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Vertical Distribution of Heavy Metal in Soil of Abandoned Vehicles Dismantling Area

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In order to study heavy metal contamination in the soil of the abandoned vehicles dismantling area, the soil samples with vertical depth 0-1000 cm were collected and the physical and chemical characterizations of heavy metals *e.g.*, Cu, Zn, Pb, Cr, Ni, Cd, Hg and As were analyzed. The correlation matrix was applied to evaluate the heavy metal contamination degree of soil samples. Moreover, the fractions of Pb and Zn in soils of various vertical depths were investigated. The results indicated that a certain degree of pollution had been caused in the superficial soil by heavy metals Cu, Zn, Pb, Cr, Ni, Cd, Hg and As, where the contamination levels of Pb, Zn, Cu excessed significantly. A combined pollution characterization of Cu, Zn, Pb, Cr, Ni, Hg and As was also presented. In addition, the concentrations of heavy metals in soils samples decreased exponentially with increasing the vertical depth, whereas the accumulated sub-standard depth of heavy metals Pb and As were still up to 150 cm. The content of exchangeable ion state of Pb was lowest. The pH control functions in species of Pb of soil were not significant. With the soil of vertical depth increasing, the ratios of oxidizable Pb and light acidic soluble Pb reduced rapidly and the residual Pb increased gradually. The exchangeable ion state Zn and weak acid soluble Zn significantly correlated with the soil pH values. The main fraction of Zn in light acidic soil was exchangeable ion state and the main fractions of Zn in neutral soil were reducible and oxidizable fractions.

Key Words: Abandoned vehicle dismantling area, Heavy metal contamination, Vertical distribution, Lead, Zinc.

INTRODUCTION

Numbers of abandoned vehicles in China have grown rapidly over the past 10 years. In 2011, over 4,000,000 vehicles were reported abandoned. Moreover, an estimated figure of 14,000,000 abandoned vehicles for the year 2020. As a result, the environmental problems associated with abandoned vehicles are becoming more acute. As the research reported[1-4], one waste accumulator with average 20 kg lead and 10 kg waste acid, 10 kg waste oil can be obtained after decomposing one discarded vehicle. Environmental impact investigations carried out on the end-of-life vehicle reveal that the heavy metals Pb, Cd, Zn and Cu, as well as waste oil, brake liquid and lubricants were the main contaminants. The spilling of vehicle fluids and the production of iron cuttings and machined pieces occurred during the mechanical processes such as pressing, grinding and separation into fractions of scrap iron. These inorganic heavy metals and organic oils penetrating into the soil result in the progressive soil contaminants, especially dismantled in the open without waterproof and protected against seepage and leaking[2,3].

The aim of this work is to evaluate the vertical variations in the contents of several metallic elements involved in the soil of discarded vehicles area with various vertical depth. Soil samples with vertical depth 0-1000 cm were collected and the physical and chemical characterizations of Cu, Zn, Pb, Cr, Ni, Cd, Hg and As were analyzed. The contaminant impact of these metals will be evaluated by determination of the total and various extractable contents, taking into account the characteristics of these soils.

EXPERIMENTAL

Site description: The area of study is located in the vehicle dismantling area, in the industrial zone of South China (Guangzhou, China). The prevailing climate is subtropical monsoon climate of coast of South China with high temperature and rain. The yearly precipitation is 1200-2000 mm. The main soil in the area is red clay with high water content.

Soil sampling and preparation: Soil samples were taken at depth intervals of 50 cm in the site situated to the dismantling area center. Abundant calcareous rock was present at a depth of 10 cm, which indicates the low degree of differentiation of the soil profile, according to the poor weathering conditions.

The samples were collected in self-locking polythene bags and were sealed in double bags. Use of metal tools was avoided and a plastic spatula was used for sample collection. The samples were air-dried before analysis. The dry soil sample was finely powdered by swing-grinding mill and then sieved to 100 mesh size (US standard). The pH was measured on a sample of 1:25 soil to deionized water on volume basis.

Metal fractionation: Chemical fractions of Pb and Zn in the soil were obtained by a slight modification of the method of the sequential chemical extraction scheme described by Tessier *et al.*[5]. The BCR sequential extraction procedure proposed by European Union standard bureau in 1992[6-8]. The experiment conditions for five extraction procedures was shown in Table-1.

TABLE-1
EXPERIMENT CONDITIONS FOR EXTRACTION PROCEDURE

Fraction	Extraction solution	Temp. (ºC)	Time (h)
Exchangeable cations	1 M $MgCl_2$ (pH 6)	25	1
Light acidic soluble	0.1 M AcOH (pH 4.9)	25	1
Reducible	0.5 M $NH_2OH{\cdot}HCl$ (pH 2.2)	60	1
Oxidizable	30 % (V/V) H_2O_2 + 1 M NH_4OAc (pH 2-3)	85	1
Residue	HNO_3 + H_2O_2 + HF	190	2

All glassware had been pre-cleaned and acid-washed before use. All reagents were of analytical grade and were used without further purification. Analysis blanks and duplicates were applied regularly. The experiments were done in duplicate. The results are based on triplicate analysis and the standard deviation is less than 5 %.

RESULTS AND DISCUSSION

Heavy metal contents of surface soils: The soil samples were analyzed according to the soil environmental background values of surface soil (0-20 cm) in Guangdong province, China[9] (Table-2). Soil samples showed, remarkably higher contents of Cu, Zn, Pb, Cr, Ni, Cd, Hg and As compared with the soil environmental background values in Guangdong province indicated the activities of dismantling vehicles affected the heavy metals contents of surficial soil remarkably. In addition, the average contents of Cu, Zn Hg and Pb in surface soil samples were 258, 828, 0.80 and 568 mg/kg, which were 17.9, 17.00, 10.6 and 16.5 times higher than the soil environmental background values in Guangdong province. The results accorded with the main pollution factors in abandoned vehicles dismantling area reported by Chicharro Martŷìn *et al.*[10]. The contents of Ni, Cr, As and Cd were also 4.6, 4.2, 5.9 and 7.2 times higher than the background values, though their relative concentration were not much higher. It demonstrated the soil was also polluted by Ni, Cr, As and Cd from the waste auto-parts and wastewater. This increase contamination may indicate possible mechanical infiltration and deposition of the contaminants originating from waste auto-parts, as well as scrap iron cutting, pressing and storing activities.

Heavy metal contents at various soil depth intervals: The heavy metals contents and pH values of soil samples with various depth were shown in Fig. 1. The heavy metal contents declined exponentially with increasing soil depth indicate possible adsorption and deposition of the contaminants particles on the soil [11,12]. This distribution characteristic has already been confirmed that the precipitation infiltration largely influenced on the heavy metal contaminants activities[13]. The concentrations of 114.69 mg/kg for Pb, 153.17 mg/kg for Zn, 55.88 mg/kg for Cr and 52.49 mg/kg for As in the soil samples with 150 cm depth were still remarkable, indicating vertical dispersion of contamination in soils. The metals speciation, leaching, soil physico-chemical properties influenced on heavy metals transportations, but the migration depth was limited and not over 200 cm. The Cd content in surface soil was higher than the soil environmental background values in Guangdong province. whereas The presence of Cd in surfacial soil was much lower than the environmental quality standard for soils of China (GB 15618-2008)[14].

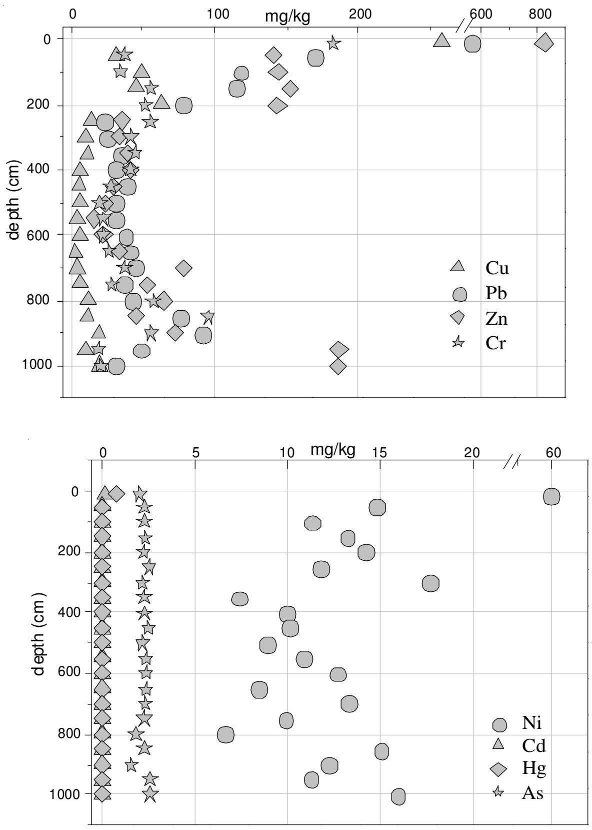

Fig. 1. Heavy metals of the soil samples in the discarded vehicles range with depth

TABLE-2
ANALYSIS OF SURFACE SOIL IN THE DISCARDED VEHICLES RANGE

Average content (mg/kg)	Cu	Ni	Pb	Cd	Cr	Zn	Hg	As
Surface soil in the discarded vehicles area	257.85	59.82	568.12	0.240	182.17	827.84	0.800	62.08
Environmental background values in Guangdong province	14.38	13.00	34.38	0.034	43.25	48.75	0.075	10.50

Pollution characteristics: The heavy metals contamination of soils were assessed based on the single factor contaminant index with the environmental quality standard for soils in China (GB 15618-2008)[14]. In this paper, data were statistically analyzed by ANOVA test using a statistical package, SPSS version 18.0. The contaminant index of soil in dismantling area contaminated by heavy metals were shown in Fig. 2 the results indicated that except Ni and Cr, other heavy metal contents were more than secondary national standards of China. It was typical heavy metal pollution in soils in the dismantling area, especially the metal Pb, Zn and Cu pollution. A tendency of a progressive decrease with depth from the dismantling site seem to verify a common origin of the metallic contamination of these soils, which is due to the dismantling activities of lead-accumulator, as well as other waste auto-parts contained Pb, Zn and Cu etc. while the soil depth higher over 50 cm, the Pb and As contaminant index were still higher 1.0, whereas other heavy metals index all lower 0.47. All index decreased lower than 0.47 while the soil depth over 200 cm, demonstrating the heavy pollution was indistinctive with the soil depth over 150 cm. It was noted that the Cr and Ni pollution had not not obviously effected on the dismantling area soil.

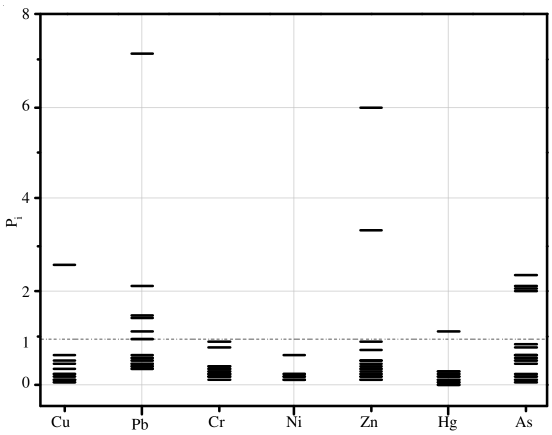

Fig. 2. Pollution index of heavy metals in soil

Significant correlation analysis of multi-metal contaminated soil: The partial correlation coefficients and significant levels between various metals were shown in Table-3 with pH and variable soil depth. It was noted that the highly significant correlation among the contents of the Cu, Zn, Pb, Cr, Ni, Cd, Hg and As determined seemed to verify a common origin of the metallic contamination of these soils, which is due to the dismantling activities of abandoned bus, truck and motorbike. The metals Pb, Zn, Cu, Hg and As containing in waste battery and discarded lamps of vehicle influenced the soil heavily.

Species of Pb and Zn: The characteristics of species Pb and Zn in soil with various depth intervals were illustrated in Fig. 3. The percentage of exchangeable species Pb changed insignificantly with the increase of soil depth and the deduction of total Pb content, whereas the contents of oxidizable and light acidic soluble species Pb decreased sharply. At the same time, the residue species Pb improved gradually. The presence of organic compounds in soil decreased with the depth may have direct and indirect effects on heavy metal mobility and reactivity. Moreover, the light acidic soil result in the decrease of the content of light acidic species Pb when the soil depth increased, because the formation of $PbCO_3$ in light acidic pH reduce the deposition of the products of $Pb_3(CO_3)_2OH_2$ and result in an decrease of soil desorption[15-17].

As shown in Fig. 3, a generalized enrichment of the superficial level (0-20 cm) and a gradual decrease with depth were observed for the target element Zn. Light acidic soluble Zn was the main species in basic pH soil, probably as a consequence of the formation of $ZnCO_3Zn_5(CO_3)_2(OH)_6$ deposition in basic soil with much free carbonate[18-20]. Moreover, the extractable contents of Zn were the main fraction in light acidic

TABLE-3
CORRELATION COEFFICIENT OF HEAVY METALS WITH THE SOIL DEPTH

	Cu	Ni	Pb	Cr	Zn	Hg	As
Cu	1	–	–	–	–	–	–
Ni	0.958	1	–	–	–	–	–
Pb	0.963	0.936	1	–	–	–	–
Cr	0.870	0.843	0.856	1	–	–	–
Zn	0.977	0.959	0.961	0.812	1	–	–
Hg	0.987	0.954	0.950	0.851	0.969	1	–
As	0.340	0.320	0.458	0.193	0.379	0.353	1

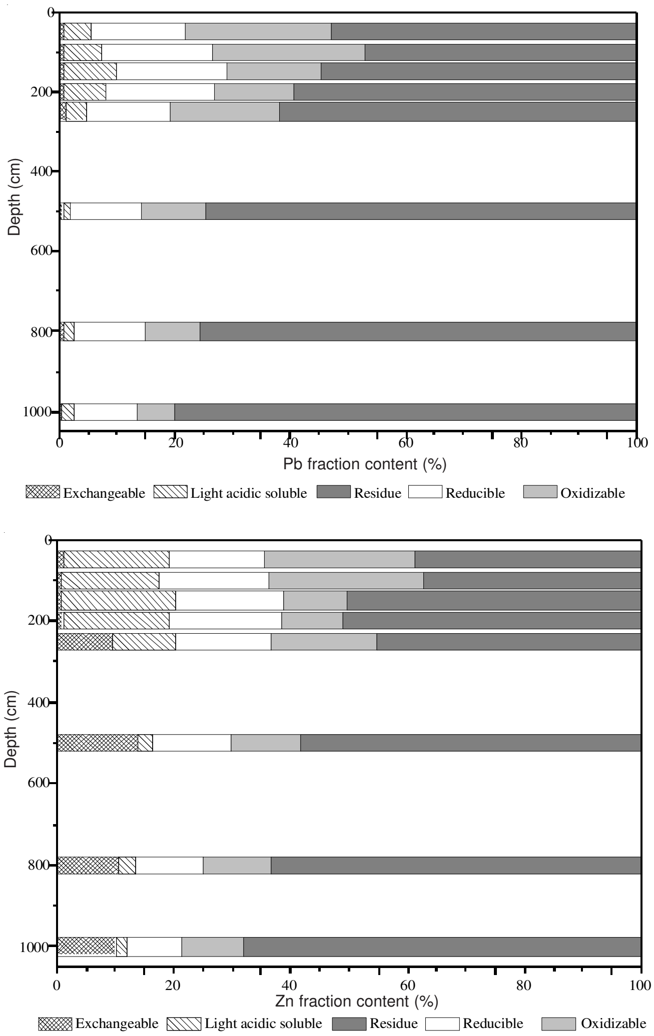

Fig. 3. Relative concentrations of Pb species with the depth of soil samples

TABLE-4
CORRELATION ANALYSIS OF HEAVY METALS WITH VARIOUS SPECIES AND DEPTH

		Depth	pH	Exchangeable cations	Light acidic soluble	Reducible	Oxidizable	Residue	
Pb	pH	-0.553	1	-0.942**	0.872**	0.549	0.250	-0.451	Zn
	Exchangeable cations	-0.566	0.033	1	-0.929**	-0.546	-0.303	0.490	
	Light acidic soluble	-0.588	0.344	0.862**	1	0.755*	0.394	-0.686*	
	Reducible	-0.841**	0.620	0.704*	0.885**	1	0.544	-0.875**	
	Oxidizable	-0.838**	0.514	0.367	0.308	0.582	1	-0.867**	
	Residue	0.887**	-0.556	-0.768*	-0.846**	-0.947**	-0.762*	1	

pH soil and the reducible and oxidizable contents of Zn were the main fraction in neutral soil. A. Chicharro Martŷìn *et al.*[10] and Barrow[21] also indicated that the formation of insoluble precipitates of heavy metal oxides and hydroxides was likely to take place under various edaphic conditions with different pH and organic content.

Table-4 illustrates the correlation analysis results of Pb and Zn with various fractions. The left bottom and right bottom present the data of Pb and Zn, respectively. No significant correlation among pH value and various contents of Pb species in the soils had been observed. The observation indicated that the pH value of soil had not remarkable influence on Pb conents with various species. However, pH values significantly influent the exchangeable and light acidic soluble Zn species in soil.

Conclusion

There was a certain degree of pollution had been caused in the superficial soil by heavy metals Cu, Zn, Pb, Cr, Ni, Cd, Hg and As, where the contamination levels of Pb, Zn, Cu excessed significantly. There was vertical dispersion of contamination in soils with 150 cm depth interval, but not over 200 cm. The contaminants in soil with multi-metals pollution characteristic mainly originate from the dismantling activities of discarded vehicles containing Cu, Ni, Pb, Cr, Zn, Hg and As in auto-parts such as waste battery and lamps.

The presence of organic compounds in soil decreased with the depth may have direct and indirect effects on heavy metal mobility and reactivity. The percentage of exchangeable species Pb changed insignificantly with the increase of soil depth and the deduction of total Pb content, whereas the contents of oxidizable and light acidic soluble species Pb decreased sharply. At the same time, the residue species Pb improved gradually. Light acidic soluble Zn was the main species in basic pH soil, the extractable contents of Zn were the main fraction in light acidic pH soil and the reducible and oxidizable fractions of Zn were the main contents in neutral soil.

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