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RESEARCH ARTICLE

Chemical forms of heavy metals in agricultural soils affected by coal mining in the Linhuan subsidence of Huaibei Coalfield, Anhui Province, China

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Abstract Total concentrations of heavy metals in soils may not be enough to understand their mobility and bioavailability. It is important to evaluate the degree of association of heavy metals with different chemical forms of soil. The sequential extraction method was applied to evaluate the mobile behavior of Cd, Cr, Cu, Ni, Pb, and Zn in 42 representative soil samples from the Linhuan subsidence of Huaibei Coalfield, Anhui Province, China. The results showed that mean concentrations of heavy metals were higher than background values of Huaibei City surface soil by a factor of 1.16 to 3.21 (Cd, 3.21; Cr, 1.19; Cu, 1.16; Ni, 1.23; Zn, 1.85) except Pb (0.89). Most of the total Cr, Cu, Ni, Pb, and Zn were present in the residual forms (above 70 %), while Cd was dominated by the exchangeable forms (42 %). The correlations analysis showed that the mobility of Cd, Cu, Pb, and Zn in soil was affected by both physicochemical properties and total metal concentrations. In contrast, the moblity of Cr and Ni of soil was mainly affected by their total metal concentrations. According to assessments by the potential ecological risk index (*RI*) and the risk assessment code (RAC), Cr, Cu, Ni, Pb, and Zn posed no or low risk. However, Cd presents high to very high risk, due to its higher exchangeable and carbonate-bound fractions.

Keywords Heavy metals · Chemical forms · Risk assessment · Coal mining · Subsidence · Agricultural soils

Introduction

The contamination of soil ecosystem by heavy metals is considered as a global environmental issue (Facchinelli et al. 2001; Solgi et al. 2012). Heavy metals in soils are originated from natural and anthropogenic sources (Facchinelli et al. 2001; Li et al. 2014). The major natural sources are parent rock materials and volcanic emissions (Blaser et al. 2000; Sun et al. 2016). The anthropogenic sources include fertilizers and pesticides (Nicholson et al. 2003; Nziguheba and Smolders 2008), agricultural and industrial waste discharges (Chabukdhara and Nema 2013; Jan et al. 2010; Silveira et al. 2003; Solgi et al. 2012), and mining (Bhuiyan et al. 2010; Li et al. 2014; Rey et al. 2013; Šajn et al. 2013). Among anthropogenic sources of heavy metals, coal mining plays a significant role. Many toxic heavy metals are released during coal mining and the burning of coal (Chen et al. 2016; Rout et al. 2013; Sun et al. 2013).

Heavy metals do not vanish in time unlike some organic materials. The soil heavy metals in the environment are relatively stable and are difficult to be removed through natural processes. Although essential for living tissues, they show toxic effect if they exceed the limit values. The most important impact of soil pollution on environmental health is that heavy metals can introduce into the food chain by plants and by their direct use or consumption by animals and human beings (Boussen et al. 2013; Dong et al. 2011; Ji et al. 2013; Li

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et al. 2014; Park and Choi 2013; Türkdoğan et al. 2003). Heavy metals taken into the human body at doses higher than the limit values proposed by the World Health Organization (WHO) are known to cause carcinogenic, teratogenic, toxic, or cardiovascular problems. Accordingly, the environmental risk of heavy metal pollution in agricultural soils by mining activities has been of great concerns.

Much attention has been focused on the investigation of the total metal concentrations in soils. Previous researches have revealed that, in most cases, soils in the vicinity of mines are contaminated severely by heavy metals. For example, in coal mine-affected agricultural soils in the northern part of Bangladesh, the average concentrations of Ti, Mn, Zn, Pb, As, Fe, Rb, Sr, Nb, and Zr exceeded the world normal averages and, in some cases, Mn, Zn, As, and Pb exceeded their toxic limits (Bhuiyan et al. 2010). In the soils around a lead and zinc smelter, the average concentrations of Pb, Cd, Hg, As, Zn, and Cu are 20, 11, 5.5, 4.6, and 3.2 times higher than the European median values, respectively (Šajn et al. 2013). In agricultural soils in non-ferrous metal mine area, high heavy metal concentrations were found in the agricultural soils closer to mines and metal smelters, and Cd and Cu were two primary pollutants in the soils with concentrations of 0.52–2.55 and 27.87–426.15 mg kg^{-1}, respectively (Liu et al. 2013). The mean concentrations of Pb, Zn, and Cd in the arable land soils around an old Spanish Pb-Zn mine were as high as 393.05, 186.09, and 2.47 mg kg^{-1}, respectively (Rodríguez et al. 2009). Although total metal concentrations may give information about the overall contamination conditions of the soil, the chemical forms of heavy metals determine their ecotoxicity, mobilization capacity, and behavior in the environment. When heavy metals are released into the soil, they are transformed into different geochemical forms through a series of physical, chemical, and biological processes (Kraemer and Hering 2004). Among these different geochemical forms, the water-soluble and carbonate forms are considered as most bioavailable, reducible bounded to Fe/Mn oxides and oxidizable bounded to organic matters may be potentially bioavailable, while the residue bounded to the soil matrix is not bioavailable (Delgado et al. 2011; Rodríguez et al. 2009). Thus, the chemical forms of heavy metals might provide much more useful information regarding the chemical nature or potential mobility and bioavailability of a particular element.

Huaibei Coalfield is one of the biggest coal-mining areas in China. The exploitation of coal resources promoted the development of the economy and society of Huaibei City, but it resulted in a large-scale coal-mining area being subsided or to be subsided, damaging the local ecological environment. In addition, heavy metal releases may increase during coal exploitation, storage, and utilization, the disposal of coal gangue and fly ash. Only one study described As, Cu, and Zn contamination in soil and wheat during coal mining in this area (Shi et al. 2013). In the present study, we investigate the Linhuan subsidence area of Huaibei Coalfield for the first time to (1) determine the chemical forms of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) by applying the sequential extraction procedure and (2) to assess the potential ecological risk of heavy metal contamination in the soils.

Materials and methods

Study area

The Linhuan coal mining area is located in warm temperate, semi-humid monsoon climate zone. The average annual temperature, rainfall, evaporation, frost-free period, and relative humidity are 14.8 °C,830 mm, 1815.6 mm, 206.9 days, and 71 %, respectively, and prevailing winds are in an southeast direction in summer, and a northeast direction in winter. Due to the exploitation of coal resources, extensive land subsidence and submergence occurs in the Linhuan subsidence area. The total subsidence areas come to 13.2 km^2 with the water area of 3.5 km^2 and water storage of 12,188,480 m^3. Meanwhile, large amounts of coal gangue and fly ash are produced during mining, washing, and coal consumption, and are usually piled around mines. In addition, in south of the Linhuan subsidence area, there are coal cleaning plant, coking plant, and coal-fired power plant which may also release heavy metals into the surrounding environment.

Sampling

A total of 42 surface soil samples (0–20 cm) were collected in the study area in July (Fig. 1). Three to five subsamples were taken with a stainless steel blade and a plastic scoop, and then mixed thoroughly to get a composite soil sample weighted about 1.0–1.5 kg. The collected soil samples were stored in a polyethylene bag, transported to the laboratory where they were air-dried at ambient temperature, and sieved through a 2-mm mesh to remove coarse debris for measuring pH, electric conductivity (EC), water content (WC), organic matter (OM) content, total N (TN), total C (TC), available potassium (AK), and available phosphorus (AP). For the determination of heavy metals, the soil samples were further ground with the agate mortar and passed through 100-mesh sieve.

Analytical method

The pH and EC were measured using pH meter and electric conductivity (sample/water = 1 g:5 ml). The WC was measured using the oven-drying method and were dried at 105 ± 2 °C for 12 h. Soil OM was determined by the potassium bichromate titrimetric method, while soil TN and TC were determined by the elemental analyzer (Element, Germany).

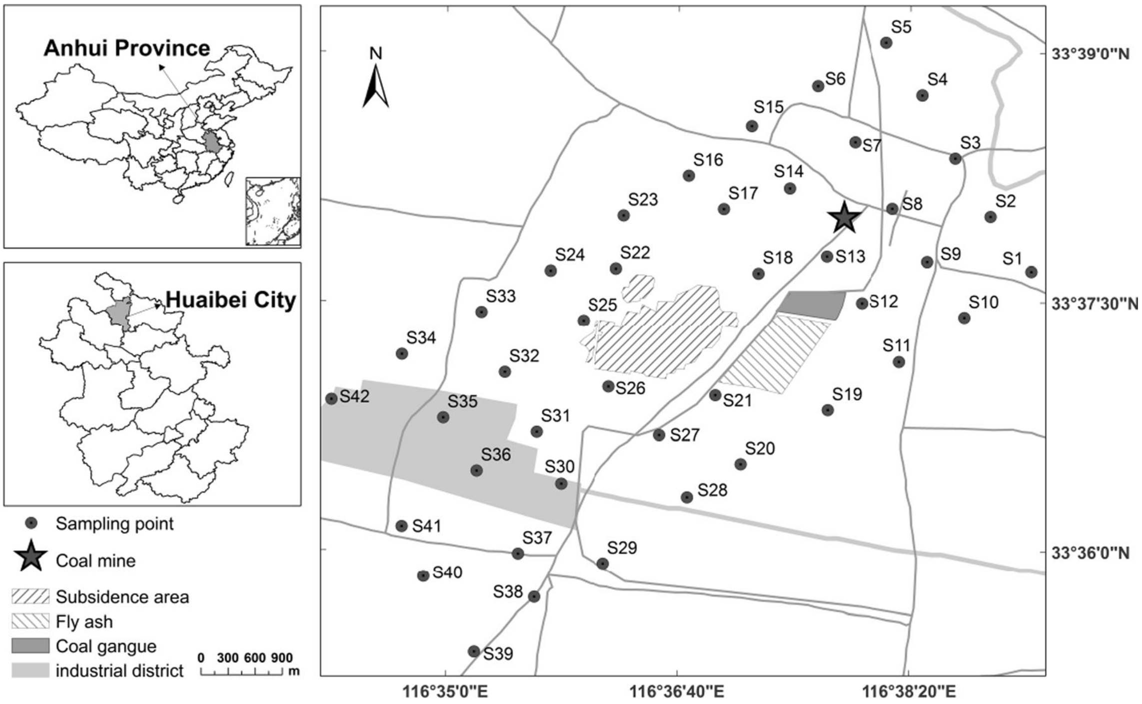

Fig. 1 Location map showing the sampling sites

The AP of samples was extracted using 0.5 mol L^{-1} $NaHCO_3$, and then determined by the molybdate blue spectrophotometric method. AK was extracted using 1 mol L^{-1} NH_4OAc, and then determined by the flame atomic absorption spectroscopy method.

The soil samples were digested with HCl, HNO_3, HF, and $HClO_4$. About 0.5 g soil sample was weighted into a cleaned Teflon vessels, 10 mL high-purity HCl was added, after initial decomposition, and 13 mL high-purity acid mixture, i.e., $HClO_4/HNO_3/HF = 3:5:5$, was used to digest the samples. After cooling, the solution was adjusted to 50 mL with 5 % HNO_3. The sample solutions were analyzed Cd, Cr, Cu, Ni, Pb, and Zn using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (XSP Intrepid II, USA). Reagent blanks and soil standard reference material (GSS-3) were processed along with the samples, and the recoveries of Cd, Cr, Cu, Ni, Pb, and Zn were 87–115, 95–99, 93–99, 106–128, 96–108, and 110–140 %, respectively.

Chemical forms of metals were measured by a sequential extraction procedure adapted from Tessier et al. (1979). The extraction was carried out in order to obtain the following: F1, exchangeable; F2, bound to carbonate; F3, bound to Fe–Mn oxides; F4, bound to organic matter; and F5, residual. A check of the results of the sequential extraction procedure was conducted by comparing the sum of the five steps (exchangeable + carbonate + Fe–Mn oxide + organic + residual) with the total metal concentration. The recoveries of Cd, Cr, Cu, Ni, Pb, and Zn were 80–121, 75–118, 82–114, 86–130, 80–115, and 80–119 %, respectively, indicating satisfactory results.

Ecological risk assessment

The potential ecological risk index (*RI*) was introduced by Hakanson (1980), according to the toxicity of elements and the response of the environment, to assess the degree of element pollution in sediments:

$$C_f^i = C_s^i \Big/ C_o^i \tag{1}$$

$$E_r^i = T_r^i \cdot C_f^i \tag{2}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

C_f^i, C_s^i, and C_o^i are, respectively, contamination factor, measured concentration, and reference concentration of element *i*, and the reference concentrations of metals in this study are Cd = 0.081, Cr = 70.8, Cu = 22.1, Ni = 32.3, Pb = 30.9, and Zn = 76.8 (AHEMC 1992). E_r^i is the monomial ecological risk factor, and T_r^i is the biological toxic factor of an individual element, which are defined as Cr = 2, Cu = Pb = Ni = 5, Zn = 1, and Cd = 30 (Yuan et al. 2014a). *RI* is calculated as the sum of the risk factors of all heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn).

The risk assessment code (RAC) is useful to assess the environmental risk using sequential extraction as a characterization method, and it has been used to assess the environmental risk of heavy metal pollution in sediments and soils (Liu et al. 2013; Nemati et al. 2011; Yuan et al. 2014b). There is no risk when the exchangeable and carbonate fractions are lower than 1 %, percentages of 1–10 % reflect low risk, 11–30 % poses medium risk, 31–50 % poses high risk, and above 50 %, the soil poses a very high risk.

The *RI* assesses potential ecological and environmental effects based on total heavy metal concentration and their toxicology, whereas RAC considers mobile proportions of metals (i.e., exchangeable and carbonate fractions) (Perin et al. 1985; Singh et al. 2005). Both methods are complementary in evaluating the mobility and toxicity of metals.

Statistical and geostatistical analyses

To identify the relationship among heavy metals in soils and their possible sources, Pearson's correlation coefficient analysis was performed (Facchinelli et al. 2001) using the commercial statistics software package SPSS version 19.0 for Windows. The correlation coefficient measures the strength of the interrelationship between two heavy metals.

Results and discussions

Spatial distribution and source analysis of heavy metals

The mean concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were 0.26, 84.3, 25.7, 39.6, 27.5, and 142 mg kg^{-1}, respectively. The mean concentrations of heavy metals in soil samples decreased as follows: Zn > Cr > Ni > Pb > Cu > Cd. The mean concentrations of these heavy metals were higher than background values of Huaibei City surface soil by a factor of 1.16 to 3.21 (Cd, 3.21; Cr, 1.19; Cu, 1.16; Ni, 1.23; Zn, 1.85) except Pb (0.89) (AHEMC 1992). In addition, the mean concentrations of these metals were higher than their background values of China soil by a factor of 1.14–3.51 (Cd, 3.51; Cr, 1.38; Cu, 1.14; Ni, 1.69; Pb, 1.17; Zn, 2.1) (CNEMC 1990), and the concentrations of Cd and Zn were higher than the Natural Environmental Quality Standard values for the soils in China (CNEPA 1995), suggesting that heavy metal concentrations in the studied soils are of the danger levels. The coefficient variations of heavy metals were comparatively low, with a decreasing order of Zn (36 %) > Cd (27 %) > Cu (22 %) > Ni (18 %) > Pb (15 %) > Cr (14 %), which suggests that the concentration levels of these metals in soils were less variable.

To identify the relationship among heavy metals in soils and their possible sources, Pearson's correlation coefficient analysis were performed as shown in Tables 1 and 2.

A significant positive correlation was found among heavy metals ($p < 0.01$) in surface soils. It can be seen that Cd showed a significant positive relationship with Cu (0.69), Pb (0.54), and Zn (0.43). Cu showed a significant positive relationship with Pb (0.40) and Zn (0.47). The strong correlations among these heavy metals indicate their common origin, possibly sourced from carbonate and sulfide minerals (e.g., sphalerite, strontianite, galena, etc.) that are associated with coal seams (Hower and Robertson 2003; Sakurovs et al. 2007). However, the concentrations of Cr and Ni showed positive relationship with each other but very weak correlations with Cd, Cu, Pb, and Zn. This indicates that Cr and Ni may have different geochemical behaviors and sources from other metals.

Significant correlations between Cd, Cu, Pb, Zn, and soil physicochemical properties were observed, which revealed that the metals may have an anthropogenic source. Significant positive correlations of Cd, Cu, Pb, and Zn with OM, TN, and TC may be due to the fact

Table 1 Descriptive statistics of total heavy metals of surface soils (mg kg^{-1}) (n = 42)

Variable	Cd	Cr	Cu	Ni	Pb	Zn
Minimum	0.16	60.7	13.8	23	20	69.2
Maximum	0.51	104	44.5	54.1	39.1	267
Mean	0.26	84.3	25.7	39.6	27.5	142
Standard deviation	0.07	11.8	5.6	7.1	4	50.5
Coefficient of variation	0.27	0.14	0.22	0.18	0.15	0.36
Soil background[a]	0.081	70.8	22.1	32.3	30.9	76.8
Soil background[b]	0.074	61	22.6	23.4	23.6	67.7
Soil environmental quality[c]	0.2	90	35	40	35	100

[a] The backgrounds of soil environment in Huaibei City (AHEMC 1992)

[b] The backgrounds of soil environment in China (CNEMC 1990)

[c] Environmental quality standard for soil (CNEPA 1995)

Table 2 Correlations between heavy metal concentrations and physiochemical properties of surface soils (*n* = 42)

Elements	Cd	Cr	Cu	Ni	Pb	Zn
Cd	1					
Cr	0.12	1				
Cu	0.69**	0.16	1			
Ni	0.07	0.58**	0.06	1		
Pb	0.54**	0.27	0.40**	0.25	1	
Zn	0.43**	0.23	0.47**	0.29	0.27	1
pH	0.30*	0.07	0.45**	0.07	0.19	0.25
EC	0.31*	0.02	0.13	0.02	0.09	0.17
WC	0.40**	−0.05	0.44**	−0.12	0.22	0.18
OM	0.58**	0.08	0.67**	−0.25	0.48**	0.36*
TN	0.46**	0.22	0.56**	−0.03	0.60**	0.36*
TC	0.61**	−0.04	0.67**	−0.26	0.39**	0.37*
AK	0.46**	0.13	0.25	0.10	0.56**	0.31*
AP	0.28	−0.02	0.22	−0.22	0.35*	−0.02

***Correlation is significant at the 0.05 level (two-tailed); correlation is significant at the 0.01 level (two-tailed)

that soil organic matter is one of the major elemental adsorbents in the soil (Quenea et al. 2009). Humic acid and fulvic acid are two major components of organic matter having strong complexation ability with trace elements (Tang et al. 2014). Comparatively, Cr and Ni showed slight correlations with other heavy metals and physicochemical properties, indicating their pedogenic nature (Chai et al. 2015; Micó et al. 2006).

Chemical forms of heavy metals in the agricultural soils

To determine the different forms of heavy metals in the soils, the leachate of each step from the sequential extraction procedure of the soils was analyzed and is shown in Fig. 2.

Different fractions of heavy metals in the soils are not equally available to plants (Morillo et al. 2007; Sundaray et al. 2011). The exchangeable fraction was considered to be easily available to plant, the carbonate fraction was susceptible to pH changes, the Fe–Mn oxide fraction was unstable under low Eh conditions, and the organic fraction could be degraded under oxidizing conditions. In contrast, the residual fraction was inert since it was not expected to be solubilized over a reasonable period of time under natural conditions (Tessier et al. 1979). The order of the bioavailability of metal fractions was exchangeable > carbonate > Fe–Mn oxide > organic > residual, and the potentially mobile fraction was considered as the sum of the first four steps (Guillén et al. 2012; Pérez et al. 2008). In the present study, the percentage of potentially mobile heavy metal fractions in the soils increased in the order of Cr (8 %) < Ni (9 %) < Zn (10 %) < Cu (20 %) < Pb (24 %) < Cd (87 %).

Cd was dominated by the exchangeable fraction, and the mean proportions associated with exchangeable, carbonate, Fe–Mn oxide, organic, and residual fractions were 42, 14, 23, 8, and 13 %, respectively. High percentage of exchangeable and bound to carbonates indicates high solubility and bioavailability, suggesting that the metal was more easily assimilated by crops. Cd in crops can transfer to the human body via the food chain and may pose a serious threat to human health. In the studied area, large amounts of coal gangue and fly ash were dumped on the surface (mine spoil), leachate from mining activities, and weathering of mine spoils may result in high concentration of Cd, as it is weakly adsorbed to the organic matter, clay, and oxide minerals when pH < 6. The results suggest that controlling the mobility of Cd is primary for agricultural soil remediation in the study area. Similar studies also found that Cd was bound in bioavailable fractions (Delgado et al. 2011; Guillén et al. 2012; Liu et al. 2013; Yang et al. 2009). Cu, Zn, and Pb had similar fraction distribution in the soils. The order of various fractions of Cu was residual (80 %) > Fe–Mn oxides (10 %) > organic (9 %) > carbonate (1 %) > exchangeable (0 %). High percentage of Cu in the residual fraction and bound to Fe/Mn oxides and organic matter fractions was also reported by Gibbs (1977). The percentage of Zn in exchangeable, carbonate, Fe–Mn oxide, and organic fractions averaged 0, 0, 5, and 5 %, respectively. Most of the total Zn was present in the residual fraction with an average of 90 %, indicating that Zn is strongly fixed in soils and its mobility is limited. The Pb in soils appeared to be associated with residual and organic fractions, accounting for 77 and 17 %, respectively. The increase of Pb in the organic fraction shows its tendency to be adsorbed by organic matter. The predominant fraction for Cu, Zn, and Pb was the residual (above 70 %); thus, these metals are less likely to harm the environment (Yu et al. 2010).

Cr and Ni were largely retained in the residual fraction (93 % for Cr and 91 % for Ni). The exchangeable proportions of Cr and Ni were very low, with mean percentages of 0 % for Cr and 1 % for Ni. Low exchangeable and high residual proportions of Cr and Ni in soils and sediments were also reported in previous studies (Delgado et al. 2011; Liu et al. 2013; Pérez et al. 2008). As heavy metals in the residual fraction are trapped in the lattice of minerals (Rodríguez et al. 2009; Shi et al. 2008), they are unlikely to be released (Nemati et al. 2011). These results indicate that the environmental risk of Cr and Ni may be low in the study area. High residual proportion of Cr and Ni also indicates that they were from a geological origin (Li et al. 2013).

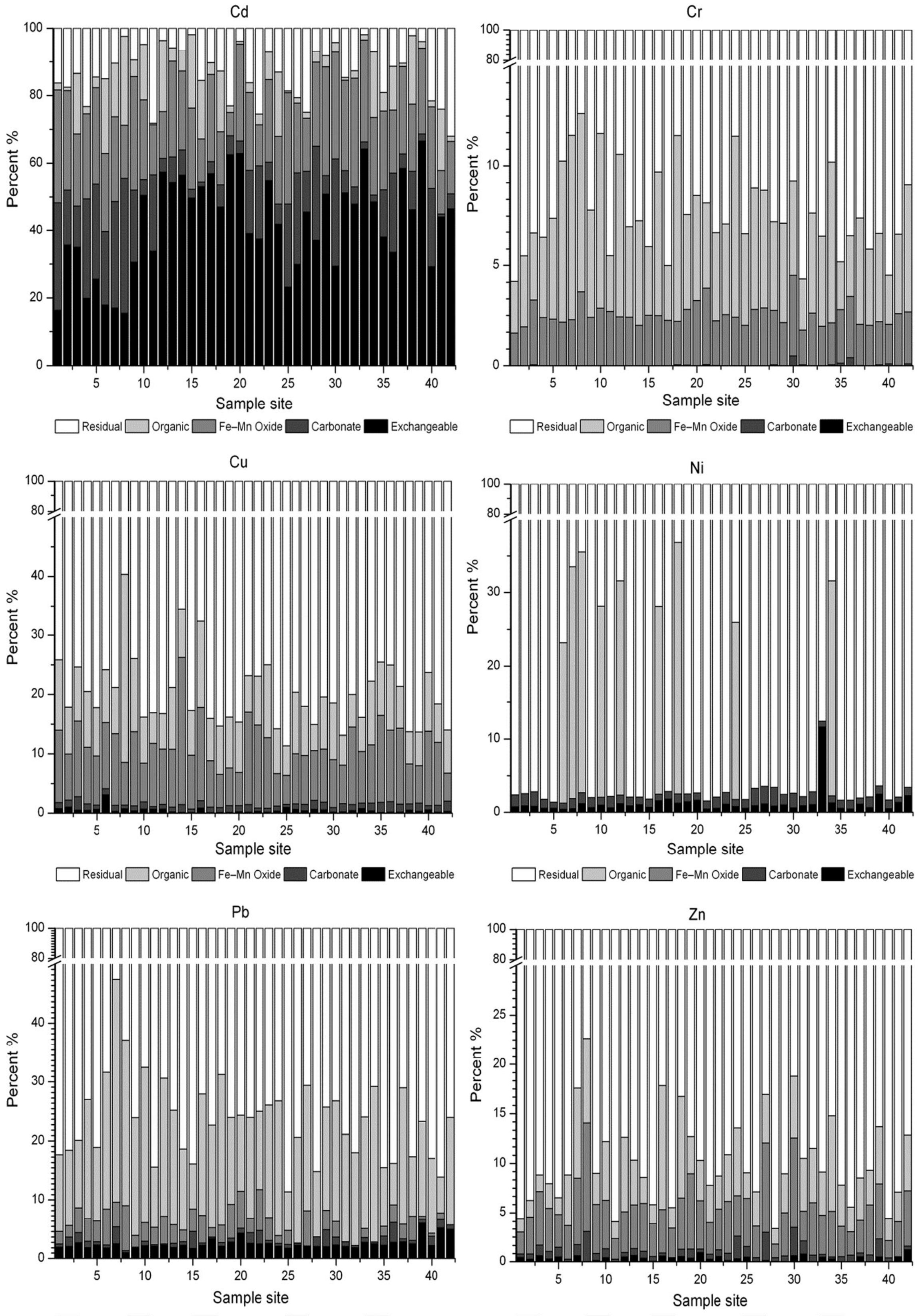

Fig. 2 The percent of heavy metal chemical forms in the agricultural soils

Behavior of heavy metals in the agricultural soils

To examine the behavior of heavy metals in the studied soils, correlations between different geochemical phases of the sequential extraction and soil physicochemical properties have been established for all soil samples (Table 3).

Significant correlations were found between chemical forms of Cd, Cu, Pb, and Zn and total metal concentrations or soil physicochemical properties. The results suggested that the behavior of Cd, Cu, Pb, and Zn in the different solid phases in soils were controlled by not only their total concentration but also soil physicochemical properties. Significant negative correlations were found between the exchangeable phase of Cd, Pb, Zn, and pH, which indicated that if pH decreased, the concentration of exchangeable phase will be increased. Soil pH has a significant influence on the environmental behavior of Cd in soil (Pérez-Esteban et al. 2014; Wang et al. 2009); a variation of pH can solubilize or immobilize Cd.

In contrast, only the residual phases of Cr and Ni were significantly positively correlated with their total metal concentrations. Total metal concentrations of Cr and Ni control their residual phases. The exchangeable phase of

Table 3 Correlations between different chemical forms of heavy metals and physiochemical properties of surface soils (*n* = 42)

		pH	Electrical conductivity	Water content	Organic matter	Total N	Total C	Available potassium	Available phosphorus	Total metal
Cd	Exchangeable	−0.72**	0.04	−0.43**	−0.04	−0.22	−0.25	−0.16	0.06	−0.08
	Carbonate	0.73**	0.28	0.54**	0.45**	0.47**	0.60**	0.42**	0.10	0.75**
	Fe–Mn oxide	0.36*	0.18	0.21	0.12	0.13	0.16	0.53**	−0.14	0.51**
	Organic	0.13	−0.08	0.41**	0.32*	0.35*	0.41**	0.16	0.32*	0.47**
	Residual	0.13	0.37*	−0.11	−0.14	−0.03	−0.12	0.16	−0.03	0.34*
Cr	Exchangeable	0.13	−0.02	0.19	−0.09	−0.04	−0.00	0.28	−0.02	0.18
	Carbonate	0.24	−0.14	−0.05	−0.23	−0.38*	−0.07	−0.34*	−0.26	−0.02
	Fe–Mn oxide	0.17	−0.11	0.17	0.19	0.31*	0.28	−0.10	0.14	0.30
	Organic	−0.14	0.01	0.10	0.29	0.31*	0.15	0.08	0.40**	0.20
	Residual	−0.06	0.05	−0.09	−0.00	0.11	−0.11	0.21	−0.02	0.91**
Cu	Exchangeable	0.35*	−0.06	0.20	0.20	0.32*	0.24	0.39*	−0.03	0.39*
	Carbonate	0.02	−0.10	0.02	0.16	−0.20	0.14	−0.17	0.03	0.34*
	Fe–Mn oxide	0.38*	−0.04	−0.00	0.16	0.16	0.14	−0.05	−0.17	0.31*
	Organic	0.29	0.01	0.58**	0.60**	0.54**	0.84**	0.35*	0.51**	0.59**
	Residual	0.30	0.18	0.36*	0.45**	0.28	0.36*	0.00	0.06	0.80**
Ni	Exchangeable	−0.35*	−0.04	−0.00	−0.13	−0.34*	−0.08	−0.05	0.03	0.02
	Carbonate	0.69**	0.14	0.29	0.01	0.25	−0.06	0.17	−0.13	0.09
	Fe–Mn oxide	0.13	−0.2	0.19	−0.09	−0.04	−0.00	0.28	−0.02	0.08
	Organic	−0.02	−0.06	0.19	0.19	0.24	0.13	−0.02	0.27	0.19
	Residual	0.06	0.18	−0.29	−0.34*	−0.15	−0.30	0.07	−0.37*	0.75**
Pb	Exchangeable	−0.71**	−0.10	−0.29	−0.12	−0.34*	−0.18	−0.30	0.27	−0.78
	Carbonate	0.31*	0.01	0.09	−0.03	−0.07	−0.03	−0.04	−0.23	0.12
	Fe–Mn oxide	0.24	0.13	0.36*	0.39*	0.65**	0.53**	0.35*	0.45**	0.54**
	Organic	0.03	−0.03	0.43**	0.43**	0.41**	0.44**	0.18	0.57**	0.57**
	Residual	0.06	0.03	0.19	0.51**	0.48**	0.49**	0.59**	0.42**	0.57**
Zn	Exchangeable	−0.47**	0.07	−0.21	−0.17	−0.16	−0.21	−0.05	0.21	0.22
	Carbonate	0.22	0.12	0.59**	0.48**	0.42**	0.69**	0.21	0.52**	0.44**
	Fe–Mn oxide	0.11	0.12	0.56**	0.54**	0.54**	0.71**	0.35*	0.68**	0.41**
	Organic	−0.08	−0.03	0.34*	0.43**	0.33*	0.49**	0.02	0.53**	0.23
	Residual	0.31*	0.14	0.23	0.43**	0.40**	0.42**	0.44**	−.005	0.89**

***Correlation is significant at the 0.05 level (two-tailed); correlation is significant at the 0.01 level (two-tailed)

Ni was negatively correlated with pH and TN, while the exchangeable phase of Cr was not affected by any physical-chemical properties and total Cr concentration. Therefore, behavior of Cr and Ni was mostly affected by their total concentrations in the soil parent material but not the soil physicochemical properties.

Assessment of heavy metal environmental risk

In order to estimate the environmental risk associated with heavy metal pollution in the study area, the soil samples were classified according to the following two methods: the potential ecological risk index (Hakanson 1980) and RAC (Perin et al. 1985) as shown in Table 4.

The assessment of heavy metal ecological risk results (Table 5) indicated that in the mining areas, the ecological risk index for all factors (*RI*) was between low to moderate risk. The mean E_r^i of Cr, Cu, Ni, Pb, and Zn values were less than 40, which is classified as low ecological risk. However, the E_r^i values of Cd in the studied area were 55.6–188, with a mean of 94, leading to moderate to high risk, suggesting that Cd would bring significant potential ecological risk in the studied area. Also, Cd was the major contributor to the ecological risk index for all factors (*RI*). The ecological risk Cd was higher than other heavy metals.

The results of RAC (Table 5) indicated that the ecological risk of Cd was highest, with all samples present high or very high risk, whereas the other heavy metals pose no or low ecological risk. Similar results of Cd in soils and sediments were also reported in other studies (Ghrefat et al. 2012; Liu et al. 2013; Yuan et al. 2014b). In our investigated region, coal exploration has been active for decades, and heavy metal emission may increase during coal exploitation, storage, and utilization. Large amounts of coal gangue and fly ash dumped on the surface may contain various heavy metals in which Cd can be long-term reserved in surface soil with high bioavailability (Kuo 1990) and bring strong ecological risk to surrounding environment. The RAC results indicate that high proportions of Cd possibly transfer from agricultural soils to crops, in accordance with the assessment of heavy metal ecological risk results by E_r^i values.

Conclusion

The concentrations, chemical forms, mobility, and environmental risk of Cd, Cr, Cu, Ni, Pb, and Zn in soils from the Linhuan subsidence of Huaibei Coalfield, Anhui Province, China, were investigated in this study. Cd is the major metal pollutant, and the mean concentration of Cd was as high as 3.21 times of background values of Huaibei City. The mean concentrations of other metals were also higher than their background values of Huaibei City surface soil except Pb. Cd and Cu in the soils were mainly from coal mining, washing, and coal consumption, while Cr and Ni were mainly from geogenic source. Both anthropogenic and geogenic sources contributed to the concentrations of Pb and Zn in the soils. Cr, Cu, Ni, Pb, and Zn were mainly present in the residual (above 70 %), while the predominant fraction of Cd was the exchangeable fraction accounting for 42 %. The mobility sequence based on the non-residual fraction decreased in the order of Cd (87 %) > Pb (24 %) > Cu (20 %) > Zn (10 %) > Ni (9 %) > Cr (8 %). The behavior of Cd, Cu, Pb, and Zn in soil was affected by both physicochemical properties and total metal concentrations. In contrast, the behavior of Cr

Table 4 Terminology used to describe the risk factor E_r^i and *RI* and RAC as suggested by Hakanson (1980) and Perin et al. (1985)

E_r^i Potential ecological risk for single regulator		*RI*		RAC	
		Ecological risk for all factors			
$E_r^i < 40$	Low	$RI < 150$	Low	RAC < 1 %	No risk
$40 \le E_r^i < 80$	Moderate	$150 \le RI < 300$	Moderate	1 % ≤ RAC ≤ 10 %	Low risk
$80 \le E_r^i < 160$	Considerable	$300 \le RI < 600$	Considerable	10 % < RAC ≤ 30 %	Medium risk
$160 \le E_r^i < 320$	High	$600 \le RI < 1200$	High	30 % < RAC ≤ 50 %	High risk
$E_r^i \ge 320$	Very high			50 % < RAC	Very high risk

Table 5 Risk assessment of soil pollution based on different chemical forms and total concentrations of heavy metals in surface soils

Sample	Cd		Cr		Cu		Ni		Pb		Zn		RI[c]
	E_r^i [a]	RAC[b]	E_r^i	RAC	E_r^i	RAC	E_r^i	RAC	E_r^i	RAC	E_r^i	RAC	
S1	C	H	L	N	L	L	L	L	L	L	L	N	L
S2	C	VH	L	N	L	L	L	L	L	L	L	N	L
S3	C	H	L	N	L	L	L	L	L	L	L	L	L
S4	C	H	L	N	L	L	L	L	L	L	L	L	M
S5	C	VH	L	N	L	L	L	L	L	L	L	L	L
S6	C	H	L	N	L	L	L	L	L	L	L	N	M
S7	C	H	L	N	L	L	L	L	L	L	L	L	L
S8	H	VH	L	N	L	L	L	L	L	L	L	L	M
S9	C	VH	L	N	L	L	L	L	L	L	L	N	M
S10	C	VH	L	N	L	L	L	L	L	L	L	L	L
S11	M	VH	L	N	L	L	L	L	L	L	L	N	L
S12	C	VH	L	N	L	L	L	L	L	L	L	N	L
S13	M	VH	L	N	L	L	L	L	L	L	L	L	L
S14	C	VH	L	N	L	L	L	L	L	L	L	L	L
S15	C	VH	L	N	L	N	L	L	L	L	L	N	L
S16	M	VH	L	N	L	L	L	L	L	L	L	N	L
S17	C	VH	L	N	L	L	L	L	L	L	L	N	L
S18	C	VH	L	N	L	N	L	L	L	L	L	L	L
S19	C	VH	L	N	L	L	L	L	L	L	L	L	L
S20	C	VH	L	N	L	L	L	L	L	L	L	L	L
S21	M	VH	L	N	L	L	L	L	L	L	L	N	L
S22	C	VH	L	N	L	N	L	L	L	L	L	L	M
S23	M	VH	L	N	L	N	L	L	L	L	L	N	L
S24	C	H	L	N	L	L	L	L	L	L	L	L	L
S25	C	H	L	N	L	L	L	L	L	L	L	L	L
S26	M	VH	L	N	L	L	L	L	L	L	L	N	L
S27	M	VH	L	N	L	L	L	L	L	L	L	L	L
S28	C	VH	L	N	L	L	L	L	L	L	L	N	L
S29	C	VH	L	N	L	L	L	L	L	L	L	N	L
S30	C	VH	L	N	L	N	L	L	L	L	L	L	L
S31	C	VH	L	N	L	L	L	L	L	L	L	L	L
S32	C	VH	L	N	L	L	L	L	L	L	L	N	L
S33	M	VH	L	N	L	L	L	M	L	L	L	N	L
S34	C	VH	L	N	L	L	L	L	L	L	L	N	L
S35	C	VH	L	N	L	L	L	L	L	L	L	N	L
S36	M	VH	L	N	L	L	L	L	L	L	L	N	L
S37	C	VH	L	N	L	L	L	L	L	L	L	N	L
S38	M	VH	L	N	L	L	L	L	L	L	L	N	L
S39	M	VH	L	N	L	L	L	L	L	L	L	L	L
S40	C	VH	L	N	L	L	L	L	L	L	L	N	L
S41	C	H	L	N	L	L	L	L	L	L	L	N	L
S42	C	VH	L	N	L	L	L	L	L	L	L	L	L

N no risk, *L* low risk, *M* moderate risk, *C* considerable risk, *H* high risk, *VH* very high risk

[a] E_r^i potential ecological risk factor

[b] Risk assessment code (Perin et al. 1985)

[c] Potential ecological risk (Hakanson 1980)

and Ni in the soil was mainly affected by their total metal concentrations. According to assessments by the potential ecological *RI* and the RAC, Cr, Cu, Ni, Pb, and Zn pose no or low risk. In contrast, the proportions of exchangeable and carbonate fractions of Cd in the soils were very high, which resulted in all samples presenting high or very high risk. More attention is needed by the environmental decision-makers.

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