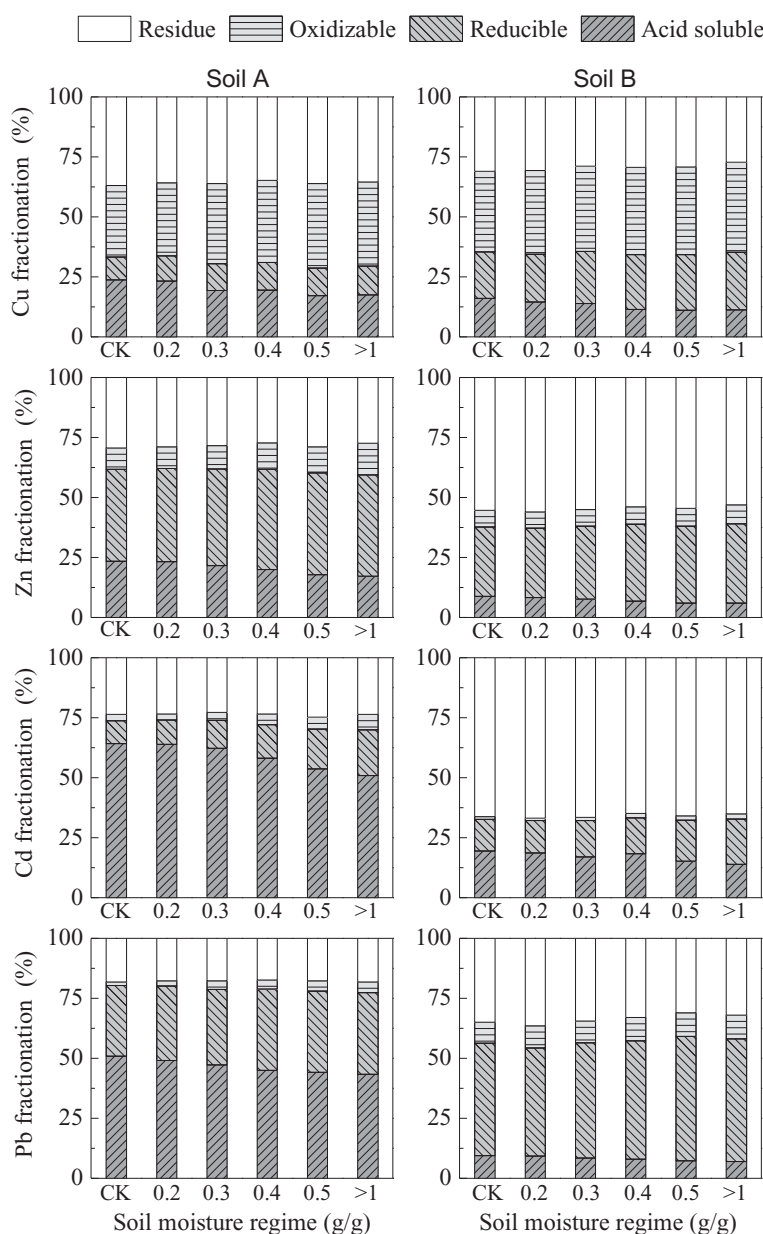

Fig. 4 – Distribution of Cu, Zn, Cd, and Pb fractions in soil A (left) and soil B (right) under different soil moisture regimes after 180 days of water incubation.
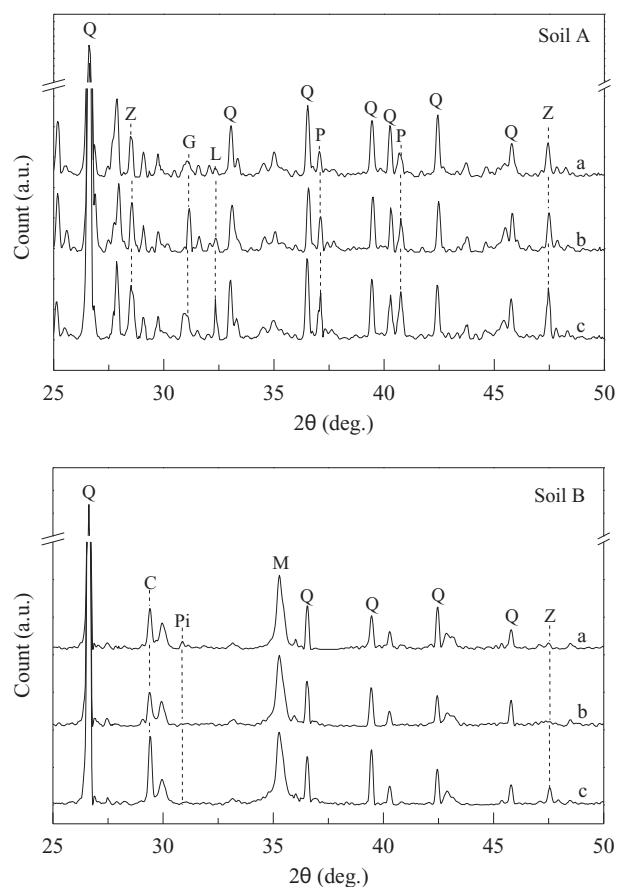
Fig. 5 – X-ray diffraction patterns for soil A and soil B. (a) Original soil. (b) Soil incubated with water at a water/soil ratio of 0.3 (W/V) for 180 days. (c) Soil after incubation under flooding conditions for 180 days. Q, quartz; G, gypsum; Z, zinc sulfide; L, lead iron oxide; P, pyrite; Pi, pirssonite; C, calcite; M, magnetite.

By definition, the RS fraction contains residual metals and those bound to silicate minerals, which is thus much more stable than the other fractions. Zheng and Zhang (2011) reported that the concentration of freshly spiked metals in the RS fraction remained unchanged after 120-day incubation. By contrast, the heavy metal content of the RS fraction decreased slightly in this study, especially for alkaline soil B, which was related to reduction of minerals due to reductive dissolution. Heavy metals fixed within the mineral matrix induced by aging effect in the long-term field-contaminated soils (Liang et al., 2016), which would release under the reducing environment, thereby caused the reduction of heavy metal in RS fraction.

2.5. Mineralogical evidence of immobilization induced by water incubation

To better understand the mechanisms underlying the immobilization of soil heavy metals induced by water incubation, mineralogical changes in the treated soils were investigated using XRD analysis (Fig. 5). To determine the mineral composition of the soils, the residue after each step of the BCR procedure was characterized via XRD analysis (Appendix A Fig. S6). Quartz, gypsum, calcite, zinc sulfide, lead iron oxide, pyrite, pirssonite and magnetite were identified. XRD analysis revealed that quartz, gypsum, pyrite and zinc sulfide were the main phases in soil A, and quartz, calcite and magnetite were the main phases in soil B.

Different XRD patterns were observed for different soil moisture regimes, with the most obvious changes in peak intensity observed for samples incubated under flooding conditions. For soil A, peak broadening at 32.40° related to lead iron oxide was due to the presence of amorphous phase and recrystallization of newly formed amorphous iron oxides, consistent with the iron oxide species and heavy metals fraction development (Figs. 3 and 4). It was also observed that the peak intensities at 28.53° and 47.50° related to zinc sulfide gradually increased with increasing soil moisture regime, which was corresponding with the development of anaerobic conditions (Fig. 2). Some studies demonstrated that SO_4^{2-} was reduced to S^{2-} under the reducing environment caused by water incubation (Pan et al., 2014, 2016; Wan et al., 2018). The formation of zinc sulfide precipitation can significantly reduce Zn mobility, thereby the leachate concentrations of Zn decreased after 180-day water incubation (Fig. 1), accompanied with a consequent increase in the proportion of the OD-Zn fraction (Fig. 4). Besides Zn, other heavy metals such as Cu, Cd and Pb might be precipitated in the form of sulfides. Only zinc sulfide was observed in our study owing to the higher total concentration of Zn among the four heavy metals. Meanwhile, an increase in peak intensity for zinc sulfide was also observed for soil B. Noted that there was little mineralogical evidence of heavy metal immobilization induced by water incubation in slightly polluted soil as their lower concentrations. The experimental results for XRD analysis, leachate concentrations and speciation analysis were highly consistent, indicating immobilization of heavy metals induced by water incubation, especially for the flooding treatment.

3. Conclusions

Two highly smelter-contaminated and aged soils were used to investigate the release of heavy metals induced by water incubation. The results indicate that addition of water increased the leaching concentrations of soil heavy metals in the initial stage and reimmobilized them after 180 days of incubation. Water incubation resulted in the leachability of Cu, Zn, Cd, and Pb in acid soil A decreasing by as much as 1.88%, 4.81%, 7.21% and 1.61%, respectively, and corresponding values in alkaline soil B decreased by 0.43%, 1.12%, 3.36% and 0.67%, respectively, illustrating the stronger immobilization of heavy metals in acid soil. The fluctuations in leachate concentrations of soil heavy metals were a consequence of several factors, including soil Eh and pH, transformation of amorphous iron oxides, and redistribution of heavy metal fractions. XRD analysis evidenced the presence of a lead iron oxide phase and the peak increasing of zinc sulfide which was

considered as a less liable fraction of heavy metals. Although, the addition of water released the heavy metals and increased the leaching risks in the initial stage, the increased risks were limited. What's more, the released heavy metals were reimmobilized and finally the leaching risk of heavy metals decreased after 180-day water incubation. This study provides new insights into assessing and managing the risk of heavy metals in highly contaminated and aged soils, especially in a closed system.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.02.026.

REFERENCES

Arao, T., Kawasaki, A., Baba, K., Mori, S., Matsumoto, S., 2009. Effects of water management on cadmium and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. Environ. Sci. Technol. 43, 9361–9367.

Bi, C.J., Zhou, Y., Chen, Z.L., Jia, J.P., Bao, X.Y., 2018. Heavy metals and lead isotopes in soils, road dust and leafy vegetables and health risks via vegetable consumption in the industrial areas of Shanghai, China. Sci. Total Environ. 619–620, 1349–1357.

Davranche, M., Bollinger, J.C., 2000a. Heavy metals desorption from synthesized and natural iron and manganese oxyhydroxides: Effect of reductive conditions. J. Colloid Interf. Sci. 227, 531–539.

Davranche, M., Bollinger, J.C., 2000b. Release of metals from iron oxyhydroxides under reductive conditions: Effect of metal/solid interactions. J. Colloid Interf. Sci. 232, 165–173.

Dittmar, J., Voegelin, A., Roberts, L.C., Hug, S.J., Saha, G.C., Ali, M.A., et al., 2010. Arsenic accumulation in a paddy field in Bangladesh: seasonal dynamics and trends over a three-year monitoring period. Environ. Sci. Technol. 44, 2925–2931.

Fang, H.W., Huang, L., Wang, J.Y., He, G.J., Reible, D., 2016. Environmental assessment of heavy metal transport and transformation in the Hangzhou Bay, China. J. Hazard. Mater. 302, 447–457.

Fulda, B., Voegelin, A., Kretzschmar, R., 2013. Redox-controlled changes in cadmium solubility and solid-phase speciation in a paddy soil as affected by reducible sulfate and copper. Environ. Sci. Technol. 47, 12775–12783.

Gaetke, L.M., Chow, C.K., 2003. Copper toxicity, oxidative stress, and antioxidant nutrients. Toxicology. 189, 147–163.

Girault, F., Perrier, F., Poitou, C., Isambert, A., Théveniaut, H., Laperche, V., et al., 2016. Effective radium concentration in topsoils contaminated by lead and zinc smelters. Sci. Total Environ. 566–567, 865–876.

Han, F.X., Banin, A., 1997. Long-term transformations and redistribution of potentially toxic heavy metals in arid-zone soils incubated: I. Under saturated conditions. Water Air Soil Pollut. 95, 399–423.

Han, F.X., Banin, A., 1999. Long-Term Transformation and redistribution of potentially toxic heavy metals in arid-zone soils: II. Incubation at the field capacity moisture content. Water Air Soil Pollut. 114, 221–250.

Han, F.X., Banin, A., Kingery, W.L., Li, Z.P., 2002. Pathways and kinetics of redistribution of cobalt among solid-phase fractions in arid-zone soils under saturated regime. J. Environ. Sci. Health A 37, 175–194.

Hu, P.J., Ouyang, Y.N., Wu, L.H., Shen, L.B., Luo, Y.M., Christie, P., 2015. Effects of water management on arsenic and cadmium speciation and accumulation in an upland rice cultivar. J. Environ. Sci. 27, 225–231.

Kashem, M.A., Singh, B.R., 2001. Metal avialability in contaminated soils. I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. Nutr. Cycl. Agroecosys 61, 247–255.

Kennou, B., Meray, M.E., Romane, A., Arjouni, Y., 2015. Assessment of heavy metal availability (Pb, Cu, Cr, Cd, Zn) and speciation in contaminated soils and sediment of discharge by sequential extraction. Environ. Earth Sci. 74, 5849–5858.

Khaokaew, S., Chaney, R.L., Landrot, G., Ginder-Vogel, M., Sparks, D.L., 2011. Speciation and release kinetics of cadmium in an alkaline paddy soil under various flooding periods and draining conditions. Environ. Sci. Technol. 45, 4249–4255.

Khaokaew, S., Landrot, G., Chaney, R.L., Pandya, K., Sparks, D.L., 2012. Speciation and release kinetics of zinc in contaminated paddy soils. Environ. Sci. Technol. 46, 3957–3963.

Kim, J., Hyun, S., 2015. Nonequilibrium leaching behavior of metallic elements (Cu, Zn, As, Cd, and Pb) from soils collected from long-term abandoned mine sites. Chemosphere 134, 150–158.

Kögel-Knabner, I., Amelung, W., Cao, Z.H., Fiedler, S., Frenzel, P., Jahn, R., et al., 2010. Biogeochemistry of paddy soils. Geoderma 157, 1–14.

Lee, S.Y., Baik, M.H., 2009. Uranium and other trace elements' distribution in Korean granite: implications for the influence of iron oxides on uranium migration. Environ. Geochem. Health 31, 413–420.

Li, T.Q., Tao, Q., Liang, C.F., Shohag, M.J.I., Yang, X.E., Sparks, D.L., 2013. Complexation with dissolved organic matter and mobility control of heavy metals in the rhizosphere of hyperaccumulator Sedum alfredii. Environ. Pollut. 182, 248–255.

Li, Z.Y., Ma, Z.W., van der Kuijp, T.J., Yuan, Z.W., Huang, L., 2014. A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Sci. Total Environ. 468–469, 843–853.

Liang, S., Guan, D.X., Li, J., Zhou, C.Y., Luo, J., Ma, L.Q., 2016. Effect of aging on bioaccessibility of arsenic and lead in soils. Chemosphere 151, 94–100.

Mcbride, M.B., 1994. Environmental chemistry of soils. Oxford University Press, NewYork, USA.

Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by a dithionite–citrate system buffered with sodium bicarbonate. Clay Clay Miner. 7, 317–327.

Mohamed, M.A., Ellis, K., Kim, C.S., Bi, X.T., 2017. The role of tailored biochar in increasing plant growth, and reducing bioavailability, phytotoxicity, and uptake of heavy metals in contaminated soil. Environ. Pollut. 230, 329–338.

Mukwaturi, M., Lin, C.X., 2015. Mobilization of heavy metals from urban contaminated soils under water inundation conditions. J. Hazard. Mater. 285, 445–452.

Pan, Y.Y., Koopmans, G.F., Bonten, L.T.C., Song, J., Luo, Y.M., Temminghoff, E.J.M., et al., 2014. Influence of pH on the redox chemistry of metal (hydr)oxides and organic matter in paddy soils. J. Soils Sediments 14, 1713–1726.

Pan, Y.Y., Bonten, L.T.C., Koopmans, G.F., Song, J., Luo, Y.M., Temminghoff, E.J.M., et al., 2016. Solubility of trace metals in two contaminated paddy soils exposed to alternating flooding and drainage. Geoderma 261, 59–69.

Plum, L.M., Rink, L., Haase, H., 2010. The essential toxin: impact of zinc on human health. Inter. J. Environ. Res. Public. Health 7, 1342–1365.

Qu, L.Y., Huang, H., Xia, F., Liu, Y.Y., Dahlgren, R.A., Zhang, M.H., et al., 2018. Risk analysis of heavy metal concentration in surface waters across the rural-urban interface of the Wen-Rui Tang River, China. Environ. Pollut. 237, 639–649.

Schroll, R., Becher, H.H., Dörfler, U., Gayler, S., Grundmann, S., Hartmann, H.P., et al., 2006. Quantifying the effect of soil moisture on the aerobic microbial mineralization of selected pesticides in different soils. Environ. Sci. Technol. 40, 3305–3312.

Shaheen, S.M., Kwon, E.E., Biswas, J.K., Tack, F.M.G., Ok, Y.S., Rinklebe, J., 2017. Arsenic, chromium, molybdenum, and selenium: Geochemical fractions and potential mobilization in riverine soil profiles originating from Germany and Egypt. Chemosphere 180, 553–563.

Ure, A.M., Quevauviller, P., Muntau, H., Griepink, B., 1993. Speciation of heavy metals in soils and sediments. an account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Int. J. Environ. Anal. Chem. 51, 135–151.

Vespa, M., Lanson, M., Manceau, A., 2010. Natural attenuation of zinc pollution in smelter-affected soil. Environ. Sci. Technol. 44, 7814–7820.

Wan, Y.N., Camara, A.Y., Yu, Y., Wang, Q., Guo, T.L., Zhu, L.N., et al., 2018. Cadmium dynamics in soil pore water and uptake by rice: influences of soil-applied selenite with different water managements. Environ. Pollut. 240, 523–533.

Williams, P.N., Lei, M., Sun, G.X., Huang, Q., Lu, Y., Deacon, C., et al., 2009. Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China. Environ. Sci. Technol. 43, 637–642.

Wu, S.C., Luo, Y.M., Cheung, K.C., Wong, M.H., 2006. Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: a laboratory study. Environ. Pollut. 144, 765–773.

Zhang, C., Yu, Z.G., Zeng, G.M., Huang, B.B., Dong, H.R., Huang, J.H., et al., 2016. Phase transformation of crystalline iron oxides and their adsorption abilities for Pb and Cd. Chem. Eng. J. 284, 247–259.

Zhao, F.J., Ma, Y.B., Zhu, Y.G., Tang, Z., McGrath, S.P., 2015. Soil contamination in China: current status and mitigation strategies. Environ. Sci. Technol. 49, 750–759.

Zheng, S.A., Zhang, M.K., 2011. Effect of moisture regime on the redistribution of heavy metals in paddy soil. J. Environ. Sci. 23, 434–443.