

Characteristics and metal leachability of natural contaminated soil under acid rain scenarios

Wenfa Tan^{1,2*}, Yuan Li¹, Lei Ding¹, Yachao Wang¹, Jiangxiang Li³, Qinwen Deng²,
Feng Guo¹, Xue Xiao¹

¹School of Resource & Environment and Safety Engineering
University of South China, Hengyang 421001, China

²Hengyang Key Laboratory of Soil Pollution Control and Remediation
University of South China, Hengyang 421001, China

³Resource and Environmental Science College
Chongqing University, Chongqing 400044, China

*Corresponding author's e-mail: nhwftan@163.com

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Abstract: Contamination of soil with heavy metals has become a worldwide environmental problem, and receives great attention. In this study, we aim to investigate soil pollution level affected by an industrial district nearby. The total amount of typical heavy metals in the soils (Hengyang Songmu Industrial Park, Hunan Province, China) was analyzed. In addition, the fraction analysis and laboratory simulation leaching via different pH rainwater was carried out to study the migration and transformation of heavy metals. The main results show that the contents of Cu, Zn, Pb, Cr and Cd in the samples were higher than the soil background values in Hunan Province. The heavy metals forms, analyzed by sequential extraction method, show that the proportion of the unstable form of Cd, Zn and Pb was more than 50%. I_{geo} values indicate that the heavy metal pollution degree of soil sample #5 at the investigated area is recorded in the order of Cd(6.42), Zn(2.28), Cu(1.82), Pb(1.63), and Cr(0.37). Cu, Zn, Pb, Cr and Cd in this area could pose a potential leaching risk to the environment which may affect the food chain and constitute a threat to human health. It would be necessary to take steps to stabilize and monitor the heavy metals in soil.

Introduction

Although Industrial Park (IP) manufactured lots of products and strengthened social development, however, the growing eco-environmental problems in IP area have become a significant reality issue. Among which, soil contamination with heavy metals is a major problem. Słowik et al. (2011) investigated the pollution and mobility of chromium and lead in floodplain sediments. The result showed that a high contents of the elements were noted in the surface layer of the sediments which may be affected by weaving industry centers in the Obra River valley in Poland between the 16th and the 19th century. Stanisławska-Glubiak et al. (2018) investigated the dynamics of changes in the metal concentrations in the soils contaminated with Cd, Pb, and Zn for a 5 year period. The authors concluded that sandy soil contamination with metals poses a potentially higher threat to humans and the environment than silty soil contamination, and the examination of the sandy soils contamination, as well as of the groundwater occurring in these areas, should be carried out at least once for 5 years, and even more often.

Soil is a dominant component in ecological systems and acts as the source and/or sinks for contaminants. Plants that

possess the ability to accumulate high levels of metals in their biomass may elevate the risk of dissemination (Jonczak et al. 2014, Lu et al. 2007). The environmental quality of soil around IP has significant effects on urban environment and health of inhabitants (Li et al. 2004). Heavy metal contamination of urban soils, especially the soil around IP, has attracted considerable attention in the world.

Heavy metals in soils, although often with high variances, may be present in several forms, with different levels of solubility: (a) dissolved (in soil solution), (b) exchangeable (in organic and inorganic components), (c) structural components of lattices in soils, and (d) insolubly precipitated with other soil components (Lu et al. 2011). The most toxic forms of these metals in their ionic species are also the most stable oxidation states, e.g. Cd^{2+} , Pb^{2+} , Hg^{2+} and As^{3+} . Many heavy metal-contaminated sites have been identified. In China, where 16.1% of the soil has been proven to be contaminated, primarily by heavy metals, and in regions characterized by heavily polluting enterprises, industrial parks, and mining areas, the contamination levels can be as high as 30% (Ministry of Environmental Protection and Ministry of Land 2014). Similar trends are also found in the United States, heavy metals are prevalent at 77% of the Superfund sites, 72% of

the Department of Defense sites, and 55% of the Department of Energy sites. In Europe, heavy metal contaminated soils encompass several million hectares, accounting for about 34.8% of the total contaminated soil (Panagos et al. 2013).

Acid rain may enhance the release of heavy metal from soils due to the cation exchange in soil with major cations (e.g., H^+ , Ca^{2+} , and Mg^{2+}) accompanied by acid deposition (Huang et al. 2005, Wen et al. 2013). With the extension of leaching time in acid rain, metals were leached, hence contaminating the groundwater and deteriorating the terrestrial and aquatic ecosystems (Ding et al. 2011). Previous studies primarily focused on the assessment of soil environment pollution with heavy metals content by means of chemical analysis, or analysis of heavy metals' behaviors from different carriers, including heavy metal adsorption by different types of materials. However, chemical monitoring alone does not always reveal the real threat connected with the presence of heavy metals in the soil environment, and the effects of acid rain on the mobility and potential risks of heavy metals based on naturally contaminated soil around IP still need further study (Baran et al. 2015).

In this study, the overall novel objective lies in the following: i) batch column experiments conducted under simulated acid rain scenarios to evaluate desorption and potential risks of widely concerned heavy metals in naturally contaminated soil, and ii) using heavy metals digestion methods combined with geochemical indicators analysis, and fraction analysis methods combined with leaching experiments

to reflect a more believable pollution situation of the heavy metals in naturally contaminated soil. The experimental results obtained highlight the importance of preliminary laboratory tests in evaluating the influence of such basic parameters as the types of contaminants, soil composition and leaching agents on the efficiency of soil washing, which can provide basis references and scientific evidence for regulators' decision-making.

Materials and methods

Soil collection

We aimed to investigate soil pollution level affected by an industrial district (Fig. 1) in Hengyang, China. Consequently, a total of eleven points were evenly distributed and selected as sampling sites surrounding the industrial concentration area. Soil samples were collected with a probe at about 1–2 m depth after shoveling out the topsoil to avoid the external interference. Three soil samples were obtained at each sampling site, which were air-dried, ground to go through a 2 mm nylon sieve, and homogenized, before preparing the soil column (Li et al. 2004). Sub-samples were further ground with an agate grinder to pass through a 0.15 mm nylon sieve, which were then used to determine selected heavy metals. The sampling area has a typical subtropical monsoonal climate, characterized by a mean annual temperature of 23.2°C to 23.7°C and a mean annual rainfall of 1300–1800 mm (Li et al. 2009).

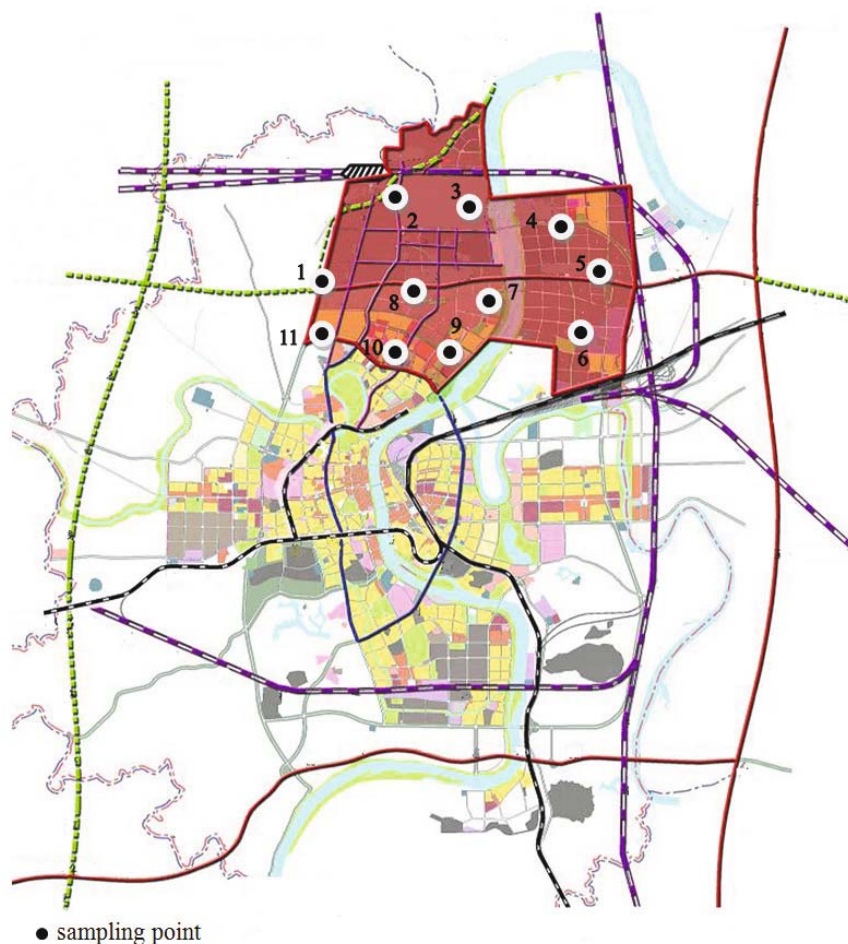


Fig. 1. Diagram of soil sampling locations in Hengyang Songmu Industrial Park, China

Preparation of simulated rain

Simulated acid rain (SAR) was prepared to reflect the characteristics of real acid rain in southern China (Huang et al. 2009). At the sampling sites, SO_4^{2-} and NO_3^- in the acid rain were 50–26 and 38–39 $\mu\text{mol/L}$, respectively, while the pH of rainfall varied from 4.18 to 7.43 (Chen et al. 2014). SAR was designed according to main ion composition and pH of the local rain water. Synthetic acid rain with the pH of 4.1, 5.6, and 7.0 was prepared from a stock H_2SO_4 – HNO_3 solution mixture (1:1.3, v/v). The concentrations of K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Cl^- , SO_4^{2-} , NO_3^- , and F^- were 6, 30, 29, 5, 41, 30, 38, 38 and 3 $\mu\text{mol/L}$, respectively.

Leaching experiment

Batch column experiments were conducted to evaluate desorption and potential risks of widely concerned heavy metals in polluted soil around IP under SAR with a range of pH values. Column experiments were performed using PVC cylinders ($\varnothing 100 \text{ mm} \times 1000 \text{ mm}$), and three parallel leaching columns were made for each experiment which were showed in Fig. 2. Glass beads ($\varnothing 6 \text{ mm}$) and quartz sand ($\varnothing 1.0$ – 2.0 mm) approximately 5 cm and 10 cm high, respectively, were packed in columns and supported on a Teflon filter (pore diameter of 5 mm). Then homogenized contaminated soil (35 cm high) was packed in after being covered with approximately 10 cm of quartz sand ($\varnothing 1.0$ – 2.0 mm) and 5 cm of glass beads ($\varnothing 6 \text{ mm}$), respectively. Each functional layer was isolated using 200 mesh nylon insulation. All materials that filled in columns were subjected to high-temperature sterilization in advance. The injection solution was delivered by a high-level water tank at a flow rate of 0–60 mL/h (Darcy flux of 12.2 cm/h) controlled by accommodating the valve. The column was flushed with SAR solution. Three parallel experiments were designed to make clear the relationship of all the factors.

Data collection and chemical analysis

The total contents of heavy metals (Cd, Pb, Cu, Zn and Cr) in soil were digested (0.5 g dry sample) with a mixture of concentrated 3 mL nitric acid, 3 mL hydrofluoric acid, and 6 mL hyperchloric acid in a polyvinyl fluoride crucible via microwave digestion (CEM MARS 5, Matthews, USA). After digestion, the sample solution was allowed to air-cool and then diluted with deionized water, followed by graphite furnace atomic absorption spectrophotometry (GFAAS-AA800, PerkinElmer Inc.) for Cd and Pb and flame atomic absorption spectrophotometry (Hitachi Z-5000) for Cu and Zn, respectively. The concentration of Cr(VI) in aqueous solution was analyzed with UV/Visible Spectrophotometer at 540 nm (Shimadzu UV-1240).

The chemical partitioning of heavy metals in soils was performed using the modified four-step BCR procedure as previously described (Li et al. 2010). According to the sequential extraction method (Rauret et al. 1999), four operationally defined chemical forms of metals were isolated as HOAc extractable, reducible, oxidizable, and residual fractions. The metal content of extracts was analyzed as described previously. The cumulative sum of four fractions was compared with the total concentration to check the recovery, and the recovery values were found satisfactory. Leachate

samples were collected at every 24 hour intervals from the bottom of columns. The total organic carbon (TOC) of soil was tested with TOC 5000A Organic Carbon Instrument.

Each sample of the soil material was analyzed in three duplicates to determine the mean value and standard deviation ($\leq \pm 5\%$). Statistical analyses were performed using SigmaPlot (v. 13.0 for Windows) and Origin 8.5 (v8.5.1 SR2).

Geochemical indicators

The Geoaccumulation Index (I_{geo}) developed initially by Muller (1979), is given by the following equation:

$$I_{\text{geo}} = \log_2 [C_n / 1.5B_n] \quad (1)$$

where C_n is the measured concentration of the metal n in the fine fraction ($< 0.063 \text{ mm}$) of the sample, and B_n is the geochemical background of the metal, n , also in the fine fraction. The factor 1.5 is used due to possible variations in background values for the metal in the environment. According to Muller (1979), the I_{geo} values are divided into classes that represent a type of sediment quality, the definitions for which are listed in Table 1.

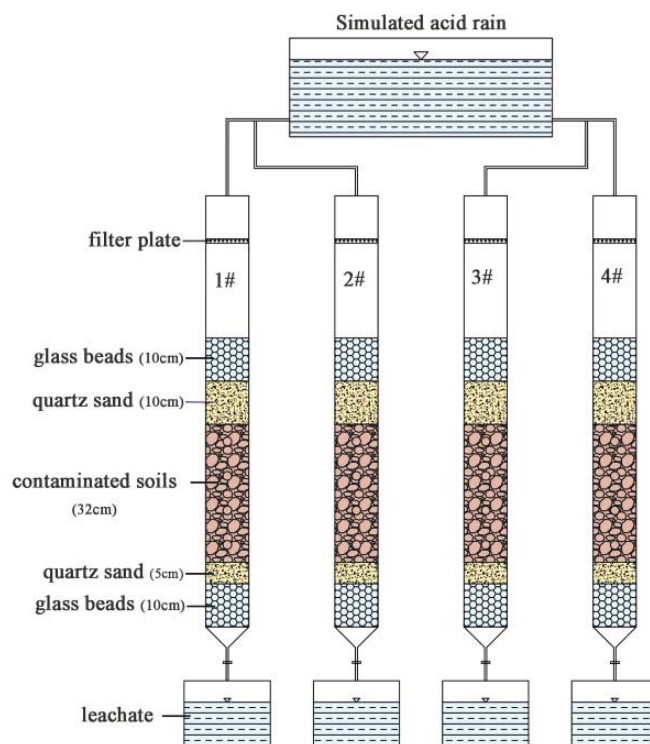


Fig. 2. Schematic diagram of the leaching experimental setup

Table 1. Classification of geoaccumulation index

I_{geo}	Class	Sediment quality
≤ 0	0	Absence of contamination
0–1	1	From absent to moderately contaminated
1–2	2	Moderately contaminated
2–3	3	From moderate to heavily contaminated
3–4	4	Heavily contaminated
4–5	5	From heavily to extremely contaminated
≥ 5	6	Extremely contaminated

Results and discussion

The content of heavy metals in samples

The total concentrations of heavy metals for soil samples prior to leaching are summarized in Table 2. The results show that the contents of Cu, Zn, Pb, Cr and Cd are much higher than the background values. This finding indicates that the soil had been affected by activities of industrial enterprises. Pollution in samples #5 and #6 is very serious, and the content of heavy metals far exceeds other samples. Especially, the contents of Cu, Zn, Pb, Cr and Cd in sample #5 are 5.3 time, 7.3 times, 4.6 times, 4.1 times and 128.6 times higher than soil background value of Hunan, respectively. The results of analyzed metals in a standard soil reference material were in good agreement with the expected values within 5%, and the relative standard deviation of replicates was less than 5%.

According to Nowack et al. (2010) and Kabala et al. (2014), metal mobility is controlled by the total metal concentration of solid phase soil, and the amount of soluble metals increased together with the increase of their total concentration. The works of other authors have confirmed that the concentrations of metals in the above ground parts and roots were correlated with the concentrations of metals in the soil determined

(Korzeniowska et al. 2017). From this perspective, Cu, Zn, Pb, Cr and Cd in this area could pose a potential leaching risk to the environment.

The index of geoaccumulation and contamination levels of heavy metals

The contamination levels of metals found in soil samples are listed in Table 3. The difference in concentrations is evident. I_{geo} is calculated using the respective concentrations observed in the fine fraction of the sample only (<0.063 mm). Based on the observed results, this study applies three different methods to calculate the I_{geo} . It has been found that the synthetic index of Cr in sample #5 was 0.37, which was 1 grade slight pollution. Cu and Pb in sample #5 were 1.82 and 1.63 which was 2 grade pollution. Zn (2.28) was 3 grade pollution. The grade of Cd is 6.42, which means extremely strong pollution level. I_{geo} values indicated that the heavy metal pollution degree and potential risk of soil at the investigated area were recorded in the following order: Cd>Zn>Cu>Pb>Cr. Caution should be taken on the multi-metal pollution since heavy metals not only pollute the surface water and groundwater, but also hurt human beings through the food chain (Hejabi et al. 2011).

Table 2. The content of heavy metals in samples [mg/kg]

Samples	Cu	Zn	Pb	Cr	Cd
#1	104.3±0.27	284.2±1.72	73.2±0.73	115.6±1.07	2.7±0.18
#2	111.6±0.14	132.3±0.94	124.7±1.03	149.6±1.49	3.8±0.23
#3	89.5±0.84	240.9±1.60	108.5±1.69	129.3±1.02	4.0±0.19
#4	95.1±0.71	103.8±0.85	63.5±0.48	133.5±1.15	3.4±0.21
#5	142.9±1.03	682.7±4.87	125.0±0.93	132.1±1.03	12.6±0.29
#6	109.4±1.92	212.6±2.10	122.4±0.74	129.6±1.92	3.9±0.12
#7	77.6±0.34	94.8±0.83	52.5±0.56	124.9±0.73	2.6±0.17
#8	64.3±0.65	102.2±1.02	52.4±0.37	136.8±0.79	3.1±0.20
#9	89.1±0.35	106.5±0.82	59.3±0.57	132.1±0.47	3.1±0.26
#10	119.4±1.23	102.2±1.14	80.7±0.43	141.4±0.32	3.9±0.38
#11	86.9±0.93	113.7±1.03	79.5±0.72	105.4±0.72	4.3±0.41
Background value of Hunan	27	94	27	32	0.098

Table 3. The index of geo-accumulation and contamination levels of five heavy metal elements

Samples	Cu	Zn	Pb	Cr	Cd
#1	1.36	1.01	0.85	0.18	4.20
#2	1.46	-0.09	1.62	0.55	4.69
#3	1.14	0.77	1.42	0.34	4.77
#4	1.23	-0.44	0.65	0.39	4.53
#5	1.82	2.28	1.63	0.37	6.42
#6	1.43	0.59	1.60	0.35	4.73
#7	0.94	-0.57	0.37	0.29	4.14
#8	0.67	-0.47	0.37	0.42	4.40
#9	1.14	-0.40	0.55	0.37	4.40
#10	1.56	-0.46	0.99	0.47	4.73
#11	1.10	-0.31	0.97	0.05	4.87
Average I_{geo}	1.26	0.17	1.00	0.34	4.72
Pollution level	Middle level pollution	Slight pollution	Slight pollution	Slight pollution	Strong – extreme strength pollution

Fraction analysis of heavy metals in soils

The heavy metals forms of soil samples #5, #6 and #11 which possess much higher pollution levels were analyzed by using BCR method. The fraction analysis of Zn, Cu, Pb, Cr and Cd in soils is depicted in Fig. 3.

For #5, #6 and #11, the greatest proportion of Cr and Cu was in the residual fraction, followed by the oxidizable fraction, accounting for over 70% of the total. Zn in sample #5 was mainly associated with the residual fraction (48.2%). Zn in #6 was mainly associated with the reducible fraction (39.5%), while it was followed by the residual fraction (36.9%). Zn in sample #11 was concentrated primarily in the residual fraction followed by the HOAc extractable fraction, 31.5% and 26.1%, respectively.

The distribution of various fractions in #5, #6 and #11 show that a considerable portion of Cd and Pb was in the reducible fraction and HOAc extractable fraction, whereas Cd in #6 was dominantly associated with the equivalent HOAc extractable fraction (46.1%), followed by the reducible fraction (30.5%). These results, however, are not consistent with previous research. Ash et al. (2015) found that reducible (Fe/Mn oxides) and oxidizable (organic matter) fractions are the most important for Cd retention, while the largest amounts of Pb were retained by oxidizable and residual fractions. The causes may be attributed to different soil properties and sampling time. The pH of soil has a significant influence on the environmental behavior of heavy metals (Guo et al. 2003, Wang et al. 2009). Onweremadu et al. (2007) revealed that the Cd concentration, compared with Pb, in the soil has a relatively higher seasonal variability. In general, heavy metals in HOAc exchangeable

fractions are considered readily mobile. The HOAc extractable fraction is approximately equal to the sum of water-soluble, exchangeable, and carbonate bound fractions, representing the most mobile and bioavailable metal pool.

Leaching experiment

The soil sample #5, which shows that pollution of heavy metals was relatively serious, has been chosen as the subject for the leaching experiment. Basic physical and chemical characters of soil sample #5 are provided in Table 4. The soils are characterized as typical red soils, and the mean moisture content, pH and TOC are 25.2%, 6.8, and 40.5 g/kg, respectively. Study on the grain diameter distribution demonstrated that samples mainly existed in grains with a diameter of 0.3–0.05 mm (80.2%). Synthetic acid rain with pH of 4.1, 5.6, and 7.0 was prepared from a stock H₂SO₄-HNO₃ solution mixture (1:1.3, v/v). SAR was made up of K⁺, Na⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻, and F⁻, which were 6, 30, 29, 5, 41, 30, 38, 38 and 3 μmol/L at the respective amounts. The results from the leaching of heavy metals in soil sample #5 are shown in Fig. 4. Generally, leaching characteristics of Cu, Zn, Pb and Cr showed different leaching properties with time increase (Esshaimi et al. 2013, Zhang et al. 2016). However, statistically speaking, pH of the synthetic acid rain impacts turns out to be small.

In terms of Cu (Fig. 4a), it was mostly concentrated in the first 2 days. After a day of leaching, leachate Cu concentration decreased from 0.45 mg/L to 0.05 mg/L (200 mL), accounting for the average of 10.2% of the total accumulative leaching amounts. Then, the leachate Cu concentration almost remained

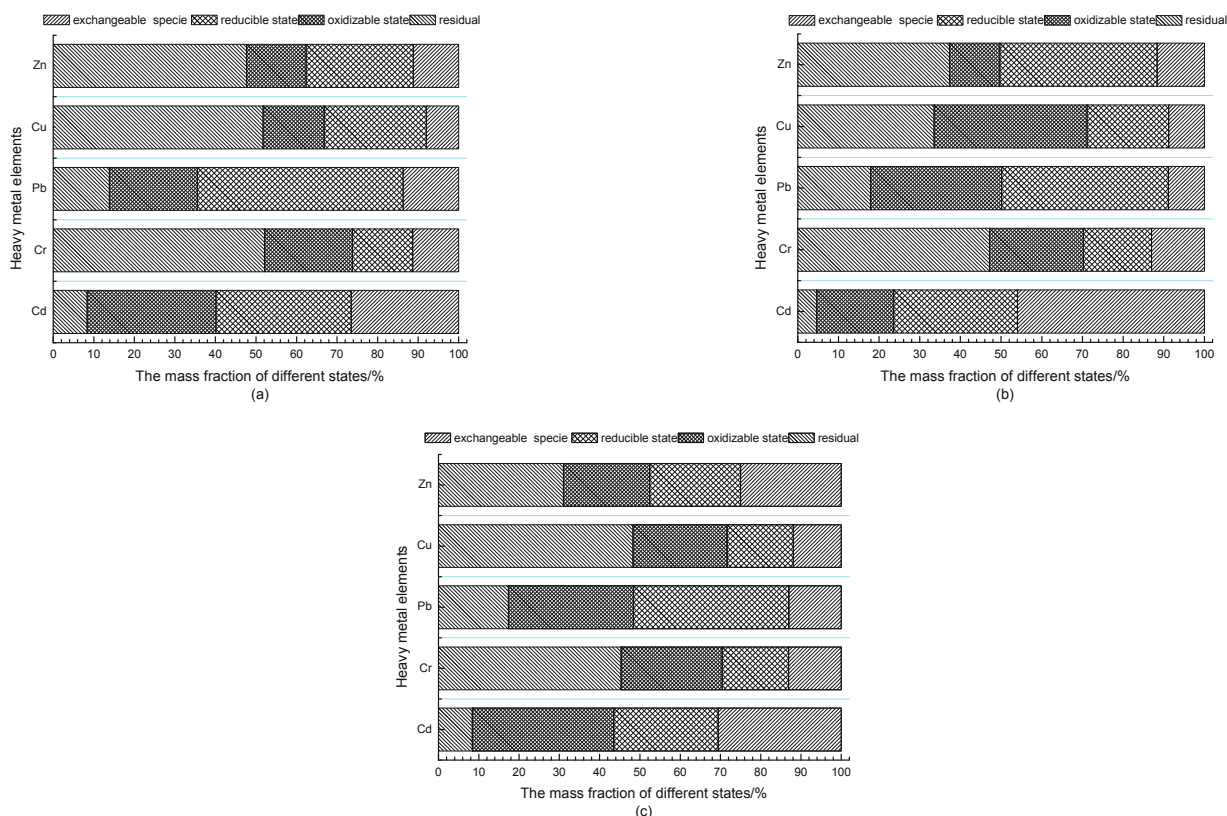


Fig. 3. Fraction analysis on heavy metal in pollution soil, soil sample #5 (a), soil sample #6 (b) and soil sample #11 (c)

Table 4. Basic physical and chemical characters of soil for column experiment

Parameters	Moisture content [%]	pH	TOC [g/kg]	Layer [m]	Textural group	Particle size [mm]		
						>0.3	0.3–0.063	<0.063
Range	23.7–28.8	6.3–7.1	31.4–56.1	subsoil	red soil	10.2%	80.2%	9.6%
Mean	25.2	6.8	40.5	(1–2)				

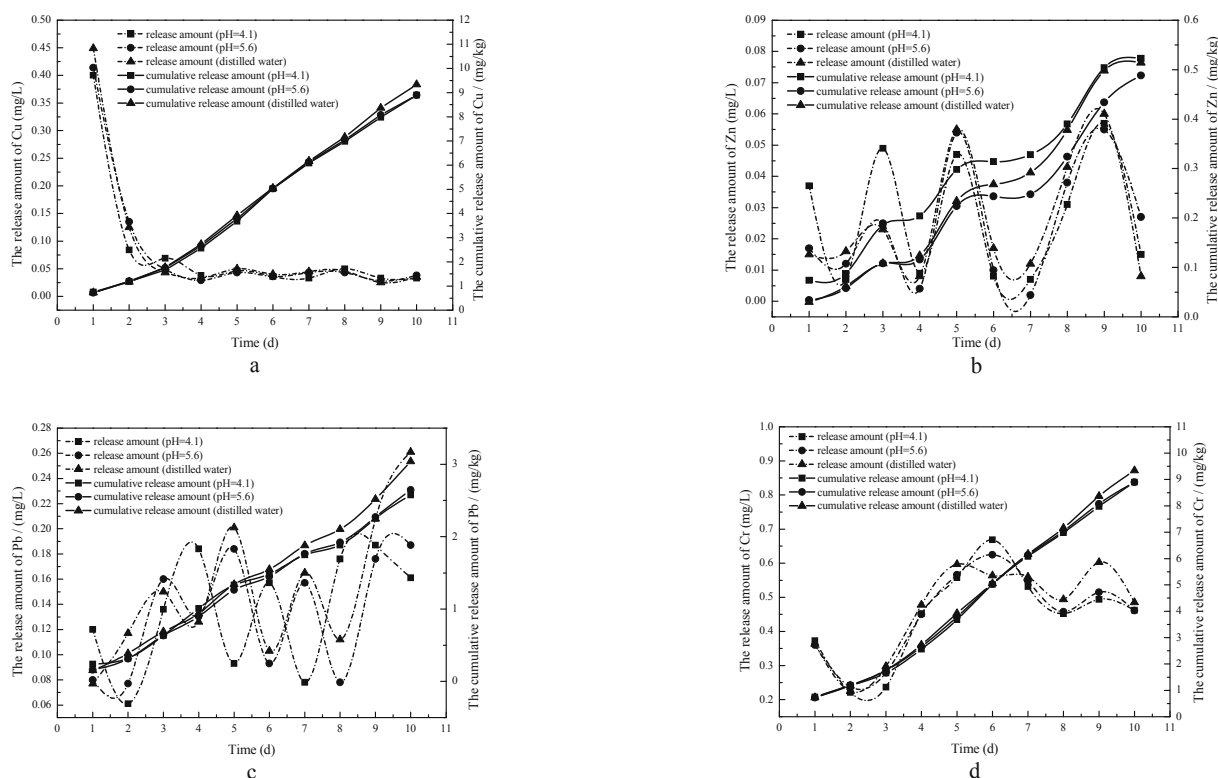


Fig. 3. The leaching curve of Cu(a), Zn(b), Pb(c) and Cr(d) in sample #5

unchanged in 0.05 mg/L. The concentration of Zn in leachates (Fig. 4b) is generally with a series of decreasing and increasing cycles. On the beginning day, the concentration decreased from 0.04 mg/L to 0.01 mg/L as leaching times increased, and yet the next day leachate Zn concentration increased and reached a peak at 0.05 mg/L, followed by a decrease. The variance of leachate Zn concentration was gentle, and maximum leachate Zn concentration was observed on day 9 (0.06 mg/L). A similar trend was observed for leachate Pb concentration as leachate amount increased, the concentration of Pb in leachates (Fig. 4c) is also generally with a series of decreasing and increasing cycles. Likewise, its maximum leachate Pb concentration was observed on day 9 (0.26 mg/L). Leaching characteristics of Cr showed different leaching properties from Cu, Zn and Pb with time increase (Fig. 4d). The concentration decreased from 0.38 mg/L to 0.21 mg/L, followed by a progressive increase until on day 6 it reached 0.69 mg/L and then remained between 0.5 mg/L to 0.6 mg/L.

The literature shows that soil pH has a significant influence on the environmental behavior of heavy metals in soil (Gray et al. 2005, Miretzky et al. 2011). However, the leaching data in this study shows that the leaching rate is less influenced by the pH of synthetic acid rain. For soil

sample #5, a certain proportion of Cu, Zn, Pb and Cr was in the HOAc exchangeable fraction and the oxidizable fraction. These fractions, in general, are considered to be readily mobile, while the properties are little affected by the pH of leachate. It is worth noting that research has proven that Cd is very mobile in the soil environment and shows potentially high toxicity for living organisms (An et al. 2004, Baran et al. 2015). However, it was found to be little dependent on pH according to the leaching data obtained in our study. This is possibly because the mobility of metals in the soil is to some extent determined by their interactions, which was confirmed by the studies of Markiewicz-Patkowska et al. (2005). Together with basic pH values, the presence of multi-heavy metal ions in the soil lead to an increase in the retention of a single metal, mainly as competitive as consequence of the ionic exchange, the principal retention mechanism of heavy metals (Esshaimi et al. 2013). Besides, metal leaching from the soil is caused, on the one hand, by leaching pH, while on the other hand, by soil properties and climate factors which also affect the mobility or immobility of metals in the soil (Stanislawska-Glubiak et al. 2018). Therefore, heavy metals usually exhibit different leaching characteristics due to different retention pattern of soil matrices.

Conclusion

The results definitely demonstrated that the contents of Cu, Zn, Pb, Cr and Cd are much higher than the background values of Hunan Province, China. A considerable portion of Cu, Zn, Pb, Cr and Cd was in the reducible fraction and HOAc extractable fraction. In addition, BCR analysis of heavy metal shows that the unstable form of Zn, Pb and Cd is more than 50%. I_{geo} values indicate that the heavy metal pollution degree and potential risk of soil at the investigated area was recorded in the following order: Cd>Zn>Cu>Pb>Cr. Column leaching via different pH rainwater confirms that heavy metal releases after acid rain leaching were strongly associated with heavy metal fractionation. Cu, Zn, Pb, Cr and Cd in this area could pose a potential leaching risk to the environment which may enter the food chain and constitute a threat to human health. It would be necessary to take steps to stabilize and monitor the heavy metals in soil.

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