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Effect of Biochar on Heavy Metal Speciation of Paddy Soil

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Abstract Biochar has great advantages and potentials on soil amendment and polluted soil remediation. In order to explore these applications, a pot experiment was carried out to research the effect of biochar on the heavy metal speciation in paddy soil and the heavy metal accumulation of paddy rice from Chengdu plain, Sichuan Province. The experimental results show that wine lees-derived biochar can efficiently increase soil pH, decrease the contents of soil exchangeable heavy metals, and promote heavy metal transformation to residual fraction. Moreover, application of biochar can reduce the accumulation of heavy metals in paddy plant, decrease the migration ability of heavy metals to the aboveground part of the plant, and consequently cut down contents of heavy metals in rice. When biochar dosage was 0.5 % in weight, the contents of soil exchangeable Cr, Ni, Cu, Pb, Zn, and Cd decreased 18.8, 29.6, 26.3, 23.0, 23.01, and 48.14 %, respectively, which all significantly differed from CK ($P<0.05$), and the contents of heavy metals in plant roots, stems, leaves, rice husk, and rice all decreased accordingly, among which Zn, Cd, and Pb decreased 10.96, 8.89, and 8.33 % respectively. When biochar dosage increased to 1 %, heavy metal contents in roots, stems, leaves, rice husk, and rice decreased further. Therefore, wine lees-derived biochar shows a great potential in remediation of heavy-metal-polluted soil, and this work provides theoretical basis for restoring heavy-metal-polluted soil using biochar.

Keywords Biochar · Heavy metal speciation · Paddy rice

1 Introduction

With economic development, environmental problems caused by human activities are increasingly serious. Among them, soil heavy metal pollution is of wide concern due to its risk on soil and human health. Soil heavy metal pollution can not only cause the decrease of soil fertility and grain yield and pollute surface water and underground water but also threaten human health through the food chain (Chen et al. 2012; Fellet et al. 2014). As a result, the amendment and remediation of heavy-metal-contaminated soil have been a research hotspot in agriculture and environment (Mani and Kumar, 2014). In China, the contradiction between population and farmland resources is increasingly acute, so it is urgent to solve the safety of agricultural production-related problems on mild and moderate polluted soils.

Due to large surface area and internal pores, biochar can not only absorb and fix soil contaminates but also improve soil physicochemical properties, reduce nutrients losses, and promote plant growth (Singh et al. 2010;

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Liu et al. 2014; Xu et al. 2013; Gao et al. 2013; Fellet et al. 2014). Biochar has been one of the research hotspots in environmental and agricultural science area (Suguihiro et al. 2013). There are important theoretical and practical significances to research the effect of biochar restoration on heavy metals in farmland soils because it can broaden the treatment method of heavy-metal-polluted soil and improve the treatment effect of heavy metal pollution. In this aspect, some researchers have implemented related work and remarkable results have been obtained, such as the work of Suguihiro et al. (2013). The effect of biochar restoration on polluted soil has a close relation to the properties of biochar and polluted soil (Liu et al. 2009; Tsai et al. 2015). But there are significant differences between different soils using different biochars.

Chengdu plain is located in the southwest of China, and it is one of the important production areas of grain and oil crops in this country. Related research showed that soil heavy metal pollution became increasingly serious in Chengdu plain due to intensive industrial production and life activities (Qin et al. 2013). In the recent 20 years, cadmium content in soil has increased by one to two times in some areas (such as Guanghan, Xindu, and Qionglai) and lead content has increased by 1.1–3.3 times in some areas (such as Xinjin, Deyang, Guanghan, and Xindu) of Chengdu plain (Li et al. 2014). Cadmium content in the farmland soil of Chongzhou has exceeded the second-level standard of Chinese soil environmental quality standard; 30.43 % of sampling sites of Chengdu plain exceeded the standard (Li et al. 2014). Therefore, it is urgent to carry out steps of soil heavy metal remediation in Chengdu plain (Yang et al. 2014). But so far, we have found few researches on the restoration of heavy-metal-contaminated soil in Chengdu plain, especially restoration by biochar. This study aims to explore the effect of wine lees-derived biochar restoration on heavy metal in paddy soil and the accumulation of heavy metal in rice so as to provide technical support for heavy metal risk reduction.

2 Materials and Methods

2.1 Experimental Materials

Experimental soil was collected from heavy-metal-polluted paddy soil near an industry-concentrating area in Chengdu plain, with a collection depth of 0–20 cm. It has been polluted by heavy metals, and the contents of Cr, Ni, Cu, Zn, Cd, and Pb in the soil were 114.28, 25.95, 38.54, 1578.67, 13.15, and 87.28 mg/kg, respectively. Jinyou 182 was applied as the experimental paddy rice.

Biochar was prepared by pyrolysis under oxygen-limited condition (Suguihiro et al. 2013). The raw material coming from a wine factory in Qionglai, Sichuan Province, was wine lees, which is made from sorghum, rice, glutinous rice, wheat, and corn, with a mass ratio of 23:37:19:17:4. Air-dried wine lees was further dried in an oven at 80 °C and crushed into a particle size of 100 meshes then weighed and compacted in crucibles and then covered with the lids. Next, these samples were pyrolyzed in a muffle furnace (the furnace heated up at 5 °C/min to 600 °C and maintained for 2 h) then cooled down at room temperature. Finally, wine lees-derived biochar was obtained (remarked as C600 hereafter).

2.2 Experimental Methods

Soil sample of 15 kg was firstly weighed in a plastic bucket then mass ratios of 0.5 % (A) and 1 % (B) wine lees-derived biochar were added separately, then water was supplemented to reach a field moisture of 75 %, and finally the mixed sample was matured for 4 weeks in order to use. During the whole growth period of rice, the water level was maintained at a depth of 3–5 cm after rice seedling transplanting. The treatment without biochar was regarded as the control (CK).

After the paddy rice was ripe, the soil and plant samples were collected. The soil samples were air-dried and crushed before heavy metal speciation determination. The plant samples were separated into roots, stems, and leaves, cleaned by distilled water, rinsed with ultrapure water, dried to constant weight in an oven at 80 °C, crushed, and finally meshed.

2.3 Items for Determination

Community Bureau of Reference (BCR) sequential extraction method was used to extract the speciation of heavy metals in soil, and the kinds of speciation were separated into exchangeable, reducible, oxidizable, and residual fractions separately (Wali et al. 2015). The extracted suspensions were filtered by 0.45-μm membranes, and heavy metal contents were determined by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) (Agilent 7700x, US). The plant samples were digested by the mixed acids of HF, $HClO_4$, and HNO_3

then filtered by 0.45-μm membranes for ICP-MS measurement.

3 Results and Discussions

3.1 The Change of Soil pH

The effect of biochar on soil pH was showed in Fig. 1. Soil pH values of the treatments with biochar were significantly higher than that of CK ($P<0.05$). The experimental results show that soil pH increases with the raising biochar dosage. It means that biochar application can effectively enhance soil pH. The reason is rooted in biochar's alkalinity, which can neutralize some acidic materials in soil. And this result is consistent with previous ones (Uchimiya et al. 2010; Ahmad et al. 2012).

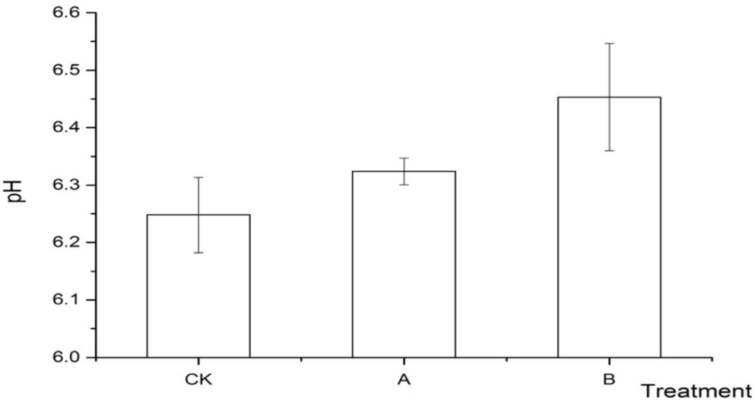
3.2 The Effect of Biochar on Soil Heavy Metal Speciation

As showed in Fig. 2, the main fraction of Cr, Cu, Zn, and Pb in CK soil was the reducible, accounting for 74.13, 53.81, 43.40, and 75.14 % of the total amount, respectively, and exchangeable Cr, Cu, Zn, and Pb only shared 0.59, 9.75, 29.09, and 4.97 %, respectively. The main speciation of Ni in CK soil was the residual, accounting for 65.01 % of the total amount. The main speciation of Cd in CK soil was the exchangeable, accounting for 60.06 % of the total amount. Compared with CK, heavy metal speciation had changed obviously. The exchangeable Cr, Ni, Cu, and Pb decreased by 19.59, 10.19, 18.66, and 17.84 %, respectively, from 0.50, 1.68, 25.01, and 5.20 mg/kg to 0.40, 1.51, 20.34, and 4.27 mg/kg, respectively, which were significantly different from CK ($P<0.05$). The reducible Cr, Ni, Cu, Zn, and Pb of the treatment with 0.5 % biochar declined obviously while the oxidizable and the residual fractions increased obviously. Compared with CK, residual Cr, Ni, Cu, Zn, Cd, and Pb increased by 2.71, 0.56, 1.41, 2.19, and 1.39 times, reaching an extremely significant level ($P<0.01$).

These results reflect that the exchangeable and the reducible Cr, Ni, Cu, Zn, Cd, and Pb in soil decrease, and the residual of these metals increases with the increase of biochar dosage, which is consistent with the research of Xu et al. (2014). Therefore, wine lees-derived biochar can decrease the contents of exchangeable heavy metals in paddy soil and promote the conversion of exchangeable speciation to residual speciation, resulting in a reduction of heavy metal migration in soil.

Heavy metals exist in several speciations after entering into the soil, and the migration ability and biological toxicity of different speciations are significantly different (Sardar et al. 2013). The speciations of soil heavy metals were separated into exchangeable, reducible, oxidizable, and residual fractions according to BCR sequential extraction method (Wali et al. 2015). Exchangeable fraction can be directly absorbed by living things because of its strong migration, and it is considered as available fraction; reducible and oxidizable fractions can transform to acid soluble species which can be utilized by living things under a certain condition, so it is considered as slow release fractions; and the residual is fixed in soil lattice, and it is hardly utilized by living things, so it is considered as and invalid fraction (Chen 2005). The more the exchangeable fraction exists, the more active the soil heavy metal is and then the higher

Fig. 1 The effect of biochar on soil pH



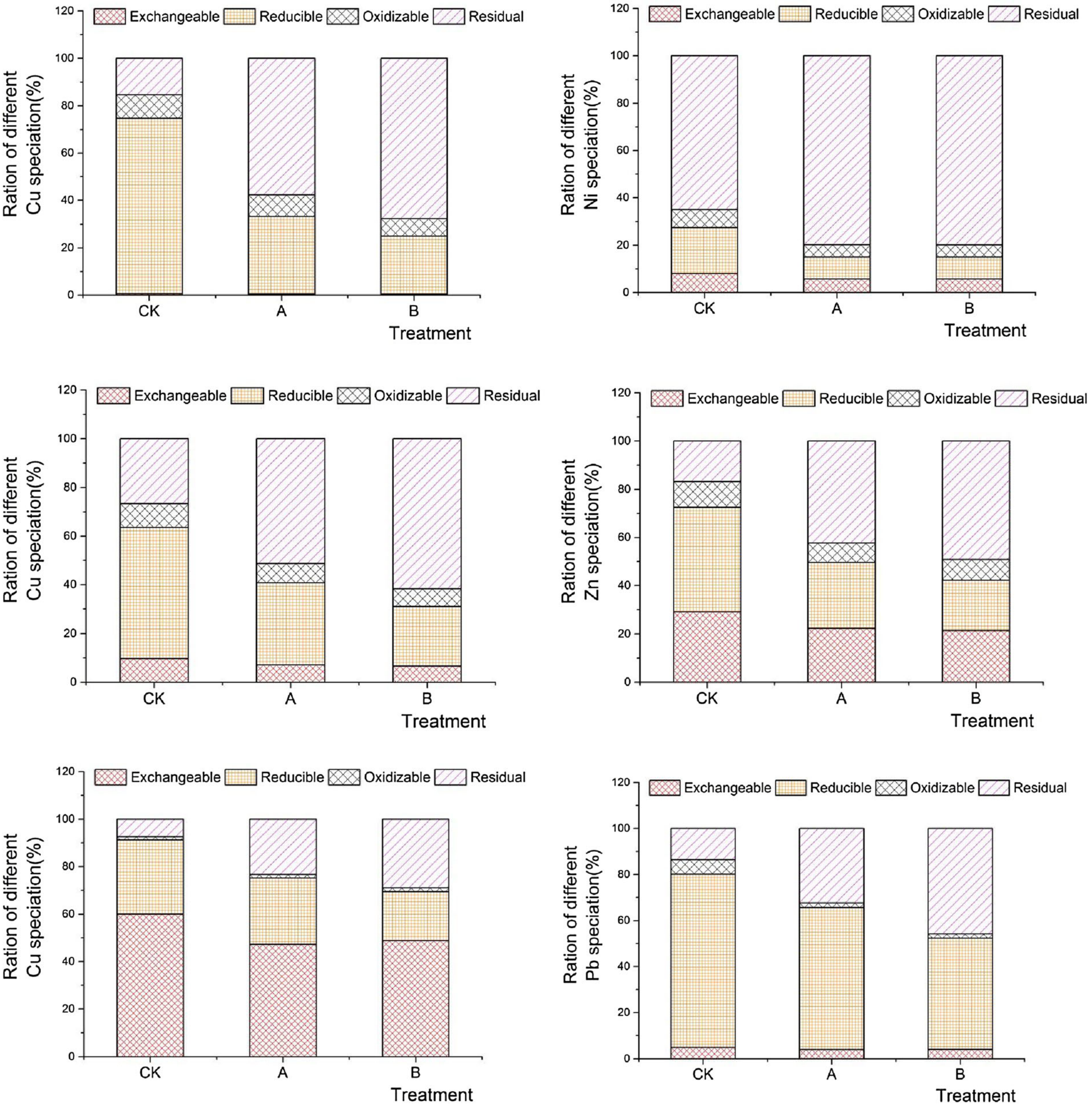


Fig. 2 Percentages of heavy metals in different speciations

the bio-availability of heavy metal is (O'Dell et al. 2007). In contrast, the more the reducible, oxidizable, and residual fractions exist, the lower the bio-availability is for the heavy metal (Reeves and Baker 2000).

The experimental results of this study showed that the exchangeable Cr, Ni, Cu, Zn, Cd, and Pb in soil decreased obviously, and the residual of these metals increased obviously after biochar application. This is because biochar application can change soil physical and chemical properties and then change the existing speciation of soil heavy metals (Yang et al. 2014). It can influence the migration, transformation, and biological toxicity through adsorption property of biochar (Chen et al. 2012). Especially, this is mainly attributed to its influence on soil pH so that biochar can promote the conversion of exchangeable fraction to residual fraction (Ahmad et al. 2012). Previous research also pointed out that soil pH could decide the dissolution-precipitation, adsorption-desorption, and other reaction progresses of soil mineral (Martincz and Motto, 2000), and the effect of pH on solubility and retention of soil mineral was greater than any other single factor (Uchimiya et al. 2010; Ahmad et al. 2012).

Biochar application can increase soil pH and the content of organic matters, which promotes exchangeable heavy metal transformation to reducible, oxidizable, and residual fractions (Xu et al. 2012). It is mainly because parts of soil acidic materials are neutralized by biochar and alkaline groups in soil solution, such as OH-, SiO_3^{2-} and CO_3^{2-}, gradually increase (Yang et al. 2015), which promotes the formation of hydroxide, silicate, and carbonate of insoluble heavy metals, and then reduce the contents of exchangeable heavy metals (Loganathan et al. 2012). Meanwhile, soil clay minerals, hydrated oxide, and a negative charge on the surface of soil organic matters increase with the increase of soil pH, so it enhances the electric adsorption capacity of heavy metal ions in soil (Salt et al. 1995; Reeves and Baker 2000). With the increase of soil pH, positive ions of soil heavy metals gradually transform to hydroxyl, and this enhances the combination of heavy metal ions and soil adsorption sites (Hou et al. 2011), so heavy metal ions can be absorbed and fixed by soil colloid. In addition, biochar directly takes part in the fixation of heavy metal ions, i.e., the oxygenic functional groups, such as carboxyl and phenol hydroxyl, combine with the surface of biochar, and this is helpful to form insoluble clathrate with heavy metal ions through chelation and complexation (Caporale et al. 2014). Another way, biochar can increase the contents of soil organic matters and soil CEC and then increase complexation of soil heavy metal ions, so it can also decrease the contents of exchangeable heavy metal (Abdel-Fattah et al. 2015). Cao et al. (2009) found that biochar could induce Pb to form $Pb_3(CO_3)_2(OH)_2$ and β-$Pb_9(PO_4)_6$ precipitation under conditions that are rich in phosphates and carbonates, respectively; meanwhile, phosphate ions carried by biochar could directly absorb heavy metal ions in soil, so it could also decrease its biological activity.

In addition, application of biochar will have significant impact on the structure of soil microbial community and then it will influence the change of soil heavy metal speciation (Huang et al. 2014). The huge surface area and porosity of biochar has great advantage on the growth of microorganisms (Bu and Xue 2014). The porosity structure of biochar can absorb a lot of organic matter, gases, soil nutrients, soil moisture, etc., which can afford a better growth environment for microorganisms (Lehmann et al. 2006). On the other hand, biochar can be combined with soil, change soil aeration structure, promote the formation of soil aggregates, and increase soil temperature (Grossman et al. 2010), so that it can promote the growth and reproduction of some soil microorganisms, especially soil *arbuscular mycorrhizae* (*AM*) *and exogenous mycorrhizae* (*EM*). Soil AM and EM can combine with heavy metals (heavy metals are stored in different parts of cells, bound to extracellular matrixes, or formed as clathrate, precipitate, and crystal through ion exchange in the progress of microorganism metabolism), which inhibit the migration of heavy metal from roots to the top parts of a plant, decreasing the toxic effect of heavy metals on plants (Gaur and Adholeya 2004; Rufyikiri et al. 2004). Additionally, biochar can significantly increase the activities of soil urease, catalase, and acid phosphatase, which can induce chelation with heavy metal ions and decrease the activities of heavy metals (Lehmann et al. 2011; Xu et al. 2014).

It is concluded that biochar application can improve soil aeration structure, promote the formation of soil aggregates, increase microorganisms metabolism, and increase soil pH and the content of organic matters, which promotes exchangeable heavy metals to transform to residual fraction and decrease the migration ability of soil heavy metals.

3.3 The Effect of Biochar on Soil Heavy Metal Availability

The effect of biochar application on accumulation of heavy metals in rice is shown in Table 1. Heavy metal contents in rice, aboveground part and underground part of the paddy plant, have changed obviously after application of biochar to paddy soil. When the biochar dosage is 0.5 % (A), heavy metal contents in paddy roots all decrease, with Cr, Cu, Zn, Cd, and Pb decreasing by 16.12, 19.53, 10.92, 21.97, 13.83 %, respectively, and they all have significant differences from CK ($P<0.05$). The contents of all heavy metals except Ni in plant stems decrease over 10 %. Compared with CK, the contents of Cr, Ni, Cu, Zn, Cd, and Pb in rice with 0.5 % biochar application have decreased; therein, the contents of Zn, Cd, and Pb have decreased by 10.96, 8.89, and 8.33 %, respectively. These experimental results also show that heavy metal contents in roots, stems, leaves, rice husk, and rice decrease faster when biochar dosage increases to 1 %; meanwhile, the contents of Cr,

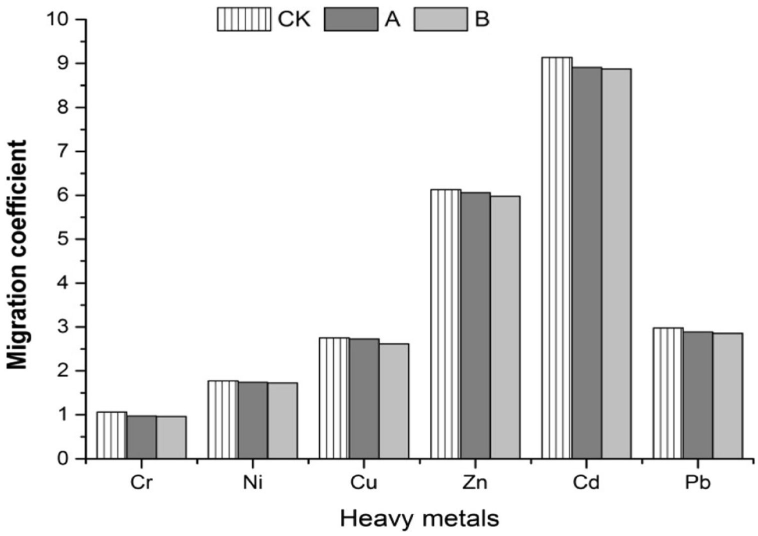
Table 1 Heavy metal contents in each part of plants (mg/kg)

Plant part	Treatment	Cr	Ni	Cu	Zn	Cd	Pb
Root	CK	21.95±1.02	21.72±2.21	32.47±2.91	39.2±1.43	18.71±2.01	14.46±1.18
	A	18.41±0.92	20.63±1.83	26.13±2.42	34.92±2.16	14.6±1.32	12.46±1.08
	B	14.49±1.13	18.92±2.01	22.26±2.01	30.18±2.15	12.55±1.02	8.11±2.01
Stem	CK	29.85±2.01	52.31±2.77	119.77±3.49	325.72±4.21	234.13±3.29	57.35±3.05
	A	20.18±3.01	48.93±3.71	95.71±2.37	288.53±3.89	178.67±65.13	48.01±2.14
	B	17.53±2.42	44.83±2.95	78.26±2.11	248.42±4.07	153.99±5.19	30.94±2.29
Leaf	CK	8.81±0.02	3.57±0.07	12.84±0.47	23.72±0.29	8.77±0.19	9.21±0.77
	A	7.64±0.21	3.24±0.03	11.85±0.29	19.21±0.31	7.76±0.24	7.74±0.38
	B	7.59±0.03	3.02±0.07	11.05±0.47	14.23±0.58	7.43±0.08	6.03±0.18
Rice husk	CK	2.06±0.18	0.84±0.02	6.69±0.31	5.24±0.22	0.64±0.06	2.03±0.28
	A	1.81±0.05	0.79±0.03.01	4.94±0.41	4.55±0.42	0.55±0.03	1.73±0.11
	B	1.45±0.02	0.77±0	4.54±0.09	4.14±0.17	0.46±0.07	1.39±0.19
Rice	CK	1.45±0.04	1.23±0.03	3.79±0.18	5.75±0.51	0.45±0.02	0.36±0.06
	A	1.42±0.03	1.20±0.06	3.53±0.21	4.82±0.17	0.41±0.08	0.33±0.03
	B	1.21±0.03	1.18±0.02	3.43±0.38	4.74±0.04	0.36±0.03	0.29±0.04

Zn, Cd, and Pb also decrease by 16.55, 16.17, 20.00, and 19.44 %, respectively, and they all have significant differences from CK ($P<0.05$); however, the contents of Ni and Cu in rice only decrease by 6.86 and 1.58 %, respectively.

The contents of Cr, Ni, Cu, Pb, Cd, and Zn in paddy plant significantly decreased after biochar was applied, and heavy metal contents in each part of plant were significantly different. Gao et al. (2013) have researched the communication of Pb in paddy plant, and their experimental results showed that the contents of Pb in each part of the paddy plant were significantly different (root>stem>leaf>rice). This paper obtained similar results that different heavy metal contents in each part of the paddy plant had significantly differences, while the trends of heavy metal contents in paddy plant with biochar application were consistent with those of CK, i.e., stem>root>leaf>rice husk>rice for Cr, Cu, Pb, and Cd and stem>root>leaf>rice>rice husk for Ni and Zn. But heavy metal contents in each part of the plant with biochar application were all lower than those of CK, and the distribution of different heavy metals in each part of the plant were more obvious. After soil heavy metals enter into root cells, one part will remain in the root, another part will enter into vessels through protoplasm flow and transport between cells, migrate to aboveground through transpiration of the plant, and accumulate in stems, leaves, and seeds, so heavy metals will redistribute in different parts after they enter the plant body (Zhong et al. 2015). The contents of heavy metals in each part of the plant are significantly different, which is mainly attributed to heavy metal type, speciation, and content (Topcuoglu, 2005). Li et al. (2014) found that heavy metals could easily accumulate in the organs of plants with strong metabolism, while they would accumulate less in nutritional organs, such as seeds or fruits. But there are significant differences between different types of heavy metals. For example, Zn and Cu are constituents of some enzymes in the plant, which can participate in the synthesis of chlorophyll, and they are essential elements for plant growth, so plants need them in their growth period. Plants will actively absorb an appropriate amount of exchangeable Zn and Cu in the soil and then transport them to the leaves (Topcuoglu, 2005). While Cd and Pb are harmful to plant growth, they will obviously affect the growth of plants after they are passively absorbed into plant roots and accumulated in nutritional organs, such as roots, stems, and leaves (Zhang et al. 2014). The experimental soil was collected from an industry-concentrating area in Chengdu plain, with high heavy metal contents, so it shows harmful influence on the growth of a plant (Qin et al. 2013). The soil structure has been improved significantly after biochar is applied (Reeves and Baker 2000; Grossman et al. 2010), and it can

Fig. 3 Migration coefficients of soil heavy metals for paddy rice



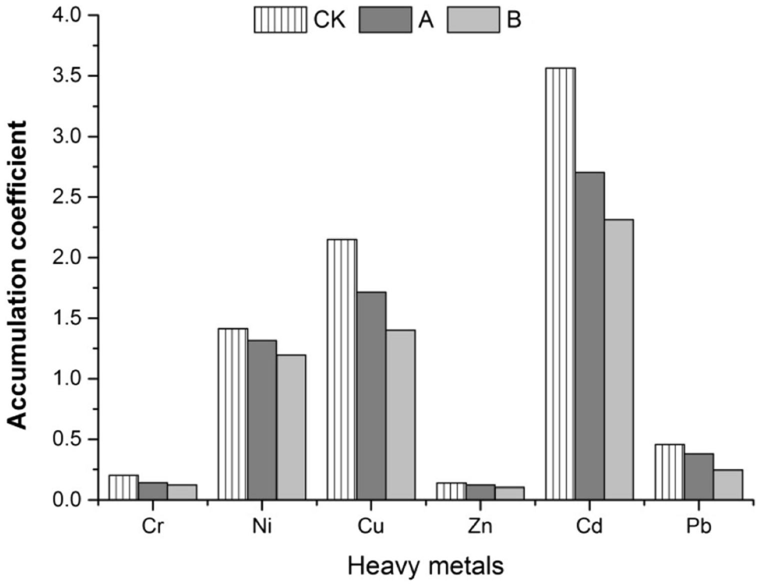
increase the soil pH and organic matter content; promote the formation of carbonate bounded form, Fe-Mn oxide form, and organic form of heavy metals (Loganathan et al. 2012); and decrease the activities of soil heavy metals (Chen et al. 2014), so it decreases the harmful effect of heavy metals on paddy plant.

It is concluded that biochar application can decrease the activities of soil heavy metals and reduce the accumulation of Cr, Ni, Cu, Pb, Cd, and Zn in paddy plants while it will not influence the migration of heavy metals in plant body.

3.4 The Effect of Biochar on Soil Heavy Metal Migration

Migration coefficient, which is used to express the migration ability of heavy metals in plants (Zhang et al. 2014), is the ratio of heavy metal content in the aboveground part of plants to those in the underground part. The bigger the migration coefficient is, the stronger the migration ability of the heavy metal is (Li et al. 2014). As illustrated in Fig. 3, migration coefficients of Cr, Ni, Cu, Zn, Cd, and Pb in paddy rice in soil range between

Fig. 4 Accumulation coefficients of soil heavy metals for paddy rice



1.06 and 9.13 for CK. When biochar was applied (treatment A and B), migration coefficients of above metals in paddy rice were gradually decreasing. The migration ability of heavy metals is closely related to biochar dosage and the categories of heavy metals. For example, when biochar dosage is 0.5 %, migration coefficients of Cr in paddy rice decrease by 8.49 % from 1.06 to 0.97, while migration coefficients of Cu decrease by 0.68 % from 2.75 to 2.73. When biochar dosage is 1 %, the migration coefficient of Cr in paddy rice decreases to 0.96, while migration coefficient of Cu decreases to 2.62.

Bioaccumulation coefficient is the ratio of certain heavy metal contents to the content of the same element in its life medium (Chen 2005). Nowadays, it is widely used to research the migration and change of heavy metals in soil-plant systems. The higher the bioaccumulation coefficient is, the stronger the plant absorption for the heavy metal is (Li et al. 2014; Lei et al. 2014). As showed in Fig. 4, biochar application can decrease the accumulation ability of Cr, Ni, Cu, Zn, Cd, and Pb in paddy rice in soil, but different dosages and different heavy metals have significant differences. When biochar dosage is 0.5 %, the accumulation ability of Cr in paddy rice decreases by 30.61 % from 0.20 to 0.16, while accumulation coefficient of Ni only decreases by 6.86 %. When biochar dosage increased to 1 %, the accumulation coefficient of Cr in paddy rice decreases by 39.28 %, while the accumulation coefficient of Ni only decreases by 15.27 %.

To sum up, wine lees-derived biochar can reduce the migration and accumulation ability of Cr, Ni, Cu, Zn, Cd, Pb, and other heavy metals in paddy rice. This is mainly because biochar application can improve soil structure; increase soil enzyme activities, pH value, and organic matter contents; promote the transformation of exchangeable metal fraction to reducible, oxidizable, and residual fractions; decrease the bioactivity of soil heavy metals; and reduce the absorption of heavy metals in paddy roots. As a result, it decreases the migration and accumulation coefficients, which is consistent with the results of Ma et al. (2015). But biochar has significantly different effects on different heavy metals, which may be attributed to the contents of heavy metals in soil, heavy metal speciation, and properties of biochar. The experimental soil was collected from an industry-concentrating area in Chengdu plain, where there were many kinds of heavy metals with high content in the soil. Meanwhile, the speciation of heavy metals has obvious differences, and heavy metal ions also have different characteristics (such as exchangeable ability of ion, hydrated ion radius, and electric quantity). All these factors, accompanied with biochar, will determin the final migration and transformation of heavy metals between plants and soil (Xu et al. 2014).

4 Conclusion

1. Biochar application can efficiently increase soil pH value; change the speciation of Cr, Ni, Cu, Zn, Cd, Pb, and other heavy metals; decrease the contents of soil exchangeable heavy metals; and increase residual fraction.
2. Biochar application can significantly decrease heavy metal contents in plant roots, stems, leaves, rice husk, and rice; weaken the accumulation ability of soil heavy metals in plant; and reduce the migration of heavy metals in plant.
3. Biochar application can decrease the contents of Cr, Ni, Cd, and Pb in rice, and heavy metal contents in rice are negatively correlated to biochar dosage.

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