The distribution characteristics and the speciation of heavy metals pollutants in soil along roadway in JiaoKe, Jiaozuo city, China

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The distribution characteristics and the speciation of heavy metals pollutants in soil along roadway in JiaoKe，Jiaozuo city, China

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Abstract: The heavy metals pollution in farm soil around the transportation skeleton line in Jiaoke was investigated.14 soil samples were collected and treated with HNO_3−HF−$HCLO_4$,then the contents of Cd、Cr、Cu、Ni、Pb 、Zn and As were determined by ICP-MS and assessed systematically, forms of the heavy metals were analyzed by Tessier method. The results indicted that the soil belonged to polymetalic compound pollution in which As、Cd and Pb were the most serious pollutants. The pollution was the heaviest in farm soil that 15m apart from the transportation line, with Nemerow index 6.1465. We found that the Nemerow index reduced with the increase of the distance. Forms of the heavy metals showed: the valid state percentage of heavy metal in soil followed the order of Pb＞Ni＞Cr＞Cu＞Cd＞Zn＞As. The forms of Ni, Cd, Zn and Pb in farm soil showed: residual fraction ＞Fe-Mn oxidizable fraction＞organic fraction＞exchangeable fraction＞acid extractable fraction, The forms of Cu and As in farm soil showed: residual fraction＞organic fraction＞Fe-Mn oxidizable fraction＞exchangeable fraction＞acid extractable fraction ; The forms of Cr in farm soil showed: residual fraction＞Fe-Mn oxidizable fraction＞organic fraction＞acid extractable fraction＞exchangeable fraction. The higher valid state and lower residual fraction percentage of Pb in soil implied that it should be paid attention to potential effects of heavy metals on regional ecosystem.

Key words: farm soil; heavy metal; the roadway in JiaoKe; speciation; Nemerow index

1 INTRODUCTION

As one of the most important natural resources, the soil is supporting all kinds of pollution from the human activity while improving the production forces for the humanity. The heavy metal elements may enter the soil by transportation, industrial emission, municipal administration and atmospheric subsidence. The accumulation of the heavy metal in soil is not only affecting growth of the plant and animal, making huge threat to the terricolous ecosystem and affecting the plant the output and quality[1], moreover, because the speciation of the heavy metal is different, the heavy metal may be released to the water body from the soil, so the surface water and groundwater will be polluted, finally, health of the human will harmed by food chain.

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The pollution of the soil and the agricultural product around the highway has been concerned[2]. Some scholars thought that the traffic can make pollution of the soil and the crops around the roadway, the heavy metal pollution around the highway has been reported in our country[2-4]. The influence to the farmland and the crop has not been valued in the countryside that the numbers of vehicles are relatively small. Jiaoke roadway is the throat to outward transport of the coal of Sanxi, by the development of road transportation in JiaoKe, which makes the heavy metal pollution quite clear, but the research of the pollution and speciation of heavy metal is still less. So, this article chooses the topsoil around the roadway in Qinyang as the object, and make analysis to the distribution characteristics and the speciation of Cd, Cr, Cu, Ni, Pb, Zn and As in soil along roadway, and grasp the environmental quality to prevent the soil pollution.

2 MATERIALS AND METHODS

2.1 sampling site description

Soil sample came from farm around the transportation skeleton line in Jiaoke, sampling cross section is vertical to the roadway, which is wide and flat, we layed sampling site away from the roadbed 5, 10, 15, 25, 35, 50, 75, 100, 150m in sampling cross section, comparison spot is away from the roadbed 500m in the north of sampling cross section, which had not pollutant source, the type and use way of soil are completely consistent with the monitoring point.

2.2 sample preparation

After the sample were air dried at room temperature, the samples were crushed to pass 1mm sieve, homogenized and stored in plastic bags prior to laboratory analysis.

The digesting procedure for the soil samples was as follows. A 0.5g pretreated sample was heated with 10ml HCl in a PTFE pot on the electrothermal plate until the final volume became 5ml, then 15 ml HF and 5 ml $HClO_4$ were added continuously heated to yellow-white pasty, after cooling down. 10ml HNO_3 and heated on the electrothermal plate. The digested sample was then poured into a 50ml volumetric flask and subsequently diluted to the mark with distilled water.

The speciation of the heavy metals were analyzed by Tessier sequential extraction.

The samples were determined by ICP-MS. The detection limits of Cd, Cr, Cu, Ni, Pb, Zn and As were 0.005, 0.074, 0.071, 0.04, 0.009, 0.052 and 0.367 ppb, respectively.

2.3 evaluation method

2.3.1 evaluation method of single factor index of pollution

Single factor index $(Pi) = Ci / Si$

Where

Pi=single factor index of i heavy metal in sample

Ci=the concentration of i heavy meatal in sample

Si=the limit values according to standard for soil

2.3.2 evaluation method of integrated index of pollution

The soil generally is been polluted by many kinds of heavy metals, so, the evaluation of soil PN pollution should be made by integrated index. There are many kinds of integrated index, Nemerow index generally is adopted.

$$PN = \sqrt{\left[\left(\max Pi \right)^2 + \left(\overline{Pi} \right)^2 \right] \Big/ 2}$$

Where

PN =integrated index of soil pollution

$\max Pi$ =the most single factor index of pollution

$\overline{Pi}$ =the arithmetic average of all single factor index of pollution

The classification standard for the soil studied(Table 1)

Table 1 The classification standard for the soil studied

Index of pollution	Classification	The standard of pollution	Polluted level
PN≤0.7	1	Safe	Clean
0.7<PN≤1	2	Warning line	Still clean
1<PN≤2	3	Light pollution	Light polluted
2<PN≤3	4	Polluted	Polluted
PN>3	5	Heavy pollution	Heavy polluted

Table 2 Heavy metal assessment standard for soil

Environment quality specification								
Heavy metals	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
pH<6.5	40	0.3	150	50	0.3	40	250	200
6.5<pH<7.5	30	0.3	200	100	0.5	50	300	250
pH>7.5	25	0.6	250	200	1.0	60	350	300

Table 3 Heavy metal concentrations in soils of farm

Elements	Distance of the sampling sites from the road way edge/m									
	5	10	15	25	35	50	75	100	150	350
Cu	34.132	34.357	35.478	34.2665	34.2665	36.342	35.1456	39.783	38.792	35.324
Pb	38.0123	41.1478	53.6423	34.0695	38.1789	24.531	23.0423	21.1476	20.1443	14.378
Cr	57.774	58.893	58.891	58.893	59.642	59.425	48.321	44.478	30.057	27.341
Ni	31.678	36.899	34.631	30.7775	26.521	24.829	23.667	22.145	20.565	19.428
Cd	1.1324	1.1678	1.2713	1.1495	1.1321	1.087	0.9891	0.8307	0.7812	0.3456
As	203.17	205.32	212.31	205.74	176.54	154.31	120.78	108.15	90.5	46.78
Zn	305.728	345.98	367.95	337.942	324.15	305.17	300.478	302.561	301.756	284.356

Table 4 Heavy metal assessments in soils of farm

Distance of the sampling sites from the way edge (m)	Single index of pollution							Integrated Index of pollution	Pollution level
	Cu	Pb	Cr	Ni	Cd	As	Zn		
5	0.17066	0.108607	0.231096	0.527967	1.887333	8.1268	1.019093	5.874454	Heavy pollution
10	0.171785	0.117565	0.235572	0.614983	1.946333	8.2128	1.153267	5.941976	Heavy pollution
15	0.17739	0.153264	0.235564	0.577183	2.118833	8.4924	1.2265	6.146542	Heavy pollution
25	0.171332	0.097341	0.235572	0.512958	1.915833	8.2296	1.126473	5.950143	Heavy pollution
35	0.171332	0.109083	0.238568	0.442017	1.886833	7.0616	1.0805	5.115225	Heavy pollution
50	0.18171	0.070089	0.2377	0.413817	1.811667	6.1724	1.017233	4.478306	Heavy pollution
75	0.175728	0.065835	0.193284	0.39445	1.6485	4.8312	1.001593	4.279151	Heavy pollution
100	0.198915	0.060422	0.177912	0.369083	1.3845	4.326	1.008537	3.151985	Heavy pollution
150	0.19396	0.057555	0.120228	0.34275	1.302	3.62	1.005853	2.646207	pollution
350	0.17662	0.04108	0.109364	0.3238	0.576	1.8712	0.947853	1.384821	Light pollution

2.4 evaluation standard

The land around the transportation skeleton line is farm, which belongs to type Ⅱ Kind of soil application function, therefore the secondary standard of “environment Quality specification" (GB15618-95)(Table 2),was adopted to classify the Nemerow index of pollution to assess.

3 RESULTS AND DISCUSSION

The digested soil sample was be measured by ICP-MS, and analyzed with software. Heavy metal concentrations and assessments in soils of farm around the roadway are shown in Table 3 and Table 4. Pollution levels of Cd，Cr，Cu，Ni，Pb，Zn and As in the soil are listed in Table 4. The results indicted that the soil belongs to polymetalic compound pollution in which As, Cd and Pb are the most serious pollutants. The pollution level away from the transportation skeleton line 0-100m belongs to heavy pollution, all Nemerow indexes are more than 3, and integrated index and the Nemerow index increased firstly then reduced with the increase of the distance. The pollution was the heaviest in farm soil that 15m apart from the transportation line, with Nemerow index 6.1465. Pollution levels of Cu，Pb，Cr and Ni is safe. Pollution level of Cd away from the way edge is polluted. Pollution levels of Cd in other sampling site are light polluted. Pollution levels of As in all sampling site are heavily polluted. Pollution levels of Zn in all sampling site are lightly polluted. From Table 4, we found that the concentrations of Cu，Pb，Cr and Ni reduced from the way edge 50m, the four heavy metals may come from tyre wear, coal ore losing and vehicle exhaust. But the concentrations of Cu has not obvious drop from the way edge, and the mean value is only 1.487 times than the soil environment background（24.1), so the pollution level of Cu is low, which is because of high environment background value. The pollution levels of Zn are light polluted, the mean value is 4.519 times than the soil environment background level, which may come from coal ore losing and tyre wear. Moreover, single index of As and Cd is high , which may be correlative with the use of farm chemical and sewage farming.

Table5 the chemical speciation of some Heavy Metals in topsoil that 15m apart from the transportation line

speciation		Heavy metals						
		Cu	Pb	Cr	Ni	Cd	As	Zn
exchangeable fraction	concentrations(mg/kg)	0.8035	0	1.4115	0.9145	0.082	0.3455	5.105
	%	2.3091	0	2.3967	2.9713	7.1335	0.1679	1.5106
acid extractable fraction	concentrations(mg/kg)	0.5255	0	2.923	0.7245	0.0065	0.1765	3.302
	%	1.5102	0	4.9632	2.354	0.5655	0.0858	0.9771
Fe-Mn oxidizable fraction	concentrations(mg/kg)	3.0925	12.865	8.850	6.8	0.1745	0.887	31.265
	%	8.8874	37.761	15.0273	22.094	15.1805	0.4311	9.2516
organic fraction	concentrations(mg/kg)	5.03	4.1845	4.1585	2.9685	0.043	1.281	17.27
	%	14.4555	12.2822	7.0611	9.645	3.7408	0.6226	5.1103
residual fraction	concentrations(mg/kg)	25.345	17.02	41.55	19.37	0.8435	203.05	281
	%	72.8378	49.9567	70.5517	62.9356	73.3797	98.6925	83.1504

According to the tessier sequential extraction, we found that five chemical speciations of Cd，Cr，Cu，Ni，Pb，Zn and As（Table 5）.

Exchangeable fraction is most active, which is easily be absorbed, used, leaching loss and moved. The concentration of exchangeable fraction of the heavy metal is lower than other fraction, form of exchangeable fraction percentage of the total quantity in soil followed the order of Cd(7.1335%) ＞ Ni(2.9713%) ＞ Cr(2.3967%) ＞ Cu(2.3091%) ＞ Zn(1.5106%)＞As(0.1679%)＞Pb(ND)；

Acid extractable fraction of the heavy metal is sensitive to soil environment especially pH, when pH dropped, the heavy metal is easily be released to the environment. On the contrary, the elevatory pH is favorable to the carbonate and co-precipitation in carbonate minerals[5]. Form of acid extractable fraction percentage of the total quantity in soil followed the order of Cr (4.9632%)＞Ni(2.354%)＞Cu (1.5102%)＞ Zn (0.9771%) ＞ Cd(0.5655%) ＞ As (0.0858%) ＞ Pb(ND).

Fe-Mn oxidizable fraction is bound by mineral or by fine particle existence, specific surface of the high-activity Fe-Mn oxidizable is large, which easily absorb positive ion and negative ion or form or co-precipitation. pH and REDOX of soil environment are influential to Fe-Mn oxidizable fraction. High pH and REDOX is favorable to Fe-Mn oxidizable fraction[5]. The concentration of Fe-Mn oxidizable fraction of Pb, Ni, Cd, Cr, Zn and Cu are high, the percentage of form of Fe-Mn oxidizable fraction in the total quantity in soil follows the order of Pb (37.761%) ＞ Ni(22.094%) ＞ Cd(15.1805%) ＞ Cr (15.0273%) ＞ Zn (9.2516%) ＞ Cu (8.8874%) ＞ As(0.4311%). The proportion of Pb, Ni, Cd, Cr are more than 10%, which explained that the four elements are more active.

The percentage of form of organic fraction in the total quantity in soil followed the order of Cu (14.4555%) ＞ Pb (12.2822%) ＞ Ni (9.645%) ＞ Cr (7.0611%) ＞ Zn(5.1103%) ＞ Cd (3.7408%) ＞ As(0.6226%).The concentration of organic fraction of Cu is most highest, because Cu is easily combined with organic matter like rock debris and mineral particle and is easily released to soil solution. There are all kinds of organic matter, like animal and plant remains、the humus and the mineral particle package which has the ability to chelate heavy metal ion, and can adhere to the surface of the mineral particle, so surface nature of mineral particle was been changed to increase the ability to absorb heavy metal[5].

The concentration of residual fraction of Cd, Cr, Cu, Ni, Pb, Zn and As are the highest, the percentage of form of residual fraction in the total quantity in soil followed the order of As (98.6925%)＞Zn (83.1504%) ＞Cd (73.3797%)＞Cu (72.8378%)＞Cr(70.5517%) ＞Ni(62.9356%)＞Pb(49.956%), the residual fraction of heavy metal primarily come from soil mineral and is stable, which is not easily be released under the natural environment and not easily be absorbed by the plant, so that the impact to the food chain is little in the whole soil-plant system[5].

Forms of the heavy metals showed: the valid state percentage of heavy metal in soil followed the order of Pb＞Ni＞Cr＞Cu＞Cd＞Zn＞As. The forms of Ni, Cd, Zn and Pb in farm soil showed: residual fraction＞ Fe-Mn oxidizable fraction ＞ organic fraction ＞ exchangeable fraction＞acid extractable fraction, The forms of Cu and As in farm soil showed: residual fraction＞organic fraction＞Fe-Mn oxidizable fraction ＞exchangeable fraction＞acid extractable fraction ; The forms of Cr in farm soil showed: residual fraction ＞Fe-Mn oxidizable fraction＞organic fraction＞acid extractable fraction＞ exchangeable fraction. The topsoil environment of Jiaoke is oxydic, so, organic fraction is easily absorbed by the plant. The higher valid state and lower residual fraction percentage of Pb in soil implied that it should be paid attention to potential effects of heavy metals on regional ecosystem.

4 CONCLUSIONS

4.1 The results indicted that the soil belonged to polymetalic compound pollution in which As、Cd and Pb were the most serious pollutants. The pollution was the heaviest in farm soil that 15m apart from the transportation line, with Nemerow index 6.1465.

4.2 Forms of the heavy metals showed: the valid state percentage of heavy metal in soil followed the order of Pb＞Ni＞Cr＞Cu＞Cd＞Zn＞As.

The forms of Ni, Cd, Zn and Pb in farm soil showed: residual fraction＞Fe-Mn oxidizable fraction＞organic fraction ＞ exchangeable fraction ＞ acid extractable fraction, The forms of Cu and As in farm soil showed: residual fraction＞organic fraction＞Fe-Mn oxidizable fraction ＞ exchangeable fraction ＞ acid extractable fraction ; The forms of Cr in farm soil showed: residual fraction＞Fe-Mn oxidizable fraction＞organic fraction ＞acid extractable fraction＞ exchangeable fraction. The higher valid state and lower residual fraction percentage of Pb in soil implied that it should be paid attention to potential effects of heavy metals on regional ecosystem.

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