Ecotoxicology and Environmental Safety 160 (2018) 67–74

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Chemical speciation and risk assessment of cadmium in soils around a typical coal mining area of China

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ARTICLE INFO

Keywords:
Chemical speciation
Ecological risk assessment
Cadmium
Soil contamination

ABSTRACT

The distribution characteristics of Cadmium (Cd) fractions in soils around a coal mining area of Huaibei coalfield were investigated, with the aim to assess its ecological risk. The total Cd concentrations in soils ranged from 0.05 to 0.87 mg/kg. The high percentage of phyto-available Cd (58%) when redox or base-acid equilibria changed. Soil pH was found to be a crucial factor affecting soil Cd fraction, and carbonate-bound Cd can be significantly affected by both organic matter and pH of soils. The static ecological evaluation models, including potential ecological risk index (PERI), geo-accumulation index (I_{geo}) and risk assessment code (RAC), revealed a moderate soil Cd contamination and prensented high Cd exposure risk in studied soils. However, the dynamic evaluation of Cd risk, determined using a delayed geochemical hazard (DGH), suggested that our studied soils can be classified as median-risk with a mean probability of 24.79% for Cd DGH. These results provide a better assessment for the risk development of Cd contamination in coal mining areas.

1. Introduction

Cadmium (Cd) contamination in the soils has attracted increasing concerns as it has potential adverse effects on crop production and human health (Durand et al., 2015; Fan et al., 2018; Nordberg, 2009; Swaddiwudhipong et al., 2007). Exposure to low levels of Cd over long periods by inhalation may result in kidney disease, whereas acute exposure to Cd can severely damage the lungs and even cause death (Hensawang and Chanpiwat, 2017). One of the principal anthropogenic sources of Cd to soil arises from coal mining. In a review of heavy metal soil contamination, Li et al. (2014a, 2014b) reported that the mean soil Cd concentration around ten coal mines from eight provinces in China was about 1.6 times higher than the national Grade II values for soil Cd (0.3 mg/kg) (GB15618-1995). Several similar studies have also been conducted in Huainan coalfield, China, where the mean concentrations of soil Cd were 2–3 times greater than the Huainan soil background value (Liu et al., 2016; You et al., 2016). Even after restoration, the soil samples from a Chinese coal-mining land were reported to have moderate to heavy Cd contamination (Niu et al., 2015). The sources for soil Cd surrounding coal mines are complex. Tang et al. (2013) found that coal combustion was the primary factor for Cd enrichment in soils (0.64 mg/kg) surrounding coal mines with coal-fired power plants. Ge et al. (2016) found that Cd migration from coal waste pile had polluted the surrounding soils. Although the total Cd concentrations in soils could provide us with valuable information about the overall degree of contamination, chemical speciation, i.e. the relative metal fraction in various chemical forms, is thought to be more informative in evaluating the environmental impact of a metal in contaminated soils (Shahid et al., 2012).

Sequence extraction (e.g. Tessier sequential extraction procedure) with a process of gradually increasing the leaching strength of the extractant has been frequently used in Cd speciation analysis in soils (Izquierdo et al., 2017; Zong et al., 2016). The extraction scheme resolves various metal forms from most mobile to most stable species including exchangeable, carbonate-bound, Fe/Mn oxide-bound, bound to organic matter, sulfide-bound, and residual forms (Tessier et al., 1979). Previous studies demonstrated that the availability of Cd was influenced by competitive adsorption-desorption processes which in turn are determined by soil properties including pH, redox potential, OM content, electric conductivity (EC), quantity and type of clay minerals, hydrous metal oxides of Fe, Al and Mn (He et al., 2017; Pietrzykowski et al., 2014; Romkens et al., 2011; Yu et al., 2016). In order to assess the combined static ecological risks of elements in soils, various geochemical indicators, including geo-accumulation index

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https://doi.org/10.1016/j.ecoenv.2018.05.022
Received 7 March 2018; Received in revised form 8 May 2018; Accepted 11 May 2018
Available online 21 May 2018
0147-6513/

(I_{geo}) (Müller, 1969), potential ecological risk index (PERI) (Hakanson, 1980) and risk assessment code (RAC) (Perin et al., 1985) have been developed on the basis of total concentration and speciation of Cd. For example, Ur Rehman et al. (2018) reported a moderate environmental risk of Cd contamination in the soils collected in the vicinity of Sewakht mines (North Pakistan) by applying contamination indices I_{geo} and PERI. Using PERI, Wieczorek et al. (2018) demonstrated a moderately ecological risk for soil Cd contamination on living components in Malopolska (South Poland). In addition, RAC was also frequently used in assessing the risk of soil Cd contamination (Isimekhai et al., 2017; Matong et al., 2016).

The transformation of Cd speciation in soils is a dynamic evolution process (Marrugo-Negrete et al., 2017; Ming et al., 2005; Xu and Yuan, 2009; Yang et al., 2005; Zhang et al., 2001), and certain amounts of mobile Cd can be stabilized by the components in the soils (Plekhanova, 2009). However, the tolerant capacity of Cd in soils is limited and varies with different environmental parameters. When the input of Cd in soil surpasses the tolerant capacity, the previously stabilized Cd could be re-activated and may result in delayed environmental hazards (Li et al., 2014a, 2014b; Sharma et al., 2007). Thus, the "delayed geochemical hazard (DGH)" model has been proposed to assess the dynamic processes and risk burst possibilities of heavy metal contaminants of soils (Dong et al., 2017; Ming et al., 2005; Zheng et al., 2015). Using the DGH model, Ming et al. (2005) demonstrated that soil chromium (Cr) near a steel company exhibited a risk of DGH burst in a large area. Subsequent studies conducted by Dong et al. (2017) and Zheng et al. (2015), showed a tendency to dynamic risk evolution of soil mercury (Hg) using the DGH model. However, as one of the pollutants with a high priority to be monitored, no previous studies on dynamic risk assessment of Cd in soils were carried out to our knowledge.

Huaibei coalfield is a nationally coal base in China, and is also one of the most important grain and fruit production district. Coal mining plays an important role in promoting the local economy, but also leads to serious deterioration of the local environments (Chen et al., 2014). The high intensity and long duration of coal mining in this area would likely lead to high Cd retention in soil, and would eventually cause potential environmental and health risks. However, very few studies have investigated the contamination characteristics of Cd associated with mining activities in Huaibei coalfield up to now (Lu et al., 2017; Shang et al., 2016; Shi et al., 2013). A comprehensive investigation of soil Cd contamination levels in the whole coal area is urgently needed to better assess the associated ecological risks.

The objectives of this study are: (1) to assess the contamination levels of Cd in soils around the coal mining area; (2) to investigate the chemical fractionation of Cd and identify its controlling factors (3) to assess both the static and dynamic ecological risk of Cd risk in soils. Our results are expected to provide a scientific basis for the soil Cd contamination control and establishment of risk management plans.

2. Methods and materials

2.1. Study area and sampling

Huaibei coalfield (33°20′ N-34°28′ N, 115°58′E-117°12′ E) is located in the northeast of Anhui province, eastern China (Fig. 1). The landscape of this coalfield is largely flat, and the terrain tilts gently from northwest to southeast. Characterized by cold and dry winters and rainy summers, this area is in the warm, semi-humid monsoon climate zone. Prevailing winds are in a southeast direction in summer, and a northeast direction in winter. The yearly average temperature and rainfall is 14.6 °C and 830 mm, respectively. The main soil types of the study area are alluvial soil, lime concretion black soil, yellow cinnamon soil and limestone soil.

The land surrounding the coal mines is mainly used as farming land for crops (wheat, soybeans, corns) and fruit trees in most of the sampling sites. A total of 186 surface soil samples (0–20 cm) were collected every 0.5–1 km at Zhangzhuang (79 samples), Linhuan (47 samples), and Yangliu (60 samples) coal mining areas in December (Fig. 1). Soils from Yongqiao district were selected as the background samples. The mining ages of these coal mines decrease in the following order: Zhangzhuang Mine > Linhuan Mine > Yangliu Mine. The locations of the sampling sites were recorded using a hand-held global positioning system (GPS). For each sampling site, three subsamples were randomly collected and stored in sealed plastic bags.

2.2. Physical and chemical analysis

After an air-drying process, all the soil samples were disaggregated before passing through a 2-mm nylon sieve for pH analysis, and through a 0.149-mm nylon mesh for the analysis of Cd and other physico-chemicals properties. Soil pH was measured in a 2:5 (w/v) soil/water mixture using a pH meter. The soil organic matter (OM) content was determined by the chromic acid titration method (Walkley and Black, 1934). Total nitrogen (TN), available phosphorus (AP), and available potassium (AK) levels were determined by Kjeldahl method, molybdate method, and alkali fusion method, respectively (Lu, 2000).

Approximately 0.1 g subsample from each soil was digested in a concentrated HNO_3-HF-$HClO_4$ mixture on a hot plate kept at a temperature of 210 °C for 3 h. The Cd concentrations in the digestion solutions were determined by graphite furnace atomic absorption spectroscopy (ZEEnit 650, Analytik Jena, Germany). The duplicates, method blanks, and standard reference materials (GSS-3 from China Geological Survey) were used to assess quality assurance and quality control. The Cd recoveries of samples spiked with standard ranged from 92% to 102%. Analysis methods were evaluated with each batch of samples (1 blank and 1 standard for each 10 samples). The relative deviation of the duplicated samples was < 6% for all batch treatments.

Tessier sequential extraction procedure was used to determine the chemical forms of Cd in representative soil samples. A summary of the procedure is given in Table S1 (Supplementary materials). Five chemical phases of Cd were classified: Cd_E, exchangeable; Cd_C, metals bound to carbonate; Cd_F, metals associated with Fe-Mn oxides; Cd_O, metals bound to OM, and Cd_S, residual. For each extraction solution and the digestion of the last residue fraction, concentrations of Cd were determined by GFAAS as well. For this extraction procedure, quality control was performed by comparing the total metal content with the sum of the Cd percentages extracted in the five fractions. The average recovery percentages of the sequential extraction ranged from 91% to 115% for Cd in soils.

2.3. Quantification of soil contamination

2.3.1. Geo-accumulation index (I_{geo})

The geo-accumulation index (I_{geo}) provides an effective method to assess the degree of Cd enrichment in soils. Its value is calculated using (Müller, 1969):

$$I_{geo} = \log_2 \frac{C}{1.5 \times B}$$

where C (mg/kg) refers to the Cd concentration in studied soils, and B (mg/kg) represents the Cd concentration in background soils. In the present study, the Huaibei soil Cd background value of Cd is adopted as the B value. Seven grades of I_{geo} were defined for the classification of soil contamination: practically uncontaminated (I_{geo} < 0); uncontaminated to moderately contaminated (0≤ I_{geo} < 1); moderately contaminated (1≤ I_{geo} < 2); moderately to heavily contaminated (2 ≤ I_{geo} < 3); heavily contaminated (3 ≤I_{geo} < 4); heavily to extremely contaminated (4 ≤ I_{geo} < 5); extremely contaminated (I_{geo} ≥ 5).

2.3.2. Potential ecological risk index (PERI)

The potential ecological risk factor (E_r) for Cd was calculated using

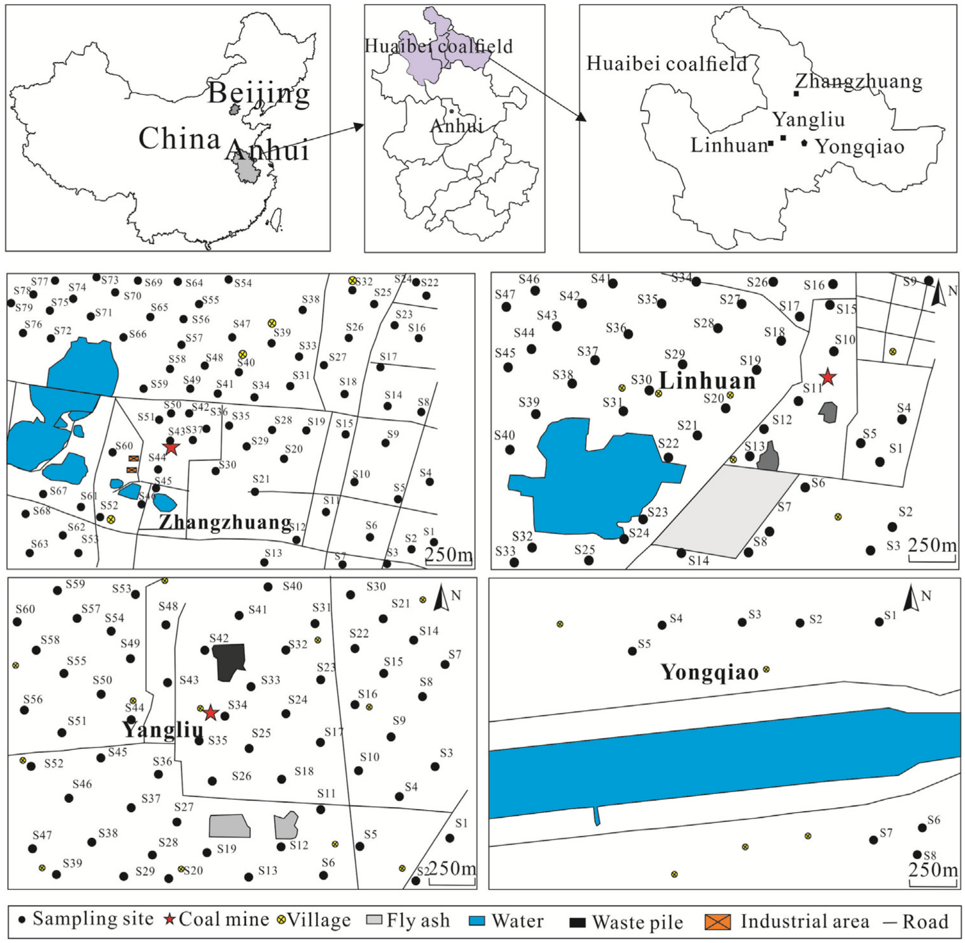

Fig. 1. Sampling locations of the Linhuan, Zhangzhuang, Yangliu and control area in the Huaibei coalfield, Anhui, China.

the equation:

$$E_r = T_r \times \frac{C}{C_0}$$

where T_r is the heavy metal toxic-response factor. This value was set at 30 for Cd (unitless) according to Hakanson (1980). C and C_0 (mg/kg) represent the content of Cd in soil samples and the Huaibei soil Cd background value, respectively. The degree of E_r is classified into five groups: low risk ($E_r < 40$); moderate risk ($40 \leq E_r < 80$); considerable risk ($80 \leq E_r < 160$); very high risk ($160 \leq E_r < 320$); Dangerous ($E_r \geq 320$).

2.3.3. Risk assessment code (RAC)

The risk assessment code (*RAC*) is used to assess the environmental risk taking sequential extraction as a characterization method. Its value is calculated using (Perin et al., 1985):

$$RAC = F_{Cd_E} + F_{Cd_F}$$

where F_{Cd_E} is the fraction of exchangeable Cd, and F_{Cd_F} is the fraction of carbonate-bound Cd. Five classes of RAC were defined for the classification of environment risk: no risk (RAC < 1%); low risk (1%≤ RAC <10%); medium risk (11%≤ RAC <30%); high risk (31 %≤ RAC < 50%); very high risk (RAC ≥ 75%).

2.3.4. Delayed geochemical hazard (DGH)

The prediction of DGH for Cd is based on a previous model developed by Feng and his coworkers (Dong et al., 2017; Ming et al., 2005; Zheng et al., 2015). As shown in Fig. S1, the X axis stands for "Total releasable content of the pollutant" (TRCP) in the soil system. Considering the natural environment and soil physical and chemical properties of Huaibei coalfield, the $TRCP_{Cd}$ in our study area refers to the fraction extracted from the first four steps of the Tessier sequential extraction procedure. The Y axis stands for "total concentration of active species" (TCAS), which refer to the concentration of some species in $TPCR_{Cd}$ that will become much more active under given environmental conditions (Chen et al., 2006). The fitting curve L_0 reflects the trend in $TCAS_{Cd}$ with the increase in $TRCP_{Cd}$, can be expressed by a non-linear polynomial as:

$$Q = a_0 + a_1C + a_2C^2 + a_3C^3 + \ldots$$

The points of the equation where the second order derivative is zero represent special critical points corresponding to the burst of DGH.

2.4. Statistical analysis

The descriptive statistical parameters were calculated with Microsoft EXCEL®. All multivariate statistical analyses, including One-way analysis of variance analysis (ANOVA) and correlation matrix (CM) were conducted using SPSS® (version 20.0). ANOVA analysis was carried out to compare differences of average soil Cd concentration among different coal mines, with a value of $P < 0.05$ indicating significant differences. CM was applied to identify the relationship between obtained soil Cd fractions and soil properties. The normality of the data set distribution each was checked using Kolmogorov-Smirnov test. Spearman's correlation coefficient was used when the data set were not normally distributed. All simulation analyses of nonlinear polynomials of the DGH model were carried out in Origin 9.0.

Table 1
Descriptive statistic of selected physico-chemical properties, total Cd contents and the percent of Cd chemical forms in soils.

Location	N		PH	OM(g/kg)	AP(mg/kg)	TN(g/kg)	AK(g/kg)	T_{Cd} (mg/kg)	Cd_E%	Cd_C%	Cd_F%	Cd_O%	Cd_R%
Zhangzhuang	79	Ranges	5.23–8.43	5.50–37.68	1.03–7.49	1.73–10.82	27.02–281.60	0.19–0.87	15.4–48.3	5.6–30.5	2.2–31.2	1.8–13.0	20.5–59.8
		A.M.	7.10	26.70	4.29	5.45	135.05	0.39	24.8	15.6	14.4	5.7	39.5
		SD	0.75	5.96	1.45	1.74	48.66	0.13	6.6	6.4	8.0	2.6	8.5
Linhuan	47	Ranges	5.33–8.25	9.35–37.78	1.46–6.85	1.56–9.25	21.60–220.23	0.12–0.74	14.7–34.8	5.7–24.3	1.2–30.6	2.6–12.6	24.9–65.0
		A.M.	6.69	23.18	4.02	5.54	134.49	0.29	23.3	11.0	16.9	5.6	43.2
		SD	0.68	5.51	1.32	1.89	50.15	0.13	5.9	4.7	9.2	2.6	8.8
Yangliu	60	Ranges	5.23–8.62	8.40–67.98	1.17–7.44	2.01–10.93	18.40–256.62	0.05–0.60	14.6–51.1	4.7–21.0	2.1–31.3	3.3–19.4	18.6–61.7
		A.M.	6.61	24.31	3.97	5.52	133.21	0.18	23.0	9.2	17.4	7.4	43.0
		SD	1.01	10.22	1.95	1.92	54.19	0.06	0.02	3.6	8.9	3.4	9.0
Mining area	186	Ranges	5.23–8.62	5.50–67.98	1.03–7.49	1.56–10.93	18.40–281.60	0.05–0.87	14.6–51.1	4.7–30.5	1.8–31.3	1.8–19.4	18.6–65.0
		A.M.	6.84	25.04	4.12	5.50	134.32	0.30	23.9	12.4	16.0	6.2	41.6
		SD	0.85	7.62	1.60	1.83	50.61	0.16	6.8	5.9	8.7	3.0	8.9
Yongqiao	8	Ranges	5.67–7.45	1.30–4.50	1.34–5.32	3.23–7.43	74.50–164.34	0.04–0.10	14.6–29.5	5.4–12.4	3.4–20.4	2.4–13.4	33.6–68.9
		A.M.	6.86	2.34	2.35	4.23	100.14	0.06	21.1	7.9	10.3	6.6	54.1
		SD	0.56	1.10	1.27	1.35	28.53	0.02	4.9	2.5	5.2	3.8	12.6

N. number of samples, A.M. arithmetic mean, SD. standard deviation, OM organic matter, AP available phosphorus, TN total nitrogen, AK available potassium.

3. Results and discussion

3.1. Descriptive statistics

The main soil properties (pH, OM, AP, TN and AK) around the studied coal mining area in Huaibei coalfield are presented in Table 1. The soil pH values (6.84) of Huaibei coalfield are weakly acidic. Among these soil samples, 62.9% of them presented acidic characteristics. The acidic soils can promote the bioavailability of Cd, whereas the basic soils can enhance the Cd adsorption (Zeng et al., 2011). In addition to soil pH, OM was another primary contributor to retain Cd in exchangeable form (Haghiri, 1974). OM contents in all soil samples around coal mining area ranged from 5.50 to 67.98 g/kg, with an average value of 25.04 g/kg. Among the three locations, the average OM contents are highest in the Yangliu area (24.31 mg/kg) and lowest in the Linhuan area (23.18 mg/kg). Some nutrient elements such as P could affect the Cd bioavailability in soils (Chen et al., 2013). The value of AP content in the studied soils varied between 1.03 and 7.49 mg/kg and had an average of 4.12 mg/kg. The TN and TK contents in soils ranged from 1.56 to 10.93 g/kg and from 18.40 to 281.60 g/kg, respectively. The large variations in some parameters (TN, AP, AK) are likely caused by differences in farming practices between soils (Liu et al., 2005). Soils from coal mining areas all have higher OM, AP, TN, and AK than those from the control area.

Fig. S2 shows the descriptive statistics of Cd contents in soils from 186 sampling sites. The Cd concentrations varied from 0.05 to 0.87 mg/kg, with a standard deviation (SD) of 0.16. The average Cd content in studied soils around coal mining area is 0.3 mg/kg, which is markedly higher than those in Yongqiao soils (0.06 mg/kg), the Huaibei soil Cd background value (0.08 mg/kg) and China soil Cd background value (0.1 mg/kg) (Table 1; AHEMC, 1992; Chen et al., 1991). According to the Soil Environmental Quality Standard of China (GB 15618–1995), ~ 71% of the soil samples were found to contain Cd concentrations greater than the upper threshold value of 0.20 mg/kg defined by Grade I soil, and ~ 49% of the soil Cd concentrations exceeded the upper threshold value of 0.30 mg/kg defined by Grade II soil (ensuring good agricultural production and maintaining human health). None of the Cd data exceeded the limit value of 1 mg/kg value defined by Grade III (ensuring the production of agroforestry and normal growth of plants). The coefficient of variation (CV = 62.0%) of soil Cd concentration is higher than 35%, suggesting that the human activities could have affected the concentrations of Cd in soils (Manta et al., 2002).

Elevated Cd concentrations in soils are largely attributed to human activities through atmospheric deposition, P-fertilizers application and sewage sludge discharge (Chen et al., 2005; Liang et al., 2017; Lu et al., 2012; Wang et al., 2015; Zhai et al., 2008). The average Cd concentrations in the soil samples are 0.39 mg/kg, 0.29 mg/kg, 0.18 mg/kg and 0.06 mg/kg for Zhangzhuang, Linhuan, Yangliu and Yongqiao, respectively. According to the ANOVA, the differences of mean Cd concentration among the three coal mines were significant ($P < 0.05$), suggesting that intensive mining activities such as coal exploitation and processing show a strong impact on Cd in soils around coal mining areas. The Cd concentrations in studied soils surrounding the coal mines lied in the middle range when comparing to the average concentrations of Cd in soils from different coal mines at national scale (0.02–1.97 mg/kg, Table S2; Fan et al., 2011; Yu et al., 2002; Ma et al., 2012; Wang et al., 2009; Ge et al., 2008; Wang and Dong, 2009; Niu et al., 2015; Jing et al., 2011; Wang et al., 2013; Jiang et al., 2014; You et al., 2015). Globally, the total Cd concentrations in studied soil are compared to soils of coal mining areas from Ptolemais-Amynteon in Greece and Pokrok in Czech Republic (Gholizadeh et al., 2015; Pentari et al., 2006), but higher than those detected in soils of coal mining areas from Sonepur Bazari in India, Oltu in Turkey and Douro in Portugal (Masto et al., 2015; Ribeiro et al., 2010; Tozsin, 2014). Overall, the Cd concentrations in our studied soils were low compared to other regions of the world (see Table S2 in supplementary materials; Ameh, 2013; Equeenduddin, 2010; Galunin et al., 2014; Kim and Chon, 2001; Ladwani et al., 2012; Pietrzykowski et al., 2014; Reza et al., 2015; Sahoo, 2011; Sadhu et al., 2012).

3.2. Spatial distribution

Fig. 2 showed the spatial distribution of soil Cd concentrations of each coal mining area with an aim of identifying the hot spots of contamination and assessing the potential sources of Cd. In Zhangzhuang coal mine, there were two obvious hotspots for Cd. One was located in the southwest, where coal mine and industrial area were located, another was located in the north of the area, where large amounts of farmlands were located. Factors, such as phosphatic fertilizers and pesticides have been shown to be important contributors of some heavy metals including Cd (Lambert et al., 2007; Maes et al., 2008), which may partially explain the presence of the Cd hotspot in the north. The soil Cd concentrations generally increased from the north to the south within this area, which may relate to the land use practices. The spatial distribution pattern of Cd in Linhuan was characterized by a high Cd concentration in northeast soils, where most of the coal mining activities existed. The lateral distribution pattern at Linhuan also showed a higher Cd concentrations in the eastern downwind soils than in the western upwind soils, suggesting that wind directions may play an important role in determining Cd distribution patterns. Yangliu coal mine also showed a similar Cd distribution pattern with the highest Cd concentrations in the vicinity of coal mine and ash yard. These

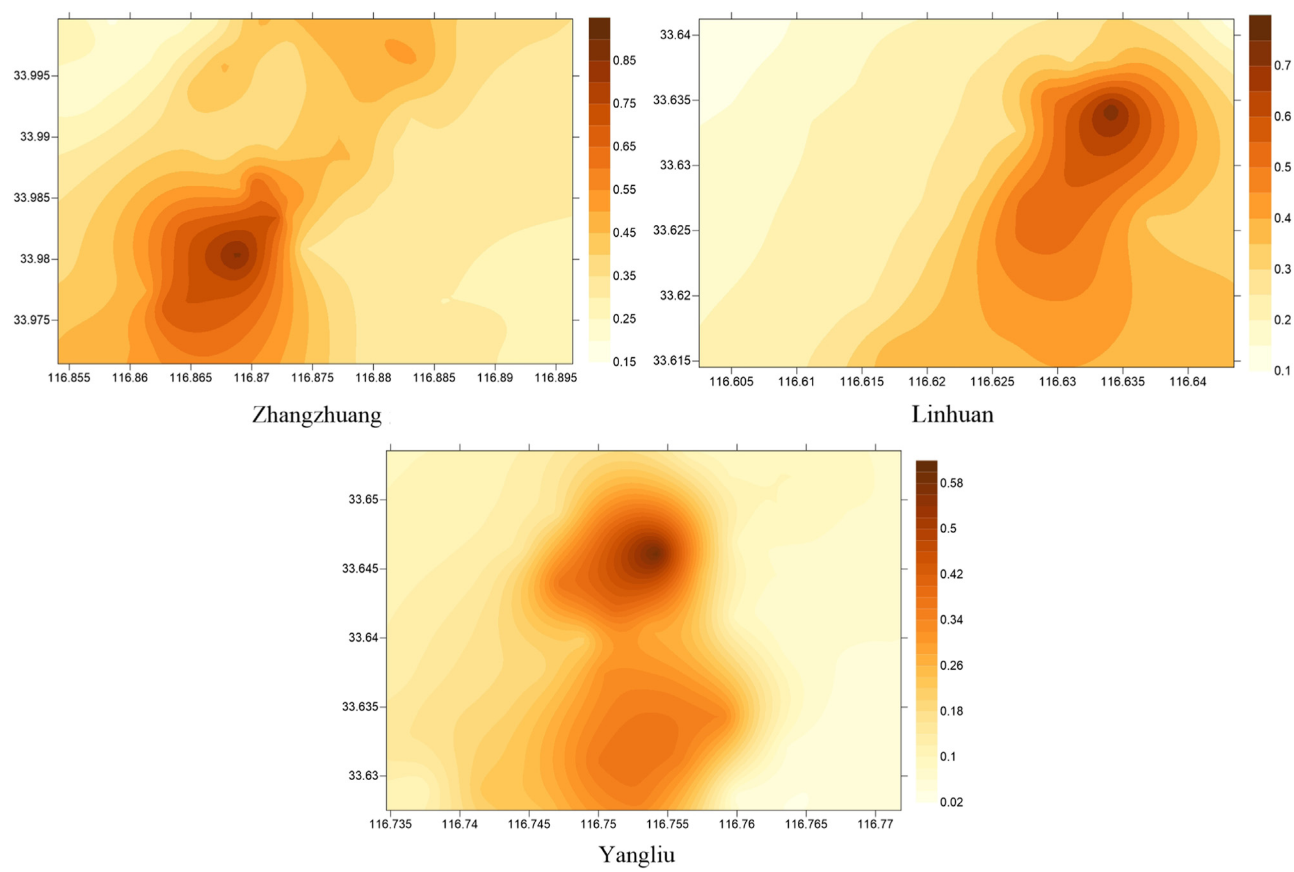

Fig. 2. Spatial distribution pattern of Cd concentrations (mg/kg) in soils around Zhangzhuang, Linhuan and Yangliu coal mines.

observations indicate that the levels and the distribution of Cd in soils are tightly correlated to coal mining activities in the study area.

3.3. Geochemical fractionation of Cd in the studied soils

Although total concentration can reflect the overall contamination of soil with Cd, the geochemical fractionation can be more informative on the mobility, bioavailability, and toxicity of Cd in soils. Using the method of Tessier sequential extraction, we examined the fractionation of Cd in the studied soils (Table 1). On average, the fractions of Cd in these soils followed the order of Cd_R (41.6%) > Cd_E (23.9%) > Cd_F (16.0%) > Cd_C (12.4%) > Cd_O (6.2%). Most of Cd was found in the Cd_R fraction, with values ranging from 19% to 65%. Previous studies have also found high fractions of Cd_R (Ma and Rao, 1997; Spence et al., 2014; Wu et al., 2013; Yu et al., 2016; Zhou et al., 2007). Both Cd_E and Cd_C fractions increased from Yangliu to Linhuan and to Zhangzhuang (an increase of coal mining history), further confirming that the elevated concentrations of Cd were resulted from mining activities.

Different forms of Cd in the soils are not equally bioavailable to plants (Chojnacka et al., 2005; Pichtel et al., 2000; Xiao et al., 2017). The order of the biological effectiveness of metal fractions was $Cd_E > Cd_F > Cd_O > Cd_C > Cd_R$. The sequential selective chemical extraction fractions of Cd can be divided into three classes based on their biological effectiveness: easily phytoavailable Cd, moderately phytoavailable Cd, and non-phytoavailable Cd. Easily phytoavailable Cd includes the Cd_E fraction. Moderately phytoavailable Cd includes Cd_F, Cd_O, and Cd_C, which can be released in a strong acid medium or under reducing conditions, and then becomes bioavailable. Not phytoavailable Cd is mainly in the residual fraction of metal, and usually cannot be utilized by organisms. The biological effectiveness of Cd in selected soils was thus evaluated according to the classification criteria above. Easily phytoavailable Cd accounts for 15–51% of Cd within the samples, moderately phytoavailable Cd accounts for 14–53%, and non-phytoavailable fraction accounts for 19–65%. Although the inert fraction was dominant in many samples, the percentage of labile Cd (24%) was also significant, indicating that Cd could be easily assimilated by crops. Notably, the percentage of moderately phytoavailable Cd ranged from 14% to 53%, suggesting that a high proportion of Cd can be assimilated by crops in a changed redox conditions and/or in acid-base equilibria.

Spearman's correlation analysis was carried out to identify correlations between the Cd fraction in selected soils and the selected physicochemical properties of soil samples (pH, OM, TN, AP, AK). Generally, the individual fraction and total Cd concentration in the soil samples varied considerably with the geochemical properties (e.g. pH and organic matter; Table 2). The results showed that pH strongly affected the adsorption/desorption and precipitation/solubilisation reactions, and has been considered as the most influential factor. Soil pH was positively correlated to the total Cd concentration or Cd_c (Table 2). The decrease in pH may potentially increase solubility and bioavailability of Cd (Antoniadis et al., 2008; Basta, 2005; Silveira et al., 2003).

Table 2
Correlations between Cd concentrations and physiochemical properties of soils.

	pH	Organic matter	Total N	Available phosphorus	Available potassium
T_{Cd}	0.46**	0.36**	− 0.04	0.19*	0.05
Cd_E	− 0.21**	− 0.11	− 0.02	− 0.22**	0.04
Cd_C	0.34**	0.21**	0.10	0.09	0.02
Cd_F	− 0.04*	− 0.13	0.00	0.05	0.03
Cd_O	− 0.08	0.23**	0.06	0.06	0.14
Cd_R	0.05	0.02	0.03	0.04	− 0.09

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

Table 3
I_{geo}, RAC and PERI assessment data of Cd in soils.

Location		I_{geo}	RAC	PERI
Zhangzhuang	Ranges	0.69–2.85	22.2–66.1%	72.68–324.86
	A.M.	1.64	40.4%	147.74
	SD	0.45	10.4%	50.33
Linhuan	Ranges	− 0.05 to 2.62	22.4–51.4%	43.37–277.53
	A.M.	1.13	34.3%	107.98
	SD	0.61	8.3%	48.40
Yangliu	Ranges	− 1.26 to 2.32	21.4–68.5%	18.84–225.08
	A.M.	0.29	32.2%	66.10
	SD	0.88	9.1%	42.67
Mining area	Ranges	− 1.26 to 2.85	21.4–68.5%	18.84–324.86
	A.M.	1.08	36.2%	111.36
	SD	0.88	10.2%	58.85

A.M. arithmetic mean, SD. standard deviation.

OM also showed high correlation with total Cd concentration and Cd_C fraction, indicating that OM may act as an important sink of Cd due to its high complexing capacity for metallic contaminants (Huang et al., 2005; Kalbitz and Wennrich, 1998). Additionally, both OM and pH significantly correlated with the Cd_F fraction, in consistent with the study by Simmons et al. (2009).

3.4. Risk assessment of Cd

3.4.1. Static risk assessment of Cd

The static ecological risk assessment of Cd in soils are based on I_{geo}, RAC, and PERI. The values of these three indexes all decrease in the following order: Zhangzhuang > Linhuan > Yangliu (Table 3). I_{geo} ranged from − 1.26 to 2.85, with a mean value of 1.08, indicating the studied soils were moderately contaminated. However, RAC analysis showed a high Cd risk in the studied soils, with a mean value of 36.2%. In consistent with the result of I_{geo}, PERI suggests a relatively moderate contamination of studied soil.

3.4.2. Dynamic risk assessment of Cd

The DGH is an efficient method for dynamic risk evolution and assessment. Under stable environmental conditions, pollutants in soil can accumulate. However, when the concentration of accumulated pollutants reaches a breakpoint, an intensive reactivation and subsequent discharge of these chronically accumulated contaminants may occur. This may cause even more hazardous ecological and environmental consequences than the initial contamination. Being quantitatively represented by a nonlinear polynomial, the DGH model thus can be applied to assess and predict the potential environmental risks of soil Cd exposure. Based on this model, the fits of data to equations were mainly determined by results of Tessier SEP. All components in the Tessier method should be involved in $TRCP_{Cd}$ except for the residual fraction (Zheng et al., 2015). In line with the DGH principle, our results showed that the Cd in soils from our study areas was well fitted to the equations of polynomials (Table 4). We defined the 'critical point of burst' in the DGH as the second derivative of each polynomial (Table 4). That is, DGH bursts may happen as long as the $TRCP_{Cd}$ is greater than the critical point, regardless of the reaction phase in the Tessier method. The possible pathways of form transformation (according to Tessier method) were proxied by the polynomials in the DGH model.

The low critical point of Cd in the DGH for the studied soils indicate a tendency of burst risk, although the concentrations of active Cd forms were relatively low. Given the fraction availability in Tessier method, the $Cd_{E+C+F+O} \rightarrow Cd_{E+F}$ path was taken as the example in our study. The regression equation was expressed as:

$$Y = 2.00E - 06X^3 - 1.80E - 3X^2 + 1.02X\,(n = 186,\ R^2 = 0.9458) \quad (1)$$

We applied this path of DGH to characterize our study, as chain reactions from $Cd_{E+C+F+O} \rightarrow Cd_{E+F}$ in this path might produce some mobile Cd fractions when DGH happened. For the equation, we set the second derivative of Eq. (1) as 0. Therefore, the calculated value of $TRCP_{Cd}$ equaled to 0.27 mg/kg.

The calculated $TPCR_{Cd}$ obtained in our study ranged from 0.18 to 0.3 mg/kg (Table 4). We then fitted every potential DGH path to the each of the $TRCP_{Cd}$ values to give reference for assessment. According to the T_{Cd} data, an average of 24.8% (ranging from 10.2% to 44.1%) of the T_{Cd} was higher than $TRCP_{Cd}$ in the study area, suggesting a medium-risk for both DGH according to the adopt DGH model, the occurrence of fraction transformation may be frequent.

4. Conclusions

In this study, the characteristics of Cd contamination in soils surrounding coal mining areas of Huaibei coalfield were investigated. Both concentrations and chemical fraction of Cd, were used to evaluate the sources and the potential ecological risks of Cd. The mean Cd concentration in studied soil samples was 0.30 mg/kg, which is nearly one order of magnitude higher than the local, regional or global soil background value. The spatial distribution pattern suggests that coal mining activities were the primary source of Cd in our study areas. The main Cd fraction in the soil samples was in the residual form, whereas a relatively high mobile fractions of Cd was also presented. The correlation analysis between Cd and the physicochemical properties of soils demonstrated that pH may strongly affect the total Cd, exchangeable Cd and Cd bound to carbonate. OM also plays a crucial role in determining the availability of Cd and its fraction distribution in soils. The static methods of ecological risk assessment (I_{geo}, PERI, RAC) showed a moderate soil Cd contamination and presented high Cd exposure risk in our study areas. Using the DGH model, low Cd critical points of burst were obtained indicating a potential risk caused by Cd and a tendency of burst of dynamical risk. Although only 24.8% of T_{Cd} was higher than $TRCP_{Cd}$ (indicating a median-risk of DGH for one path of the chain reactions), the large variation (10.2–44.1%) suggests that high concentrations of Cd may be accumulated in some areas, and high amounts of accessible Cd may be potentially released. This could lead to much

Table 4
Fitting equations and characteristic values of Cd in the studied soils.

Potential DGH path		DGH models	Statistical characteristics		The critical points of DGH burst	
		Y is $TCAS_{Cd}$; X is $TRCP_{Cd}$ (mg/Kg)	R^2	F	$TRCP_{Cd}$	$TCAS_{Cd}$
Cd_{ECFO}	Cd_{EFO}	$Y = 2.00E-06X^3-1.80E-03X^2 + 1.02X$	0.9583	6816.53	0.30	0.20
Cd_{ECFO}	Cd_{EF}	$Y = 2.00E-06X^3-1.60E-03X^2 + 0.89X$	0.9458	4840.95	0.27	0.16
Cd_{ECO}	Cd_{ECF}	$Y = 2.00E-06X^3-1.80E-03X^2 + 1.43X$	0.9176	2723.43	0.30	0.32
Cd_{ECO}	Cd_{EO}	$Y = 4.00E-06X^3-2.60E-03X^2 + 0.97X$	0.9679	7014.46	0.22	0.13
Cd_{ECO}	Cd_{E}	$Y = 4.00E-06X^3-2.20E-03X^2 + 0.78X$	0.9581	4626.68	0.18	0.09
Cd_{ECF}	Cd_{EFO}	$Y = 3.00E-06X^3-2.30E-03X^2 +1.16X$	0.9481	5463.62	0.26	0.20
Cd_{ECF}	Cd_{EF}	$Y = 3.00E-06X^3-2.30E-03X^2 + 1.00X$	0.9528	5567.44	0.22	0.16
Cd_{EC}	Cd_{EO}	$Y = 6.00E-06X^3-3.6E-03X^2 +1.15X$	0.9514	4611.08	0.20	0.14
Cd_{EC}	Cd_{E}	$Y = 5.00E-06X^3-2.7E-03X^2 +0.90X$	0.9657	5666.18	0.18	0.10

more serious environmental consequences. Our study indicates that environmental risks of heavy metal contamination may be underestimated using static assessment methods, and highlights the necessity of the application of dynamic methods, such as DGH model, in environmental risk assessments.

Acknowledgements

This work was supported by the National Basic Research Program of China (973 Program, 2014CB238903) and the National Natural Science Foundation of China (NO. 41672144, 41402133). We acknowledge editors and reviewers for polishing the language of the paper and for in-depth discussion.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2018.05.022.

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