



# Effect of soil pH and organic matter content on heavy metals availability in maize (*Zea mays* L.) rhizospheric soil of non-ferrous metals smelting area

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Received: 26 February 2019 / Accepted: 27 August 2019 / Published online: 14 September 2019  
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**Abstract** Maize plant tissues and rhizosphere soil were collected from an agricultural area around the Huludao Zinc Plant in Liaoning Province, China, to investigate the effects of soil pH and organic matter content on heavy metal concentration and accumulation in different types of maize tissues. The mean pH of the soil samples was 7.02 (range 5.74–7.86), and the mean organic matter content was 31.03 g kg<sup>-1</sup> (range 18.80–52.20 g kg<sup>-1</sup>). The average Cu, Zn, Pb, and Cd contents in soil were 2.92, 6.72, 7.95, and 16.28 times greater than the corresponding background values, respectively. The geo-accumulation index indicated that the soils were uncontaminated to moderately contaminated by Cu, moderately to strongly contaminated by Pb and Zn, and strongly contaminated by Cd. The average

available Cu, Pb, Zn, and Cd contents in the soil samples were 16.34, 6.997, 69.77, and 0.190 mg kg<sup>-1</sup>, respectively, while their bioavailability coefficients were 28.53%, 1.65%, 40.44%, and 10.83%, respectively. The respective mean Pb and Cd concentrations in grain samples were 0.341 and 0.342 mg kg<sup>-1</sup>, which exceeded the maximum concentrations permitted by the Chinese National Standard. Thus, the maize grain is not safe for consumption and poses potential risks to human health. With the exception of Cu, the combined effect of pH and organic matter content had a stronger influence on the availability of heavy metals in soil compared with either factor alone. Cd uptake in maize plant tissues was affected by the combination of soil pH, organic matter content, and bioavailable Cd content in soil; however, the combination of these three factors had only slight effects on Cu, Zn, and Pb absorption in maize tissues.

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10661-019-7793-5>) contains supplementary material, which is available to authorized users.

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**Keywords** Physicochemical properties · Available metals · Metal accumulation · Soil-maize system · Non-ferrous smelting areas

## Introduction

The heavy metal pollution of agricultural soils results from various anthropogenic activities including the burning of fossil fuels, metal mining and smelting, excessive use of chemical fertilizer and pesticides, wastewater irrigation, and the discharge of sewage sludge that is rich in heavy metals (Shukla et al. 2011; Ma et al. 2013; Islam et al. 2015; Xu and Zhang, 2017).

In China, approximately 20% of agricultural land has been contaminated by heavy metals, and this percentage is predicted to increase over the next few decades (Li et al. 2014b).

Heavy metals are one of the most toxic inorganic pollutants to organisms in the environment because of their non-biodegradation and bioaccumulation, making them persistent hazards in the environment (Singh et al. 2010; Nabulo et al. 2011). Heavy metals contamination in soil can adversely affect plant growth and reduce yield (Seleiman et al. 2013; Shen et al. 2013). Even worse, the consumption of polluted plants by livestock can result in detrimental effects to human health due to bioaccumulation in the food chain (Williams et al. 2011; Mani et al. 2012).

Recent studies have demonstrated that heavy metal accumulation and their toxicity are not dependent on the total heavy metal concentration, and heavy metal accumulation in plants tends to depend on the availabilities of the heavy metals in soils (Chen et al. 2014; Lee et al. 2015), which are generally influenced by the adsorption and desorption characteristics of the soil (Monterroso et al. 2014; Zhang et al. 2017). The bioavailability of heavy metals is associated with several factors, among which, soil pH and organic matter (OM) content are critical (Xu et al. 2015). Scotti et al. (1999) reported that the solubility and bioavailability of zinc (Zn), cadmium (Cd), nickel (Ni), and copper (Cu) are negatively correlated with soil pH because the soil pH affects solubility and speciation in soil solution (Zhao et al. 2010; Zeng et al. 2011). OM content in soil has been shown to increase the uptake of lead (Pb) and mercury (Hg) by roots (Xu et al. 2015), determine the nutritional status of soil, and keep heavy metals in an exchangeable form and chelate with heavy metals to increase metal bioavailability (McCauley et al. 2009). However, studies on the combined effects of soil pH and OM content are limited.

Maize is one of the three main grain crops in the world and is globally important for food, feed, and energy security (Seleiman et al. 2013). The planting area and annual yield of maize in Huludao city, Liaoning Province, China, were  $1.449 \times 10^5$  ha and  $7.25 \times 10^5$  t in 2016, respectively. However, there is little concern about the factors that influence heavy metal availability in the maize rhizosphere soil. Therefore, it is imperative to estimate the effects of pH and OM content on the availability and uptake of heavy metals by maize to minimize the toxic effects and bioaccumulation of

heavy metals in the food chain. Currently, information about heavy metal availability in maize-soil system in China, especially around the Huludao smelting area, is limited. In addition, the combined effect of pH and OM content on heavy metal accumulation in maize has seldom been reported.

Thus, we studied the rhizosphere soil and maize plants collected from an area of maize planting near the largest zinc plant in Asia. This site is polluted with large quantities of metals, including Cu, Zn, Cd, and Pb presenting a significant risk to local human health (Zheng et al. 2007). The specific objectives were to (1) determine the concentrations of available Cu, Pb, Zn, and Cd in soil samples along with their uptake in maize plants; (2) explore the effects of pH and OM content on heavy metal availability; (3) evaluate the combined effects of soil pH, OM content, and available heavy metal contents on the accumulation of heavy metals by maize; and (4) provide a theoretical basis for utilizing metal-polluted soils in agricultural production.

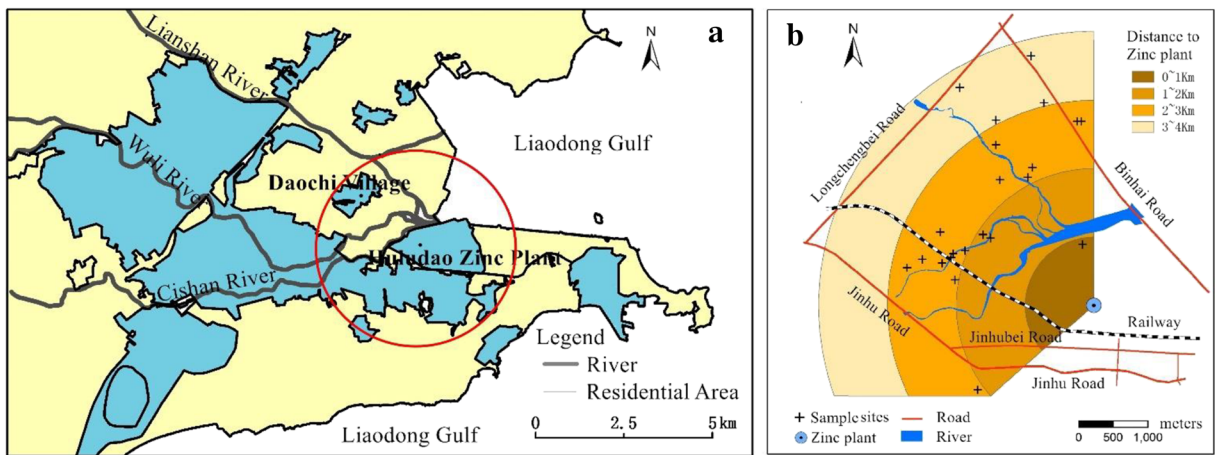
## Materials and methods

### Background of the sampling area

As the largest zinc smelter in Asia, the Huludao Zinc Plant (HZP) is situated in the southeastern part of Huludao city (40° 56' N, 120° 38' E), Liaoning Province, northeast China. Huludao city has a typical continental monsoon climate with an average annual temperature of 8.7 °C and average annual rainfall of 590 mm. Daochi village, which is located 2–4 km away from the HZP, has a population exceeding 3000 and is notorious for extremely high rates of several types of cancer.

### Sampling methods and preparation

Rhizosphere soil and maize plant samples were collected from the cornfields of Daochi village in the autumn of 2015 (Fig. 1). At least three mature maize plants were removed from the ground in each sampling site. Rhizosphere soil was sampled by gently shaking the maize plant following the method reported by Xiao et al. (2017). The soil samples were analyzed, since plant root-soil-microbe interactions are known to affect a range of properties, including OM content, pH, cation exchange capacity, and microorganisms, which in turn influence heavy metal availability and accumulation in



**Fig. 1** Locations of the study area (A) and the sampling sites in maize fields of Daochi (B)

plants (Zhang et al. 2016; Antoniadis et al. 2017). For each soil sample, six subsamples were collected and mixed thoroughly before being stored in plastic bags. Sampling locations were determined using global positioning system (GPS) throughout the sample collection process.

The soil samples were air-dried at room temperature and then grounded before being passed through a 100-mesh nylon sieve for chemical analysis. These maize plant samples were subdivided into four parts (root, stem, leaf, and grain) and then washed thoroughly using ultrapure water to prevent the surface soil from affecting the metal concentrations in the roots. After drying to a constant weight in an oven at 70–80 °C, the maize tissues were milled into fine powders for the measurement of heavy metal contents (Noli and Tsamos, 2016).

**Measurement of soil pH, OM content, and heavy metal contents**

Soil pH was examined using a pH meter with a soil-to-water ratio of 1:2.5 (Leici, Shanghai) as reported by Sun et al. (2013a). OM content was measured using the method of Walkley-Black (Schnitzer 1982).

The total concentrations of Cu, Pb, Zn, and Cd were determined by HF–HNO<sub>3</sub>–HClO<sub>4</sub> digestion (Liu et al. 2013). The available metals were extracted by adding 10 ml of a mixture of 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>, 0.05 mol L<sup>-1</sup> EDTA-Na<sub>2</sub>, and 0.1 mol L<sup>-1</sup> TEA (Zeng et al. 2011) to polypropylene tubes containing 5 g of soil. The polypropylene tubes were shaken at 60 rpm for 3 h on a reciprocal shaker. The suspension was centrifuged at 3000 rpm for 20 min and the obtained supernatant liquid

was used to measure the available contents of heavy metals. The concentrations of the extracted Cu, Zn, and Pb in soil samples were determined by flame atomic absorption spectrometry (FAAS; AA-6300C, Shimadzu, Japan), and Cd was analyzed using graphite furnace atomic absorption spectroscopy (AA-6300C, Shimadzu, Japan).

**Heavy metals content in maize**

The heavy metals in the three replicates of each maize sample were digested by HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> (Gebrekidan et al. 2013). The contents of Cu, Zn, and Pb in the maize samples were tested by flame atomic absorption spectrometry (FAAS; AA-6300C, Shimadzu, Japan), and Cd was tested by using graphite furnace atomic absorption spectroscopy (AA-6300C, Shimadzu, Japan).

**Quality assurance and control**

Standard reference materials GBW07443 (GSF-3) and GBW10011, which are formulated by the Center of National Standard Reference Material of China, were used to validate the heavy metal contents measured in the soil and plant samples. The recoveries of Cu, Pb, Zn, and Cd were 85–103%, 90–109%, 87–102%, and 96–110%, respectively. Analytical reagent blanks were evaluated to ensure the accuracy of the heavy metal analysis. All of the samples were tested in triplicate. The heavy metal contents in the blank samples were found to be below the detection limit. The relative standard deviation (RSD) of duplicate samples was routinely 4–8%.

## Statistical analysis

The geo-accumulation index ( $I_{\text{geo}}$ ) was used to assess the contamination levels of heavy metals in soil samples (Zahra et al. 2014; Aiman et al. 2016) that was estimated as Eq. 1:

$$I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \quad (1)$$

where  $C_n$  is the contents of every heavy metal in the test soil, and  $B_n$  is background heavy metal content. In this study, the background value for the soil in Liaoning Province was used as  $B_n$  (CNEMC 1990). The factor 1.5 was used to analyze variations in background values. The standard classifications of  $I_{\text{geo}}$  reported by Muller 1969 (see Table S1 in the Supplementary Material) were used in this study.

The bioconcentration factors (BCF) of heavy metals in the root (RCF), stem (SCF), leaf (LCF), and grain (GCF) material were used to indicate the acropetal translocation of Cu, Pb, Zn, and Cd in the maize plants as presented in Eqs. 2–5 (Zhang et al. 2017):

$$\text{RCF} = \frac{C_{\text{root}}}{C_{\text{soil}}} \quad (2)$$

$$\text{SCF} = \frac{C_{\text{stem}}}{C_{\text{soil}}} \quad (3)$$

$$\text{LCF} = \frac{C_{\text{leaf}}}{C_{\text{soil}}} \quad (4)$$

$$\text{GCF} = \frac{C_{\text{grain}}}{C_{\text{soil}}} \quad (5)$$

where  $C_{\text{soil}}$ ,  $C_{\text{root}}$ ,  $C_{\text{stem}}$ ,  $C_{\text{leaf}}$ , and  $C_{\text{grain}}$  are the total heavy metals total concentrations in soil, and maize root, leaf, stem, and grain tissues, respectively.

Pearson correlation coefficients were used to test the associations between soil heavy metal content and the single factors soil pH and OM content. Stepwise linear and non-linear regressions were used to predict the combined effect of soil pH and OM content on heavy metal availability in the soils. Microsoft Excel 2010 was used to manage the data in this study. Statistical analyses were performed using SPSS 19.0 and Origin 8.0.

## Results and discussion

### Soil pH and OM content in soil

The mean soil pH was 7.02 (range pH 5.74–7.86), and 58% of the samples was acidic (pH 5.74–7.0) (Table 1). Soil acidity depends on soil texture, parent material, vegetation, and topography (Sun et al. 2013a). Additionally, acidic soil pH may be related to the use of large quantities of mineral fertilizers, especially nitrogen fertilizers, and the low application of fresh organic matter (Guo et al., 2010). The alkaline pH observed in the remaining 42% of samples may be related to the enzymatic reactions in the soil (Li et al., 2013).

The mean OM content was 31.03 g kg<sup>-1</sup> (range 18.80–52.20 g kg<sup>-1</sup>), indicating that the OM content in the maize rhizosphere soil was generally high, and the nutrition level of the soil was good.

### Effects of soil pH and OM content on Cu, Pb, Zn, and Cd availability

As demonstrated in Table 1, the mean values of total contents of Cu, Zn, Pb, and Cd were 57.90, 426.7, 167.8, and 1.758 mg kg<sup>-1</sup>, respectively; these values were 2.92, 6.72, 7.95, and 16.28 times greater than the corresponding background values in Liaoning Province, respectively. According to the  $I_{\text{geo}}$  values of heavy metals, the soils were uncontaminated to moderately contaminated by Cu, moderately to strongly contaminated by Pb and Zn, and strongly contaminated by Cd.

The available contents of Cu, Zn, Pb, and Cd in soil samples were extracted using EDTA, and the available contents were 16.34, 6.997, 69.77, and 0.190 mg kg<sup>-1</sup>, respectively. The bioavailability coefficients of Cu, Zn, Pb, and Cd were 28.53%, 1.65%, 40.44%, and 10.83%, respectively (Table 1). Among the studied metals, Zn showed the lowest mobility and bioavailability in the study area, which might be attributed to the soil conditions (e.g., high carbonate content) (Gibson, 2012). The results are consistent with the founding of Lee et al. (2015), who reported that Pb and Cd are highly mobile and bioavailable, thereby posing a potential environmental risk.

As demonstrated in Table 2, the correlation analysis indicated that the availabilities of Zn, Pb, and Cd were negatively affected by soil pH ( $P < 0.05$  or  $P < 0.01$ ), with the strongest relationship observed for Zn and Pb. These findings are consistent with the results of Brokbarthold et al. (2012) and Soares et al. (2015), who reported negative

**Table 1** pH values, organic matter contents, total and extractive heavy metal contents, and bioavailability indices of heavy metals in maize rhizosphere soil

Items		Mean	Minimum	Maximum	SD	CV (%)	$B_n$ (mg kg <sup>-1</sup> )	$I_{geo}$
Soil property	pH	6.999	5.74	7.86	0.585	8.354	–	–
	OM	31.03	18.8	52.2	9.358	30.16	–	–
Cu	Total	57.9	9.81	93.4	20.4	35.2	19.8	0.96
	Extractive	16.3	7.95	20.6	3.35	20.5	–	–
	BC	28.5	16.7	50.7	8.8	30.9	–	–
Zn	Total	427	297	471	34.6	8.11	63.5	2.16
	Extractive	7	6.51	7.36	0.22	3.16	–	–
	BC	1.65	1.51	2.42	0.18	11	–	–
Pb	Total	168	46.9	312	55	32.7	21.1	2.41
	Extractive	69.8	33.4	106	19.7	28.2	–	–
	BC	40.4	22.9	65.9	11.2	27.7	–	–
Cd	Total	1.76	1.49	2.09	0.13	7.62	0.11	3.44
	Extractive	0.19	0.13	0.23	0.03	15.8	–	–
	BC	10.8	7.88	12.9	1.57	14.5	–	–

$B_n$ , background heavy metal content;  $I_{geo}$ , geo-accumulation index (mg kg<sup>-1</sup>); OM, organic matter content (g kg<sup>-1</sup>); Total, total heavy metal concentration (mg kg<sup>-1</sup>) in soil; Extractive, EDTA-extractable heavy metal concentration (mg kg<sup>-1</sup>) in soil; BC, bioavailability coefficient (%)

correlations between soil pH and the availabilities of Zn and Pb in soil. Previous studies indicated that the available concentration of Cd in soil increases with decreasing soil pH (Li et al. 2014a; Yu et al. 2016). Furthermore, the absorption of Cd by plants was shown to depend on the plant’s tolerance to low pH conditions (Hattori et al. 2006) because low pH conditions can inhibit plant growth and decrease the amount of Cd absorbed (Yu et al. 2016). However, no association between pH and EDTA-extractable Cu content was observed in this study, indicating that pH has no significant effect on available Cu content in maize rhizosphere soil.

Similar to previous studies, we found a positive correlation between Zn content and OM content in soil ( $P < 0.05$ ); however, no associations with OM content were found for the other heavy metals (Table 2). Zeng et al. (2011) reported that the bio-availabilities of Cu, Pb, and Zn were positively correlated with OM content due to the effects of OM on element mobilization in soil (Antoniadis et al. 2017). OM influences the mobility and availability of soil heavy metals by supplying organic chemicals to the soil solution as synthetic chelates, increasing heavy metal availability (McCauley et al. 2009). However, the available contents of Cu, Pb, and

**Table 2** Pearson correlation coefficients between soil property and extractable heavy metal content

Parameter	Soil property		Available heavy metal concentration (mg kg <sup>-1</sup> )			
	pH	OM	Cu	Zn	Pb	Cd
pH	1					
OM	0.119	1				
Cu	- 0.233	0.036	1			
Zn	- 0.701**	0.411*	0.737**	1		
Pb	- 0.611**	0.147	0.800**	0.913**	1	
Cd	- 0.433*	0.171	- 0.113	- 0.091	- 0.015	1

OM, organic matter; \* $P < 0.05$  level; \*\* $P < 0.01$

Cd were not correlated with OM content ( $P > 0.05$ ); therefore, we hypothesized that the availability of heavy metals in maize rhizosphere soil may be affected by the synergistic effect of soil pH and OM content.

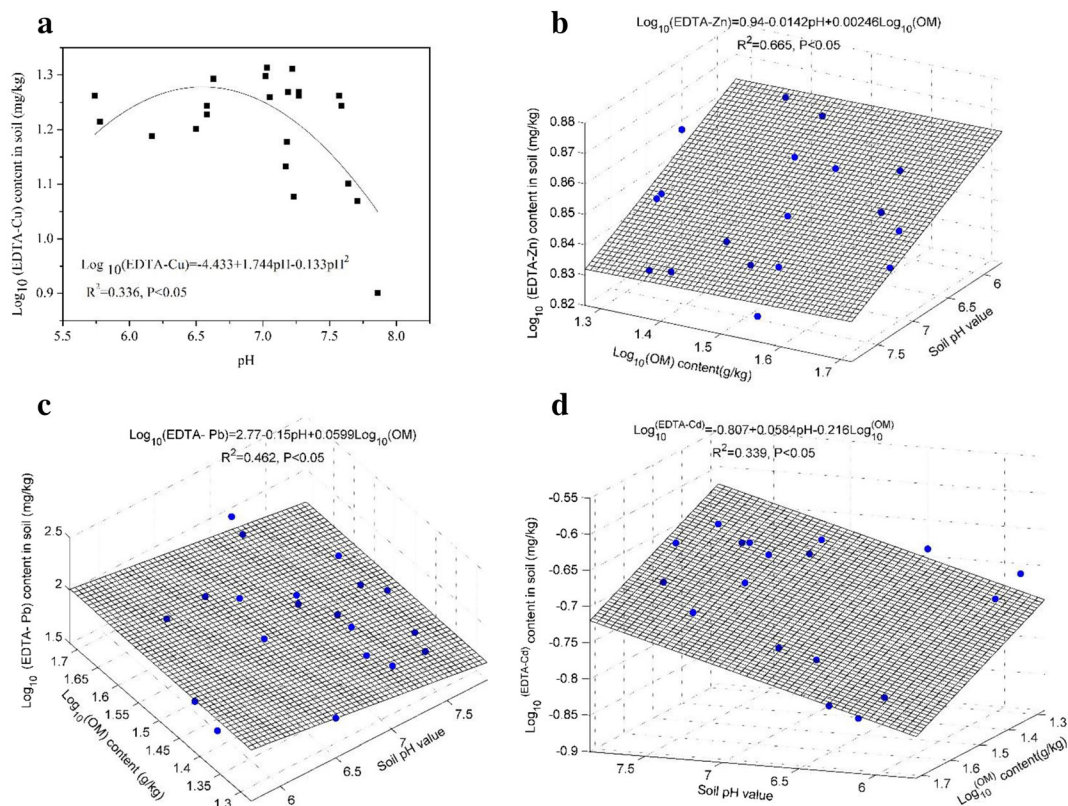
Based on stepwise multiple linear regression of the effects of pH and OM content, the combined influence of soil pH and OM content was more strongly associated with the available Zn, Pb, and Cd contents in soil compared with soil pH or OM content alone (Fig. 2(B–D)). In contrast, soil pH was the primary factor affecting the available content of Cu (Fig. 2(A)). These results suggest that soil pH and OM content may act synergistically to determine the availability of Zn, Pb, and Cd in maize rhizosphere soil, while the synergistic effect is not important for Cu.

Correlation analyses between the heavy metal concentrations indicated interactions among Cu, Zn, and Pb; no associations involving Cd were found (Table 2). Xiao et al. (2017) also reported the positive correlation between available Cd, Ni, and Cr contents in soil and Cu availability; however, the underlying

mechanisms of these interactive effects between bio-available heavy metals in soil remain unclear (Huang et al. 2016).

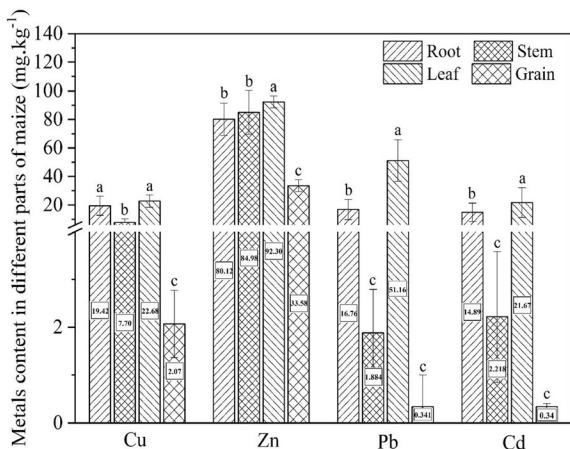
### Heavy metal contents in maize plant tissues

The contents Cu, Pb, Zn, and Cd varied among the different maize tissue, with the highest and lowest contents of Cu, Pb, and Cd found in leaf and grain tissues, respectively (Fig. 3). Metal smelting at HZP has led to the contamination of the surrounding atmosphere (Lu et al. 2010). Additionally, a previous study showed that atmospherically deposited metals can accumulate in plants via leaf absorption (Gan et al., 2017), which might explain the higher metal contents observed in maize leaf tissue. In contrast, Carbonell et al. (2011) found that more Cu, Pb, and Cd accumulated in maize roots than in aerial plant parts in a greenhouse experiment. This discrepancy might be attributed to differences in cultivation conditions between the field and greenhouse.



**Fig. 2** Multiple linear regression of soil pH and organic matter on available concentration of Cu (a), Zn (b), Pb (c) and Cd (d). The original data of EDTA-extractable heavy metals contents and

organic matter contents in soil samples were Log10-transformed to ensure homogeneity of variances



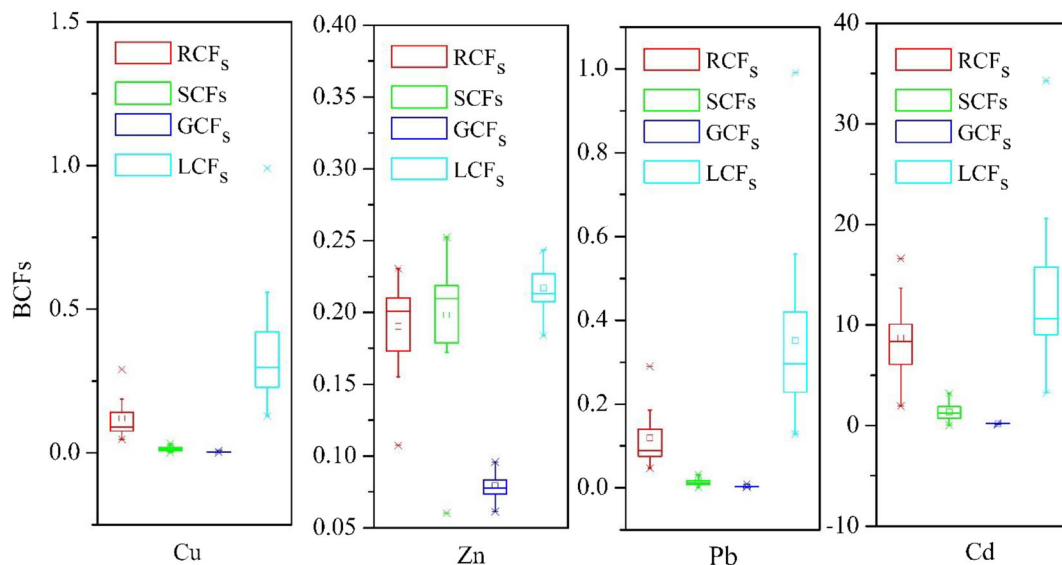
**Fig. 3** Contents of Cu, Zn, Pb, and Cd in different maize tissues. Lower-case letters indicate differences in heavy metal content between tissue types at  $P < 0.01$

As the edible portion of the plant, maize grain is relevant to the human diet. In this study, the mean Pb and Cd concentrations in grain tissue were 0.341 and 0.342 mg kg<sup>-1</sup>, respectively, both exceeding the maximum concentrations (0.20 and 0.10 mg kg<sup>-1</sup>, respectively) permitted by the Chinese National Standard (GB 2762-2017). Thus, the results suggested that maize grain collected from plants cultivated in heavy metal-contaminated soils may not be safe for consumption and pose potential risks to human health. High metals accumulation in rhizosphere soil reinforces metal translocation into maize grains (Wang et al. 2006; Seleiman and Kheir 2018).

The BCFs of heavy metals represent the metal uptake behavior of maize. In this study, the BCFs decreased in the order of LCF > RCF > SCF > GCF for Cu, Pb, and Cd, and in the order of LCF > SCF > RCF > GCF for Zn (Fig. 4). For Cu, Zn, Pb, and Cd, the highest BCF was observed in leaf tissue, whereas the lowest BCF was found in grain tissue for all metals. The widespread distribution of stomata on leaves, along with the high rate of evapotranspiration on the leaf surfaces, may lead to the greater accumulation of heavy metals in maize leaf (Chen et al. 2017). Conversely, the lowest accumulation in grain tissue may result from the additional barriers to translocation compared with in leaf and stem tissues (Sun et al. 2013b). We also found that the BCF values varied among different metals with Cd having the highest BCFs indicating that maize plants may have a strong capacity for Cd accumulation as indicated by Zhuang et al. (2009) and Zhan et al. (2014).

#### Metals' accumulation in maize plant and its influential factors

Multiple stepwise linear regression was employed to identify the combinatorial effects of pH, OM content, and soil EDTA-extractable metal content on heavy metal accumulation in maize tissues (Table 3). The accumulation of Cd in maize root, grain, and leaf tissues was affected by the combination of soil pH, OM content, and bioavailable content of Cd in soil (Table 3). The combined influence of soil pH and soil OM content affected



**Fig. 4** Bioaccumulation factors of heavy metals in maize tissues

**Table 3** Multiple linear regressions of pH, organic matter and soil EDTA-extractable metal content on accumulation of metals in maize tissues

Metal	Equation	R <sup>2</sup>	P value
Cu	$\text{Log}_{10}^{(\text{Root})} = 0.177 + 0.858\text{log}_{10}^{(\text{EDTA-Cu})}$	0.265	< 0.05
	$\text{Log}_{10}^{(\text{Stem})} = 0.336 + 0.059\text{pH} + 0.003\text{log}_{10}^{(\text{OM})} + 0.091\text{log}_{10}^{(\text{EDTA-Cu})}$	0.052	0.157
	$\text{Log}_{10}^{(\text{Grain})} = -2.008 + 0.447\text{log}_{10}^{(\text{EDTA-Cu})}$	0.228	< 0.05
	$\text{Log}_{10}^{(\text{Leaf})} = 1.784 - 0.015\text{pH} - 0.226\text{log}_{10}^{(\text{OM})}$	0.247	< 0.05
Zn	$\text{Log}_{10}^{(\text{Root})} = 3.014 - 0.006\text{pH} - 0.215\text{log}_{10}^{(\text{OM})} - 0.890\text{log}_{10}^{(\text{EDTA-Zn})}$	0.155	0.062
	$\text{Log}_{10}^{(\text{Stem})} = 5.117 - 0.062\text{pH} + 0.111\text{log}_{10}^{(\text{OM})} - 3.446\text{log}_{10}^{(\text{EDTA-Zn})}$	0.107	0.082
	$\text{Log}_{10}^{(\text{Grain})} = 1.373 + 0.031\text{pH} - 0.059\text{log}_{10}^{(\text{OM})}$	0.258	< 0.05
	$\text{Log}_{10}^{(\text{Leaf})} = 2.587 - 0.08\text{pH} - 0.055\text{log}_{10}^{(\text{OM})} - 0.577\text{log}_{10}^{(\text{EDTA-Zn})}$	0.102	0.151
Pb	$\text{Log}_{10}^{(\text{Root})} = 1.061 + 0.035\text{pH} - 0.182\text{log}_{10}^{(\text{OM})} + 0.084\text{log}_{10}^{(\text{EDTA-Pb})}$	0.203	0.057
	$\text{Log}_{10}^{(\text{Stem})} = 1.867 - 0.089\text{pH} - 0.675\text{log}_{10}^{(\text{OM})}$	0.312	< 0.05
	$\text{Log}_{10}^{(\text{Grain})} = -1.225 + 0.410\text{log}_{10}^{(\text{EDTA-Pb})}$	0.239	< 0.05
	$\text{Log}_{10}^{(\text{Leaf})} = 2.904 - 0.38\text{pH} - 0.364\text{log}_{10}^{(\text{OM})}$	0.275	< 0.05
Cd	$\text{Log}_{10}^{(\text{Root})} = 1.475 + 0.05\text{pH} - 0.909\text{log}_{10}^{(\text{OM})} - 0.302\text{log}_{10}^{(\text{EDTA-Cd})}$	0.384	< 0.05
	$\text{Log}_{10}^{(\text{Stem})} = -0.941 + 0.583\text{log}_{10}^{(\text{EDTA-Cd})}$	0.442	< 0.05
	$\text{Log}_{10}^{(\text{Grain})} = 0.962 - 0.012\text{pH} - 0.168\text{log}_{10}^{(\text{OM})} + 0.495\text{log}_{10}^{(\text{EDTA-Cd})}$	0.488	< 0.05
	$\text{Log}_{10}^{(\text{Leaf})} = 1.408 - 0.007\text{pH} - 0.761\text{log}_{10}^{(\text{OM})} - 0.48\text{log}_{10}^{(\text{EDTA-Cd})}$	0.384	< 0.05

Root, Stem, Grain, and Leaf, heavy metal content in the respective plant parts; OM, organic matter; the original data of EDTA-extractable heavy metals contents and organic matter content in soil was  $\text{Log}_{10}$ -transformed to ensure homogeneity of variances

the accumulation of Cu in leaf, Zn in grain, and Pb in stem and leaf material. EDTA-extractable contents of Cu, Pb, and Cd in soil had greater effects on root and grain Cu, grain Pb, and stem Cd concentrations than either soil pH or OM content; extractable metal was positively associated with the metal content in maize tissues, in agreement with the previous study of Xiao et al. (2017).

## Conclusions

This study demonstrated that the rhizosphere soil of maize that had been contaminated by Cu, Zn, Pb, and Cd in fields near the HZP in Liaoning Province has been contaminated to different degrees. This contamination should receive more attention to prevent adverse effects to human health. The correlation analysis suggested that the available contents of Cu, Zn, and Pb were negatively correlated with soil pH, while OM content was positively associated with Zn availability. The combined effect of soil pH and OM was more strongly associated with available Zn, Pb, and Cd contents in soil compared with either factor alone.

The contamination levels of Pb and Cd in maize exceeded safety thresholds, indicating a potential health risk for humans. The degree of accumulation of Cd in maize tissue was mainly determined by the combined effects of soil pH, OM content, and Cd availability. The effects of other soil properties (e.g., electrical conductivity, oxidation-reduction status, and cation exchange capacity) on bioavailability of heavy metals in maize remain to be investigated.

**Funding information** The authors appreciate the support of the National Natural Science Foundation of China (No. 41722110 and No. 41571474), the Jilin Province Natural Science Foundation of China (No. 20170101203JC), and 135 Breeding Project of Chinese Academy of Sciences, Northeast Institute of Geography and Agroecology (No. Y6H2081001).

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