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

Siwei Cheng[a,b], Guijian Liu[a,b,*], Chuncai Zhou[a], Ruoyu Sun[c]

[a] CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China
[b] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, Shaanxi, China
[c] Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

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

---

[*] Corresponding author at: CAS Key Laboratory of Crust-Mantle Materials and the Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China.

E-mail address: lgj@ustc.edu.cn (G. Liu).

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

(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 ($0 \leq I_{geo} < 1$); moderately contaminated ($1 \leq I_{geo} < 2$); moderately to heavily contaminated ($2 \leq I_{geo} < 3$); heavily contaminated ($3 \leq I_{geo} < 4$); heavily to extremely contaminated ($4 \leq I_{geo} < 5$); extremely contaminated ($I_{geo} \geq 5$).

2.3.2. Potential ecological risk index (PERI)

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