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Distribution, Morphologic Analysis and Characterization of Cadmium in Different Contaminated Soil Particle Sizes

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Abstract:

In this study, five soil particle sizes from the Liupanshui City and in Jiyuan City contaminated soils were separated by the physical screening method. The effects of particle sizes on distribution, morphologic analysis and characterization of soil Cd were investigated by BCR continuous extraction, principal component analysis (PCA), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). The results showed that soil Cd content in fine particle size (<0.15mm) was higher, especially the acid-extracted Cd content in LPS soil and the residual content Cd in JY soil increased obviously with the decrease of particle size. Meanwhile, pyrite was found in soil particle size of LPS soil; However, these characteristics were not found in JY soil, indicating that the former soil was rich in Fe and sulfide elements, which was easy to enrich sulfide or heavy metals.

Keywords: *Soil, Cadmium, XRD, FTIR, Ecological risk.*

I. INTRODUCTION

Mineral resources, one of the basic guarantees of human production and life, play an important role in national economic and social development [1, 2]. However, in the process of mining, beneficiation and smelting, a large number of heavy metals are also released into the surrounding environment and spread to the surrounding areas by atmospheric deposition, precipitation, leaching, acidification and other human activities. It resulted in heavy metal pollution of the soil around the mining area. The pollution of heavy metals in China is grim, with 7.0% of over-limit ratio for cadmium (Cd) contaminated sites. The harm of Cd to soil and plants can be enriched and transformed by the food chain, and

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ultimately harm human health [3].

Soil is a mixture of particles of different sizes. The composition of soil particles varies from places. The migration and transformation of heavy metals are closely related to the size of soil particles. For example, the fine soil particles in soil could be blown to the atmosphere due to the transportation of wind [4, 5]; Soil fine particles combined with heavy metal pollutants could also penetrate into groundwater by the action of rain, which might cause heavy metal pollution of groundwater [6]. Therefore, heavy metal interacting with soil fine particles could bring potential risks to the environment and human health by different ways. To evaluate the activity and potential environmental risks of heavy metals in soil particle sizes, it is helpful to understand the migration and transformation characteristics of heavy metal, and then provide strategies for soil remediation.

In this paper, the long-term Cd-contaminated soils from the Liu Panshui City and Ji Yuan City contaminated soils were studied, and five soil particle sizes (0.9-2 mm, 0.3-0.9 mm, 0.15-0.3 mm, 0.075-0.15 mm and <0.075 mm) were separated by the physical screening method. The effects of particle sizes on distribution, morphologic analysis, characterization of Cd in contaminated soils were investigated by BCR continuous extraction, principal component analysis (PCA), X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR), and aims to provide a reference for remediation and risk assessment of Cd in contaminated soils.

II. MATERIALS AND METHODS

2.1 Site Description and Physical Screening of Soil

The contaminated soils from the Liupanshui city and Jiyuan city were collected respectively, which were representative contaminated agricultural soils by smelteries. Soil samples they were collected from 30 sample points respectively, and then samples were mixed. 10 kg of topsoil with a depth of 0-20 cm was collected from the two places. The Cd content is 11.8 mg/kg in Liupanshui (LPS) city and 11.2 mg/kg Jiyuan city (JY), respectively.

The physical screening method for soil particle sizes was used in the experiment. Soil particle sizes were isolated by shaking of 200 g of air-dried 2-mm soil on a column of sieves with pore sizes of (0.9-2, 0.3-0.9, 0.15-0.3, 0.075-0.15, and <0.075 mm using nylon mesh. After physical screening, the soil particle sizes collected were the following: 0.9-2, 0.3-0.9, 0.15-0.3, 0.075-0.15, and <0.075 mm, respectively. The collected soil particle sizes were air-dried at room temperature.

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2.2 Soil Analysis

The forms of Cd in soil are extracted continuously by BCR [7]; Soil total Cd contents are digested with nitric acid-hydrofluoric acid-perchloric acid [8]; the contents of Cd in the solution are measured by flame atomic absorption spectrophotometer. Under the scanning range of 5-60, the mineral phase composition of soil is measured by X-ray diffractometer (D8 ADVANCE, Germany), and the diffraction data is processed according to Jade 6 software. GSS-3 (yellow brown soil) standard soil sample is used for quality control, and the recovery rate of Cd is in the range of 90%-110%.

2.3 Data Processing

Excel 2016 was used for statistical analysis of data; SPSS 18.0 was used to test the differences among different treatments. PCA were analyzed by R language pack.

III. RESULTS

3.1 Contents and Form Distribution of Cd in Soil

From fig 1, it can be seen that the content of Cd in soil increases with the decrease of particle size, and there are obvious differences in the change of Cd content, which may be related to different pollution sources. The lead and zinc smelting in LPS sampling point adopts indigenous smelting, and the heavy metal is mainly the soil pollution caused by slag leaching by rainwater or wastewater discharge. Soil Cd content increased obviously at 0.15-0.3 mm size. When the particle size decreasing from 0.075-0.15 mm to < 0.075 mm, the increasing trend of Cd content decreased. The Soil Cd in JY mainly come from atmospheric deposition. Soil Cd content increased at particle size of 0.3-0.9 mm and 0.075-0.15 mm; When the particle size < 0.075 mm, the contents of Cd in LPS and JY soils reached the highest, which were 12.5 mg/kg and 11.3 mg/kg, respectively. The reason may be that organic matter in wastewater or clay minerals in soil play an important role in the accumulation of metals in fine-grained soils.

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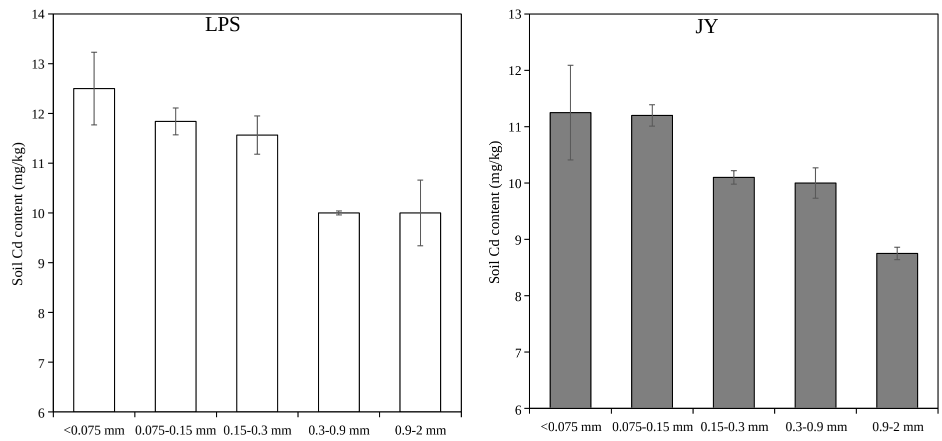

Fig 1: the Cd contents in different soil particle sizes of LPS and JY

BCR sequential extraction method has been widely used to determine the form of metal element in soil particles, and its bioavailability is acid extraction state, reducible state and oxidizable state in turn [9]. It can be seen that the content of acid-extracted Cd in LPS and JY soil is higher Fig 2. With the decrease of soil particle size, the contents of LPS acid-extracted and reducible Cd increase obviously. Except for residual Cd in soil, soil particle size has no significant effect on the form content of Cd in JY soil. The results show that the bioavailability of Cd in LPS and JY soils is high, and the particle size has a significant influence on the bioavailability of Cd in LPS soils.

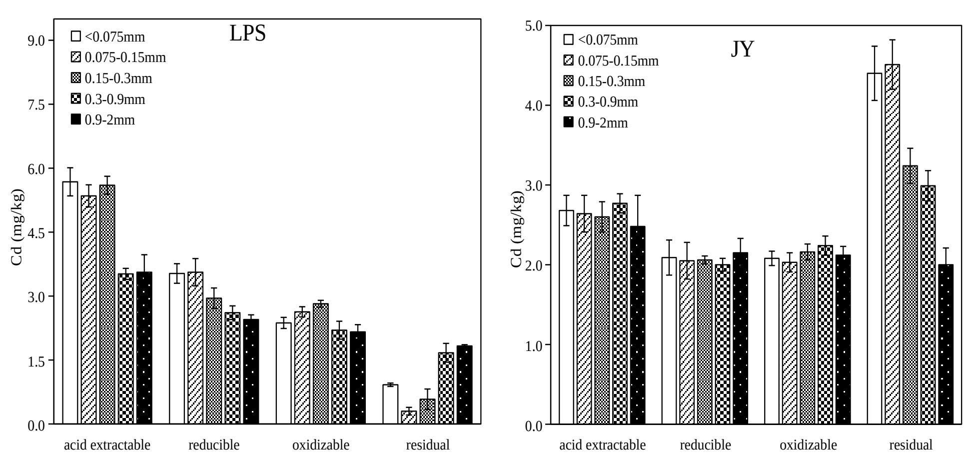

Fig 2: the distribution of Cd content in different soils particle sizes

3.2 The PCA Analysis of Cd in Different Soil Particle Sizes

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In addition, through the PCA analysis of soils, it can be seen that the contribution rates of the first principal ammxis (PC1) and the second principal axis (PC2) in LPS soil are 63.0% and 15.1%, respectively. Among them, those of soil samples with particle sizes of <0.075mm, 0.075-0.15mm and 0.15-0.3mm, 0.3-0.9mm and 0.9-2mm are closer. Similarly, the contribution rates of the first principal axis (PC1) and the second principal axis (PC2) in JY soil are 37.1% and 21% respectively. It can be seen that the soil particle sizes are obviously divided into < 0.075mm and 0.075-0.15mm, 0.15-0.3mm and 0.3-0.9mm, 0.9-0.2 mm Fig 3. The above results show that the particle sizes of soils can be divided into three groups, which may be because the environmental instability affects the properties and composition of soil with different particle sizes. The specific influencing mechanism needs to be further explored.

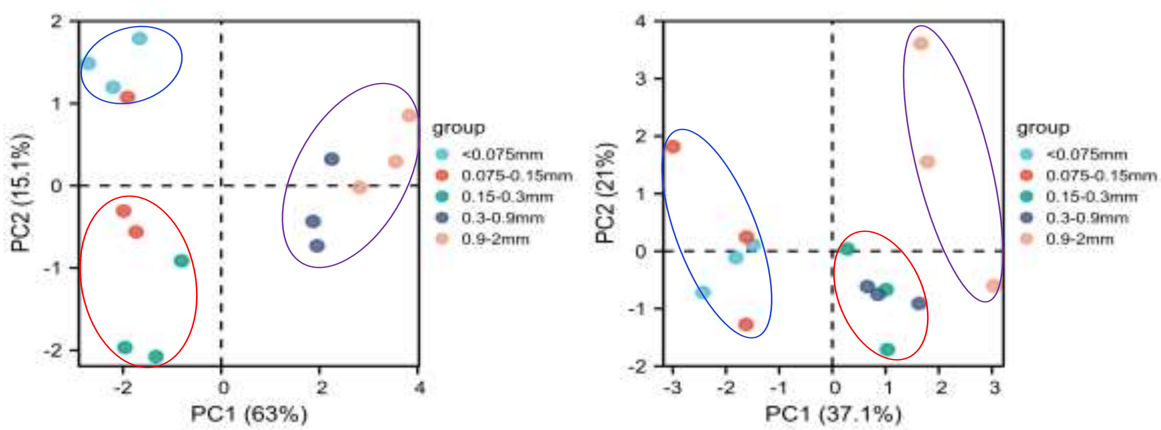

Fig 3: the PCA analysis

3.3 Component Phase Change and Heavy Metal Release Characteristics of Soil

Fig 4. shows X-ray diffraction of soil with particle sizes of 0.9-2mm, 0.15-0.3mm and < 0.075mm. The particles of LPS contaminated soil mainly contain quartz, kaolinite, anatase and pyrite minerals. The particles of JY contaminated soil mainly contain quartz, chlorite, illite, potash feldspar, plagioclase, and calcite minerals. There are significant differences between JY and LPS soils. However, the characteristic peak of XRD pattern appears amorphous, and a strong burr peak appears at the tangent of XRD pattern, which indicates that the decrease of particle size reduces or breaks crystalline minerals. This further indicates that soil components with smaller particle size may have high dispersion degree, poor crystal form, and increasing release and dissolution of heavy metals. The leaching of wastewater could dissociate the soil with larger particle size into small particle components and destroy the soil mineral crystals, so that the heavy metals adsorbed on the mineral surface would be released the soil, which be adsorbed by the fine particles with larger specific surface area. In addition, hydroarsenite, vanadium,

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iron and lead are also found in the particles of JY soil, which shows that it is obviously affected by smelting activities.

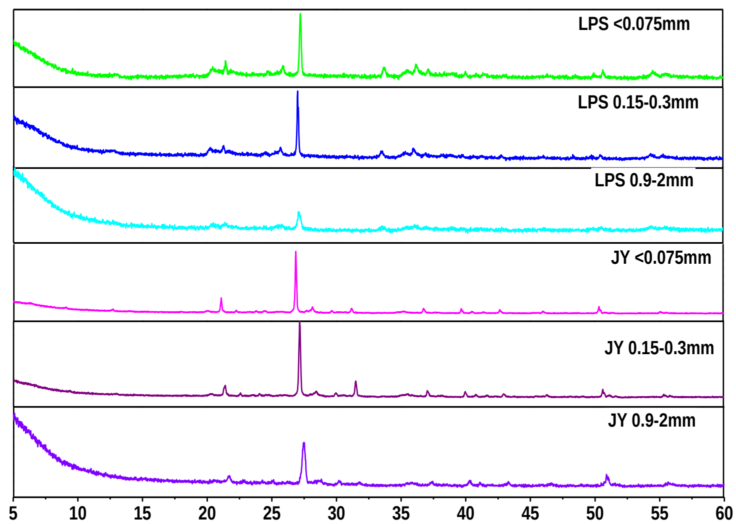

Fig: 4 soil XRD analysis

Fig 5. is FTIR analysis of soil with particle size of 0.9-2mm and < 0.075mm. There are many similar bands in FTIR spectra of soils with different particle sizes, and there are corresponding changes when the particle size < 0.075mm, which may be related to the change of organic matter content and types in soils [10]. The absorbance has a peak at 3419-3444 cm^{-1}, which is mainly the O-H stretching vibration of phenolic compounds. There are two peaks at about 2900 cm^{-1} corresponding to the tensile vibration of aliphatic chain -CH2 and CH3 groups. There are obvious double peaks at 2300~2400cm^{-1}, which indicates that the fine particles of contaminated soil contain triple bonds of carbon and nitrogen. The peak at 1615-1635cm^{-1}may be the C=O vibration of aromatic compounds and carboxyl groups or the interaction between free water and organic matter or clay components [11, 12]. The peak values of tensile bands are 1031,800-780,529-523 and 469-472 cm^{-1}, which indicates the bending vibration in the Si- O-Si plane, the existence of bridge bonds between Si-O-Si tetrahedrons, the deformation of Si-O-Al/Mg and the bending vibration of Si-O. Therefore, the similar wave bands in this area indicate that similar minerals (such as quartz, smectite, illite and kaolinite) may exist in soils of different particle sizes, which is closely related to the release of heavy metals [13].

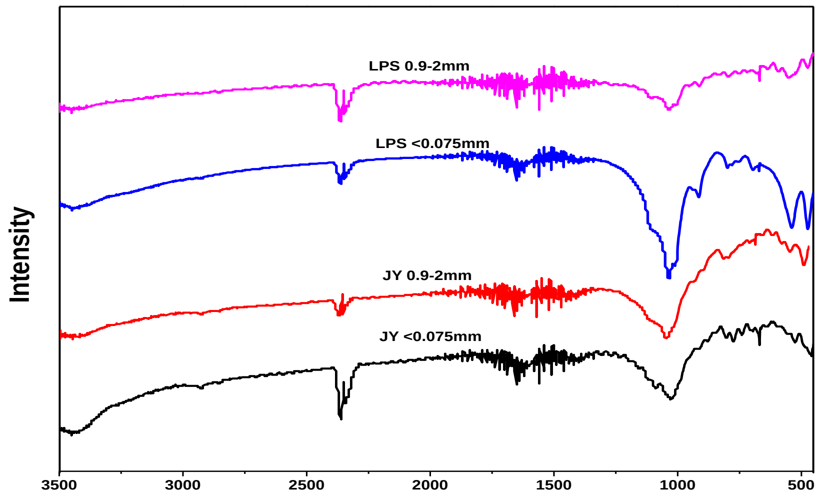

Fig 5: soil FTIR spectrum analysis

Soil particle sizes the distribution of Cd n Liupanshui City and Jiyuan City contaminated soil. The contents of Cd in the soils both exceeded the screening values in the soil environmental quality control standard of agricultural land soil pollution risk (Trial) (GB 15618-2018). With the decrease of soil particle size, the contents of Cd increased, and the contents of Cd in fine soil particles were significantly higher than those in coarse soil particles. The content of acid-extracted and reducible Cd in fine particles in the Liupanshui soil increased, while that in Jiyuan soil had similar changes, which may be related to the composition of soil mineral species, organic matter content or pollution sources. The specific reasons need to be further explored. Especially, the harm of Cd-containing fine particles in the contaminated soil by smelters should be paid to attention.

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