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Distribution of Heavy Metals in Different Size Fractions of Agricultural Soils Closer to Mining Area and its Relationship to TOC and Eh

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Abstract -The concentrations of As, Cd, Cr, Cu, Pb, Zn were analyzed in the bulk and six particle size fractions of soil samples from a village near mining area, southwest of Jiangxi Provence. The relationships of heavy meals concentrations with total organic carbon (TOC), redox potential (Eh) have been investigated. Total heavy metal concentrations ranged from 318 mg/kg to 1215 mg/kg dry weight. The highest total heavy metal concentration occurred in <0.05 mm size fraction. The maximum individual heavy metal concentration was in <0.05mm size fraction too. The similar trends of distribution of individual heavy metal indicate source homology. The maximal TOC and Eh contents were found in <0.05 mm size fraction. Strong positive linear relationship between total heavy metal and TOC or Eh has been demonstrated, with a correlation coefficient of 0.99 and 0.53, respectively. Concentration and toxicity of heavy metal in fine particle are higher than the coarse particle.

Keywords: Heavy metal; Distribution; Soil size fraction; TOC; Eh

1. Introduction

Mining activities and metal smelting have been the main sources of hazardous heavy metals (El Khalil et al., 2008; Rodríguez et al., 2009). With the rapid economic development in the past 30 years in China, booming mining industry has caused a series of environmental problems. Agricultural soils near mining area are often contaminated by heavy metals due to irrigation and flooding (Cheng et al., 2011). Due to toxicity, persistence and bioaccumulation of heavy metals, remediation of heavy metal-contaminated soil becomes a major environmental concern (Dong et al., 2010).

Finding out the distribution of heavy metals in soil is the premise of soil remediation by soil washing and subsequent land reuse. Previous research has conducted to determine the spatial distribution pattern of heavy metals in soils and sediments, and a few researched the distribution pattern of heavy metals in different size fraction. But few researches on the distribution of heavy metals in different soil size fractions and relationship between heavy metals and soil characteristics. So many studies have demonstrated the accumulative effect of metals in soil and sediment. And most indicated that heavy metals concentrated in the fine size fraction(Ajmone-Marsan et al. 2008; Yu and Li 2011).Other results are slightly different, Chen et al. (2013) found the maximum content of most metals in particle size was at 0.002~0.001 mm, instead of <0.001 mm. Sager et al. (2012) has similar findings. High inclination of joint connection between heavy metals and TOC brought difficulties for environmental remediation. Positive correlation between heavy metals concentrations and TOC was found in most relative researches. And soil Eh was found to be an important factor controlling the dynamics of studied compounds and elements, it can be the dominating factor affecting metal fate (Du Laing et al. 2009). Frohne et al. (2011) reported Eh correlate significantly with Cd, Ni, Cu, Zn and Mn. However, there were few reports about the research on its relationship to distribution of heavy metals in different soil size fractions.

The objective of this research is to examine heavy metals distribution among different size fraction of soil samples from farmland closer to mining area. Besides, we also analyzed the effects of TOC and Eh contents on the distribution of heavy metals.

2. Materials and Methods

2. 1. Study Area and Soil Sampling

The soil samples used in this study were collected from a village in southwest of Jiangxi, China, which is abundant in mineral and is honored as the village of tungsten for hundred years. They are all from cultivated soils and the samples were taken from the surface layer (0-20 cm). The soils were air-dried, ground, and passed through a 2-mm screen to remove rocks, roots, and other large particles, and then stored in polyethylene bags before analysis.

2. 2. Size Separation

Soil samples were separated into six fractions(<0.05 mm, 0.05-0.075 mm, 0.075-0.22 mm, 0.022-0.5 mm, 0.5-1 mm, 1-2 mm)by dry sieving. The mass of each soil size fraction was weighted to calculate the mass fraction.

2. 3. Soil Characteristics and Metal Analysis

Basic soil physicochemical properties, such as pH, water content, density, cation exchange capacity(CEC) were determined by standard procedures (Lu, 2000), total organic carbon(TOC) and soil redox potential(Eh) were measured using a TOC analyzer (Elementar, Germany) and a soil Eh analyzer(STEH-200, China). Experiments were carried out in duplicate.

The total concentrations of metals(As, Cd, Cr, Cu, Pb, Zn) in bulk soils and different particle size fractions were analyzed by ICP-AES after using a strong acid(HNO_3-$HClO_4$) pseudo-total digestion method(Lee et al., 2006). Reagent blanks and analytical duplicates were also used where appropriate to ensure the accuracy and precision of the analysis. The recovery rates for most metals in the standard reference material were around 75-110%. Experiments were carried out in duplicate.

3. Results and Discussion

3. 1. Soil Characteristics

Figure 1 presents the distribution of the bulk soil. The results indicated that the particle size fraction of bulk soil presented normal distribution. Particles in the range of 0.22-0.5 mm had the highest value and accounts for 35.20%, followed by particles of 0.5-1 mm and 0.075-0.22 mm which contributed 24.20% and 23.46%, respectively. Particles larger than 0.075 mm contributed 92.88% of the total soil mass, more than 50% of the sum dry weight, the bulk soil sample is sandy soil (Chang et al., 2007). Some of soil properties are listed in Table 1, the soil has a relatively low TOC, CEC and Eh. So from the perspective of remediation, it is adaptable to soil washing method.

Table. 1. The physicochemical property of bulk sample.

	Water/%	density/g·cm^{-3}	pH	Eh/mV	CEC/cmol·kg^{-1}	TOC/g·kg^{-1}
Bulk	1.09±0.05	2.45±0.01	5.15±0.08	148±4	5.85±0.09	2.65±0.21

The characteristics of the each size fraction were presented in Table 2. Particle size fraction had the greatest influence on the soil TOC and Eh, the coefficient of variation (CV) were both 0.6, which was far above CV of pH and CEC. With the augment of particle size, TOC decreases to a lowest value, 1.5-1.7 mg·kg^{-1}, before the increase at <0.05 mm particle size. As important organic colloid, TOC can form colloid structure with small particle size, which is combined closely with organic and inorganic matters alternately (Lee et al., 2006;).Although changes of CEC was not remarkable, it had the similar changing trend, with lowest value, 5.2-5.6 cmol·kg^{-1}, at 0.22-0.5 mm particle size and highest value 7.0-7.2 cmol·kg^{-1} at <0.05 mm. Though the high value of metal concentration, TOC and Eh in <0.05 mm size fraction, the percent mass contributions of them were very low and all below 5%. For total heavy metals and TOC, the percent mass contributions were greatest in the 0.075-0.22 mm size fraction, while for Eh, the greatest contribution value was in the 0.22-0.5 mm size fraction.

Table. 2. The physicochemical property of different soil size fractions.

Particle size/mm	1-2	0.5-1	0.22-0.5	0.075-0.22	0.075-0.05	<0.05	CV
pH	5.0±0.0	5.2±0.0	5.3±0.0	5.4±0.0	5.4±0.0	6.0±0.0	0.06
Eh/mV	142±3	152±4	146±2	155±2	173±3	452±3	0.60
CEC/cmol·kg^{-1}	6.8±0.1	6.4±0.3	5.4±0.2	6.6±0.2	7.1±0.1	7.1±0.1	0.09
TOC/mg·kg^{-1}	4.3±0.1	1.6±0.1	2.1±0.1	3.9±0.0	7.1±0.1	8.5±0.1	0.60

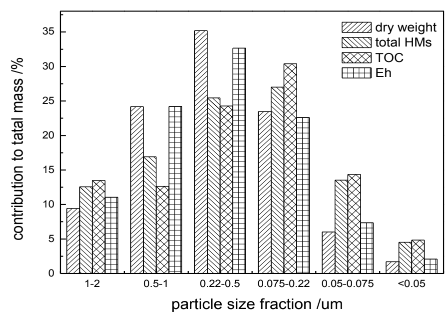

Fig .1. Relative contribution of individual size fractions to composite soil dry mass, sum heavy metals, TOC and Eh content.

3. 2. Heavy Metal Distribution in Soil Size Fractions

Concentrations of heavy metals (As, Cd, Cr, Cu, Pb, Zn) were measure for the bulk sample and each size fraction. Concentrations of As and Cd were 227.63 mg·kg^{-1} and 2.00 mg·kg^{-1}, which is 5 and 8 times higher than the second grade standard of Environmental quality standards for soils (2008), while other heavy metals were under the level of quality standards. The concentrations and distribution patterns of 6 heavy metals in different soil size fractions are plotted in Fig.2.The data are the mean value of duplicated samples. The highest total heavy metal concentration occurred in the <0.05 mm size fraction, and the particle size of 0.5-1 mm had the lowest metal concentrations. Although metal concentration varied greatly among the six size fractions in samples, the distribution patterns of each metal are similar, which indicate the source homology (Zhen et al., 2014), moreover, combined pollution promotes synergistic effect. With the increasing of particle size, heavy metal concentrations first decreased then increased. The particle size of 0.5-1 mm had the lowest concentration of As, Cd, Cr, Cu, with the value of 156.44, 4.13, 33.49 and 15.24 mg·kg^{-1}, respectively. While 0.22-0.5 mm to Pb, Zn, 31.65 mg·kg^{-1} and 70.78 mg·kg^{-1}. The finest size fraction (<0.05 mm) had the highest concentration for all the 6 heavy metals, the similar observation was found in other researches (Li et al. 2011; Chen et al., 2011).

Although there is no uniform international standard of soil particle partitioning, research results of heavy metal distribution of different particle size are similar. Owing to larger specific surface area in fine particle size fraction, it has stronger adsorption ability of heavy metals than coarse particle, so occurrence of heavy metals is preferably on the fine fraction. The large concentration variations of heavy metals were probably controlled by temperature, pH, Eh, ionic strength and other factors, so heavy metal content in soil is not entirely increases with the decrease of the particle size. The trend was also found in our research (Fig.1.). The distribution of metal elements is not only related to soil particle size fraction, but also to the mineral composition in soil. In the coarse particles, there contains different native mineral composition which reflects the original sedimentary environment of the chemical composition of the earth, meanwhile primary mineral itself contains metal elements (Chen et al.,2014;Chen et al.,2011). The soil samples were collected from a village near mines in southwest of Jiangxi, so they might be affected by ore , so the heavy metals concentration of coarse fraction is relative high.

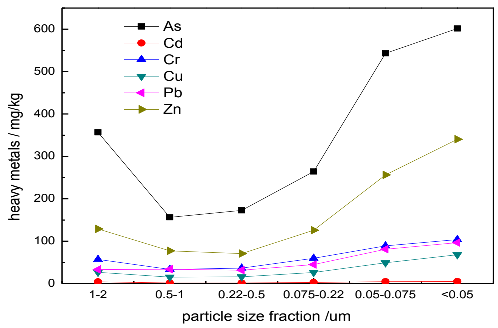

Fig. 2. Distribution patterns of heavy metals in different soil size fractions.

3. 3. Correlations of Heavy Metal Versus TOC and Eh

Total heavy metal concentrations versus TOC and Eh was plotted as followed to further examine the relationship between distribution of heavy metal and soil characteristics (Fig.4). Strong correlations exist between total heavy metals versus TOC, and the linear regression correlation coefficient between total heavy metal concentrations versus TOC is much larger than it versus Eh. The linear regression correlation coefficient between total heavy metal and TOC is very high, the value is 0.99. TOC can not only be as measured of the productivity of soil, but also affect behavior and mobility of metal element relying on specific adsorption and surface coordination with organic matter (Liu et al., 2008). Correlation analysis showed that TOC can strongly adsorbed with heavy metals, and this is similar to the viewpoint reported by predecessors (Chen et al.,2014). Though small proportion of TOC in soil, its adsorption capacity on metal cation is far more than any other mineral gel. So more TOC in soil, more heavy metal adsorbed here and slower migration of heavy metals. Meanwhile, the linear regression correlation coefficient between total heavy metal concentration versus Eh is much lower, only 0.53. Research has shown that environmental factors such as soil Eh, pH and changes of nutrient elements together lead to changes of behavior and activities of heavy metal (Yamaguchi et al., 2011). Under two different conditions of flooded and dried, changes of soil Eh can affect valence state of As and its behavior, and corresponding impact on available form of As (He et al., 2010; Rothwell et al., 2009). The Eh value of <0.05 mm is particularly high, so toxicity of heavy metal in fine particle is higher than the coarse particle. The linear regression equation and correlation coefficient of individual heavy metal versus TOC and Eh are also given in table 3. As seen from the table, the linear correlation of every single heavy metal versus TOC and Eh had the same trend with linear correlation of total heavy metal, the ranges of correlation coefficient are 0.88-0.99 and 0.28- 0.69 , respectively.

4. Conclusions

It is the premise of soil remediation and land reuse to figure out the distribution of heavy metal in contaminated soil. The concentrations of 6 heavy metals ranged from 318 $mg \cdot kg^{-1}$ to 1215 $mg \cdot kg^{-1}$ dry weight in the six soil size fractions and present the distribution of firstly decreased then increased with the increasing of particle size. The distribution patterns of each metal are similar. The size fractions of 0.22-0.5 mm have higher percentages and contributed 35.20% of the total heavy metal mass. The maximum TOC and Eh content were found in <0.05mm size fraction. Despite relatively low contents in soil, TOC plays an important role in the sequestration of heavy metal. Linear correlation relationships between total and single heavy metal concentration are better explained versus TOC than Eh content, which means TOC could be the dominant adsorbent of heavy metal in soil samples.

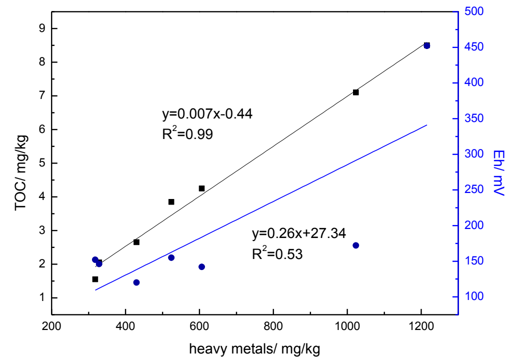

Fig. 4. Total heavy metals concentration versus TOC/Eh of the bulk and different size fractions in the soil.

Table. 3. Linear correlation relationships between single heavy metal concentration versus TOC and Eh content.

Heavy metal	Heavy metal versus TOC	Heavy metal versus Eh
As	y=0.01x-0.56(R^2=0.98)	y=0.47x+35.52(R^2=0.42)
Cd	y=1.70x-0.96(R^2=0.86)	y=51.01x+34.30(R^2=0.28)
Cr	y=0.09x-1.68(R^2=0.99)	y=3.33x-11.32(R^2=0.50)
Cu	y=0.13x+0.18(R^2=0.96)	y=5.04x+32.32(R^2=0.69)
Pb	y=0.09x-0.58(R^2=0.88)	y=3.58x+6.85(R^2=0.58)
Zn	y=0.03x+0.34(R^2=0.96)	y=0.95+42.31(R^2=0.65)

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