Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

Particle-Size Distribution of Lead and Environmental Risk Assessment in Agricultural Soils Contaminated by Different Smelters

Lei Shi[1,2], Shuaixia Liu[1,2]*, Bo Huang[1], Qiming Zheng[1], Mengjuan Ma[1,2], Xianggang Feng[1], Yanlin Cheng[1], Mingze Li[1]

[1]College of Environmental and Biological Engineering, Henan University of Engineering, Zhengzhou 451191, Henan, China

[2]Zhengzhou Key Laboratory of Mine-Soil Remediation, Zhengzhou 451191, Henan, China

*Corresponding Author.

Abstract:

Soil particle size was an important factor for the transformation of soil heavy metals and environmental risk. However, the impact of soil particle on the allocation, and environmental risk of lead (Pb) in contaminated soil by different smelters was seldom addressed. In the study, 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) from the soil polluted by different smelters were separated by the physical method, respectively. The impact of particle size on soil Pb, and ecological risks were investigated by BCR continuous extraction and redundancy analysis. The results showed that soil pH, SOM, CEC and EC increased with the decrease of particle size, except JY soil EC. The reducible Pb content in contaminated soil increased with decreasing particle size. Furthermore, soil Pb had a high accumulation index and potential ecological risk in different soil particle sizes. Therefore, effective measures should be taken to the risk control for agricultural soil contaminated by smelters.

Keywords: *Soil, Heavy metal, Particle size, Ecological risk assessment.*

I. INTRODUCTION

Smelting would generate heavy metal contamination[1]. It is grim in cultivated land in China, with 19.4% of over-limit ratio of contaminated sites, of which 1.5% for Pb. Pb are non-essential elements of plants, which are easily uptaked by crops and endanger human health[2-3]. Soil is composed of different particle sizes. Natural fine particles with particle sizes less than 250μm are called soil fine particles. Soil particle size plays an important role in regulating the effectiveness and toxicity of heavy metals[4].

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

It is great significance to study the content and form transformation of Pb in different soil particle sizes to assess their potential risks.

In recent years, wet method is often used to extract the content distribution and chemical forms of heavy metal with different particle sizes from soil and surface dust[5]. Although different particle sizes of soils can be obtained by this method, the process is complicated and the interaction between soil and water may change the soil properties, the content of heavy metal, and the evaluation of environmental risks. At present, researchers pay more attention to the distribution and morphological changes of heavy metals in small-sized soils, but there are few reports on the soil properties, heavy metal morphology, and potential environmental risk evaluation of different-sized soils. Especially, the distribution characteristics of Pb in agricultural soils polluted by different lead-zinc smelters in central and western China with different particle sizes and the potential environmental and ecological risk evaluation need further discussion. Therefore, this study selects agricultural soils polluted by lead-zinc smelters in Liupanshui City, Guizhou Province in the west and Jiyuan City, Henan Province in the central part as the research objects: (1) Studying the change law of soil properties and the distribution characteristics of Pb contents with different particle sizes; (2) Discussing the forms and influencing factors of Pb in soils with different particle sizes; (3) Exploring the potential environmental and ecological risks of Pb in the agricultural soil polluted by different smelters and finally providing scientific basis for risk control of agricultural soil around smelter.

II. MATERIALS AND METHODS

2.1 Collection and Treatment of Soil Samples

In November, 2019, farmland topsoil in Muguo Town and the Erxuanchang District of Dawan Town, Liupanshui City (LPS), and farmland topsoil in Kejing Town, Jiyuan City (JY) were collected respectively. They are representative agricultural soils polluted by lead and zinc smelting. For the soil samples (HJ/T 166-2004), they were collected from 30 sample points respectively according to the sampling method of multi-density random layout. After sampling, the soil samples were mixed. 10 kg of topsoil with a depth of 0-20 cm was collected from the two places for laboratory use.

In the laboratory, pour the soil on clean paper, crush it with a rubber hammer, spread it evenly, remove plant residues and gravel from the samples, and air-dry it at room temperature. The air-dried soil samples were ground by the quartering method, then rolled and sieved by nylon sieves of 2.00 mm, 0.90 mm, 0.30 mm, 0.15 mm and 0.075 mm, respectively, to obtain soil samples with particle sizes of 0.9-2.0 mm, 0.30-0.90 mm, 0.15-0.30 mm, 0.075-0.15 mm and < 0.075 mm respectively. Soil properties are shown in TABLE I.

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

TABLE I. Soil physical and chemical properties

Location	pH	EC(μS·cm)	CEC(cmol·kg^{-1})	SOM (%)	Total Pb(mg/kg)	Total Zn(mg/kg)	Total Cu(mg/kg)	Total Cd(mg/kg)
LPS	4.93	80.2	10.26	6.94	122.2	232.6	55.25	11.8
JY	8.01	70.5	6.48	4.36	138.7	221.4	32.83	11.2

2.2 Analysis of Soil Samples

Soil pH is measured by pH meter with water-soil ratio of 1:2.5; the EC of soil is measured by the Electrode Method for Measuring Soil Electrical Conductivity; SOM in soil is measured by potassium dichromate external heating method ($K_2Cr_2O_7$-H_2SO_4). CEC of soil is measured by ammonium acetate method[6]; the forms of heavy metals in soil are extracted continuously by BCR[7]; the total heavy metals in soil are digested with nitric acid-hydrofluoric acid-perchloric acid; the contents of Pb in the solution are measured by flame atomic absorption spectrophotometer[8]. GSS-3 (yellow brown soil) standard soil sample is used for quality control, and the recovery rate of Pb is in the range of 80%-120%.

2.3 Environmental Risk Evaluation

2.3.1 The calculation formula of the geoaccumulation index is:

$$I_{\mathrm{geo}} = \log_2\left(\frac{C_{\mathrm{f}}^{\mathrm{i}}}{1.5 \times B_i}\right) \tag{1}$$

Wherein, C_f is the measured content of heavy metal i (mgkg-1), B_i is the soil pollution control value (mgkg-1) of heavy metal i. 1.5 is the correction coefficient for the change of background value caused by rock difference and Igeo is the geoaccumulation index.

2.3.2 The activity coefficient (MF) and potential ecological risk of heavy metals in soil is evaluated. The calculation formulas are as follows:

$$\mathrm{MF} = \frac{\mathrm{F1} + \mathrm{F2} + \mathrm{F3}}{\mathrm{TM}} \tag{2}$$

Wherein: [F1], [F2], [F3] and TM are acid extracted state, reducible state, oxidizable state and total amount of heavy metals (mg/kg), respectively.

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

$$C_f^i = \frac{C_s^i}{C_r^i} \tag{3}$$

$$E_r^i = T_r^i \times C_f^i \tag{4}$$

Wherein: C_f^i is the single pollution coefficient; C_s^i is the measured content of heavy metal element in the sample (mg/kg). C_r^i is the reference value of heavy metal elements. In this study, the background values of topsoil in Guizhou Province and Henan Province were used as references. T_r^i is the toxicity coefficient of Pb (Pb=5). E_r^i is the single potential ecological risk index of heavy metal element i.

2.4 Data Processing

Excel 2016 was used for statistical analysis of data; SPSS 18.0 was used to test the differences among different treatments. RDA was analyzed by Conoco 5.0.

III. RESULTS

3.1 Analysis of Soil Properties with Different Particle Sizes

Soil pH increased with the decrease of particle size. The particle size< 0.075 mm, the pH values of LPS and JY soil were the highest, which were 4.91 and 8.34 respectively. When the soil particle size decreased from 0.90-2.00 mm to 0.30-0.90 mm, the content of LPS soil organic matter and EC value increased. However, SOM content and EC value of JY soil first increased and then decreased. Soil organic matter contents with particle size of 0.30-0.90 mm to < 0.075 mm were 5.01%-6.01% and 3.51%-5.48% respectively in LPS and JY (except JY with particle size of 0.075-0.15mm). The high content of organic matter indicates that soil particles have strong affinity for heavy metals. The CEC of LPS increased, among which the CEC of soil increased to 16.5 cmol/kg at particle size of 0.15-0.30 mm, followed by 15.5 cmol/kg at particle size of 0.075-0.15 mm and 16.3 cmol/kg at particle size< 0.075 mm; the CEC value of JY soil increased significantly at particle size < 0.075 mm. The result shows that particle size has a great influence on soil physical and chemical properties[9].

3.2 Contents and Form Distribution of Pb in Soils with Different Particle Sizes

Heavy metal exceeded the standard of crops, posing a potential threat to the health of local residents[10]. From Fig 1, it can be seen that the content of Pb in soil increases with the decrease of particle size, and there are obvious differences in the change of Pb content, which may be related to

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

different pollution sources. The lead and zinc smelting in LPS sampling point adopts indigenous smelting, and the heavy metal pollution is mainly the soil pollution caused by slag leaching by rainwater or wastewater discharge. The contents of Pb increased obviously at particle size of 0.15-0.3 mm. At the particle size decreasing from 0.075-0.15 mm to < 0.075 mm, the increasing trend of heavy metal content decreased. The pollutants Pb in JY soil may come from atmospheric deposition. The Pb content obviously increased when the particle size decreased from 0.075-0.15 mm to < 0.075 mm. When the particle size < 0.075 mm, the contents of Pb in LPS and JY soils reached the highest, which was 130.6 mg/kg and 151.2 5 mg/kg, respectively. The reason may be that organic matter in wastewater or clay minerals in fine-grained soils[11-13]. Based on the enrichment trend of heavy metals in fine soil particles, the soil particle size should be considered in the risk evaluation of heavy metal pollution in smelters.

TABLE II. Soil properties with different particle sizes

Particle sizes(mm)	pH		SOM(%)		EC(μS/cm)		CEC(cmol/kg)	
	LPS	JY	LPS	JY	LPS	JY	LPS	JY
<0.075	4.91±0.02a	8.34±0.03a	6.07±0.8a	4.15±0.2b	155.5±9.6a	105.7±4.0bc	15.5±1.3ab	5.3±0.5a
0.075-0.15	4.81±0.04b	8.27±0.03ab	5.9±0.9a	3.51±0.2c	158.3±13.3a	98.00±7.0c	16.3±0.7ab	4.4±0.5b
0.15-0.30	4.83±0.02b	8.26±0.05ab	6.00±0.7a	5.48±0.10a	156.7±8.3a	116.5±8.5ab	16.5±1.9a	4.7±0.2b
0.30-0.90	4.80±0.02b	8.11±0.04c	5.01±0.3a	4.07±0.2b	141.7±5.8a	119.7±9.2b	13.8±1.8b	5.2±0.3ab
0.90-2.00	4.81±0.03b	8.23±0.07b	3.59±0.3b	3.43±0.03c	120.1±9.2b	126.7±2.9a	9.5±0.6c	4.6±0.3b

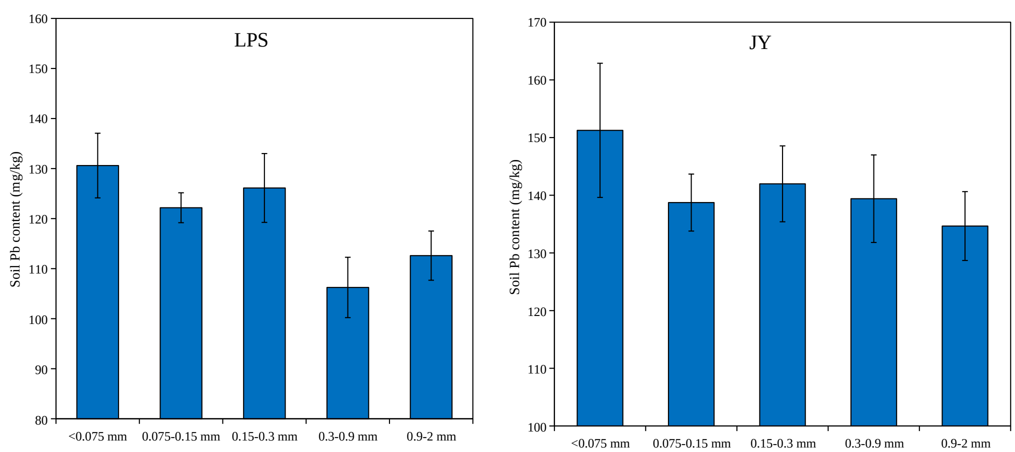


Fig 1: The Pb contents in different soil particle sizes of LPS and JY

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

BCR continuous extraction method is usually used for the heavy metal form. The form and content of Pb in soils is quite different. The content of reducible Pb increases with the decrease of particle size, and it is significantly higher than that of acid-extracted, oxidizable and residual Pb (Fig 2). Pb is easily adsorbed by soil minerals or organic matter and CEC[14]. When Pb interacts with the surface of soil minerals, it has a high affinity with the soil with high organic matter content[15], which is consistent with the change trend of organic matter content in Table I. Based on the above results, it can be seen that Pb in soils with different particle sizes have high bioavailability, and effective measures should be taken to control them.

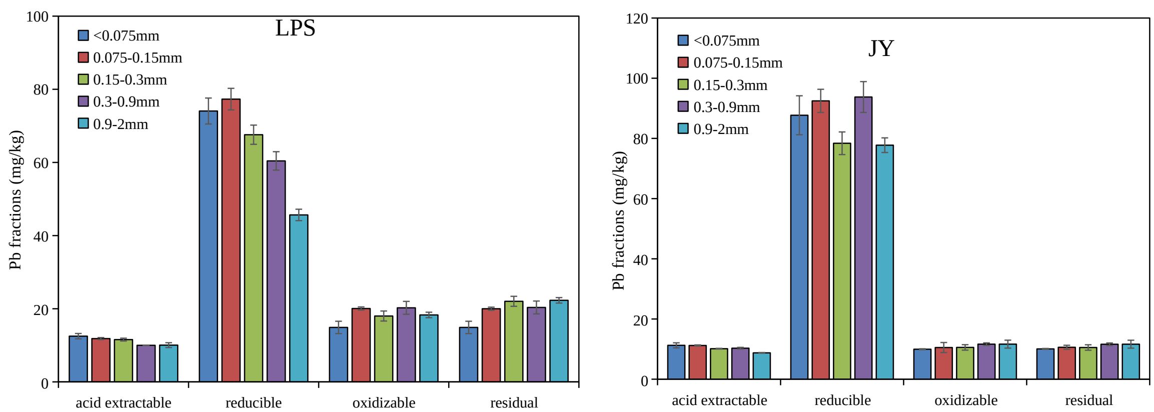
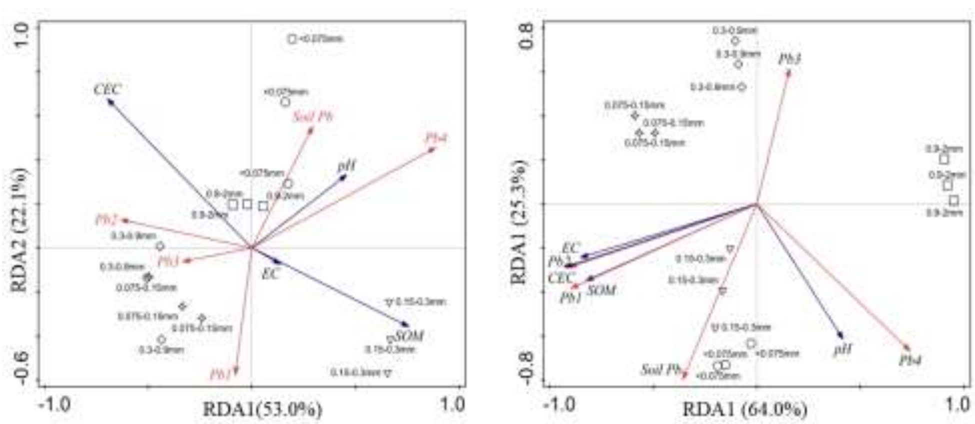


Fig 2: The distribution of soil Pb fractions content in different particle sizes

3.3 Analysis of Correlation between Heavy Metals in Soil and Environmental Factors



Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

Fig 3: The RDA analysis of soil Pb and environmental factors

Fig 3 shows the analysis of RDA between Pb in soil and environmental factors. The interpretation rates of the first principal axis and the second principal axis of LPS in soil are 53.0% and 22.1% respectively (Fig 3). The main influencing factors of the first axis are SOM and pH, and the main influencing factor of the second axis is CEC; Acid-extracted Pb are negatively correlated with soil pH and CEC. Oxidizable and reducible Pb are positively correlated with CEC, whereas negatively correlated with SOM. In JY soil, the rates of interpretation of Pb by the first principal axis and the second principal axis are64.0% and 25.3% respectively. The main influencing factors of the first axis are SOM, CEC and EC, and the main influencing factors of the second axis is pH. Acid-extracted and reducible Pb is positively correlated with soil CEC, SOM and EC. However, Oxidizable Pb is negatively correlated with pH, CEC, SOM and EC.

3.4 Environmental Risks of Heavy Metals in Different Soil Particle Sizes

Geoaccumulation index (I_{geo}) is an evaluation of heavy metal pollution in soil. As shown in Table III, the I_{geo} of Pb increase with the decrease of particle size. Among it, the I_{geo} in LPS soil is 0.1-0.31 respectively and the pollution degree is slight, whereas there is no Pb pollution in JY soil. The types and activities of heavy metal could affect the absorption of plants. In LPS soil, with the decrease of particle size, MF of Pb is gradually rise; while MF of Pb in JY soil is no obvious rule of change. The result shows that the activity coefficient of Pb in LPS soil is higher; however, the result is opposite in JY soil, which may be related to the high content of exchangeable, reducible and oxidizable Pb and the high pollution level. According to the results of potential ecological risk evaluation, in the finer particles of soil, the single pollution coefficient (C_f) and the potential ecological risk index (E_r) of Pb are larger than those of Coarse-grained soil. To sum up, the geoaccumulation index, activity coefficient and potential ecological risk of elements in soils are different. But in fine particles, the geoaccumulation index, activity coefficient and potential ecological risk increase (except the activity coefficient of Pb in JY soil). Therefore, soil Pb content finer particle sizes should attract enough attention for further study.

TABLE III. The ecological and environmental risk assessment of Pb

Location	Evaluation Index	<0.075mm	0.075-0.15mm	0.15-0.3mm	0.3-0.9mm	0.9-2mm
LPS	I_{geo}	0.31	0.22	0.26	0.02	0.10
	MF	0.78	0.89	0.79	0.85	0.67
	C_f	1.87	1.75	1.80	1.52	1.61

Forest Chemicals Review
www.forestchemicalsreview.com
ISSN: 1520-0191
September-October 2021 Page No. 159-167
Article History: Received: 22 July 2021 Revised: 16 August 2021 Accepted: 05 September 2021 Publication: 31 October 2021

	E_r	9.33	8.73	9.01	7.59	8.04
JY	I_{geo}	-0.76	-0.88	-0.85	-0.87	-0.92
	MF	0.72	0.82	0.70	0.83	0.73
	C_f	0.89	0.82	0.84	0.82	0.79
	E_r	4.45	4.08	4.18	4.10	3.96

In conclusion, particle size significantly affects the properties of soil contaminated by smelters in Liupanshui City and Jiyuan City, the distribution of Pb in soil particles and the environmental risk evaluation. Except for the EC in Jiyuan soil, pH, SOM, EC and CEC in the soil increased with the decrease of particle size. The Pb content in fine soil particles was higher than those in coarse soil particles. Among different particle sizes, the content of reducible Pb was relatively high. The specific reasons need to be further explored. The values of I_{geo}, C_f and E_r show that Pb have a very high risk level in the fine particles. In addition, based on the enrichment trend of Pb in fine soil particles, the influence of soil particle size should be considered in the risk evaluation of the soil contaminated by heavy metal from smelters.

ACKNOWLEDGEMENTS

This research was supported by Key R&D and Promotion Projects of Henan Province, China (Grant No. 212102310067), National Innovation and Entrepreneurship Training Program for College Students (Grant No. 202111517009) and Doctoral Fund of Henan University of Engineering (Grant No. D2020006).

REFERENCES

[1] Chen R, Chai L, Wang Y, et al. (2012) Degradation of organic wastewater containing Cu-EDTA by Fe-C micro-electrolysis. Transactions of Nonferrous Metals Society of China 22:983-990.

[2] Zhao FJ, Wang P (2020) Arsenic and cadmium accumulation in rice and mitigation strategies. Plant and Soil 446:1-21.

[3] Tma B, Tong ZA, Zhu LA, et al (2020) Prediction models for rice cadmium accumulation in Chinese paddy fields and the implications in deducing soil thresholds based on food safety standards. Environmental Pollution 258:113879.

[4] Wu T, Li XP, Cai Y, et al. (2017) Geochemical behavior and risk of heavy metals in different size lead-polluted soil particles. China Environmental Science 37(11):4212-4221

[5] Huang B, Yuan Z, Li D, et al. (2020) Effects of soil particle size on the adsorption, distribution, and migration behaviors of heavy metal (loid)s in soil: a review. Environmental Science: Processes Impacts 22:1596-1615

[6] Lu RK (2000) Soil agrochemical Analysis methods. Beijing: China Agricultural Science and Technology Press

[7] Yan DM, Guo ZH, Huang FL, et al. (2020) Effect of calcium magnesium phosphate on remediation paddy soil contaminated with cadmium using lime and sepiolite. Environmental Science 41(3):1491-1497

[8] Shi L, Guo ZH, Peng C et al. (2019) Immobilization of cadmium and improvement of bacterial community in contaminated soil following a continuous amendment with lime mixed with fertilizers: A four-season field experiment, Ecotoxicology and Environmental Safety 171:425-434

[9] Tang Z, Wu L, Luo Y, et al. (2009) Size fractionation and characterization of nanocolloidal particles in soils. Environmental Geochemistry and Health 31(1):1-10

[10] Li YL, Chen WP, Yang Y, et al. (2020) Heavy metal pollution characteristics and comprehensive risk evaluation of farmland across the eastern plain of Jiyuan city, Acta Scientiae Circumstantiae 40(6):301-308

[11] Wang N, Yao JJ, Gao YZ, et al. (2012) Particle size distribution in yellow-brown soil: Fractionation and characterization, China Environmental Science 32(12):2253-2260

[12] Bartz W, Górka M, Rybak J, et al. (2021) The assessment of effectiveness of SEM- EDX and ICP-MS methods in the process of determining the mineralogical and geochemical composition of particulate matter deposited on spider webs. Chemosphere 278: 130454

[13] Quenea K, Lamy I, Winterton P, et al. (2009) Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water. Geoderma 149(3-4):217-223.

[14] Elliott HA, Liberati MR, Huang CP (1986) Competitive Adsorption of Heavy Metals by Soils. Journal of Environmental Quality 15(3):214-219

[15] Appel C, Ma LQ, Rhue RD, et al. (2008) Sequential sorption of lead and cadmium in three tropical soils. Environmental Pollution 155(1):132-140