The incubation experiment consisted of CK (without organic materials amendment) and 8 organic material treatments including A1, A2, S1, S2, A1+S1, A1+S2, A2+S1 and A2+S2. In which A1 and A2 represent 22.5 t/hm^2 and 45.0 t/hm^2 of fresh alfalfa amendment respectively, and S1 and S2 represent 4.5 t/hm^2 and 9.0 t/hm^2 of air-dried rice straw amendment respectively. For each treatment/control, organic material as designed was mixed with 1kg soil (oven-dry basis) thoroughly and packed into 2L plastic container, then 4 mg Cd (as $CdCl_2$) was added into soil as solution and mixed evenly. The mixture was incubated

Effect of Alfalfa (*Astragalus sinicus*) and Rice Straw Additions on Cd Fractions and Activity in Acidic Soil Under Flooded Condition

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Abstract

In China, cover crop and crop straw are widely used to improve soil fertility, and Cd is a common contaminant in arable soils. In this study, soil incubation experiment was carried out to investigate the effect of alfalfa (*Astragalus sinicus*) and/ or rice straw on Cd-fractions in acidic yellow-red soil under flooded condition. The results showed that Cd in acidic yellow-red soil was mainly distributed in residue fraction (Res-Cd) regardless of organic material addition, followed by strongly bound organic Cd (SBO-Cd) and exchangeable Cd (Exch-Cd) fraction, with a small portion being associated with carbonate bound Cd (CARB-Cd) and weakly bound organic Cd (WBO-Cd) fraction. Soil Cd fractionation changed with incubation time. SBO-Cd and Res-Cd increased and then decreased. Exch-Cd and WBO-Cd increased but the iron and manganese oxide bound Cd (Ox-Cd) decreased significantly at 120 d of incubation, as compared with 40 d or 80 d of incubation. However, CARB-Cd had little change within 120 d of incubation. All the treatments showed similar variation trend, but Cd fractions at A1 treatment with 22.5 t/hm^2 of alfalfa addition changed less than other treatments with incubation time extension. Compared with CK, adding alfalfa or rice straw alone or together reduced the ratio of water soluble Cd and Exch-Cd to total Cd by 22.7~60.4%, but increased the ratio of Res-Cd and SBO-Cd to total Cd by 13.9%~43.2% within 120d of incubation. A1 treatment resulted in the lowest percentage of high activity Cd regardless of incubation time and the highest percentage of low activity Cd especially at 120 d of incubation, obviously different from other treatments. The results indicated that application of alfalfa and rice straw have potential for immobilizing Cd in acidic yellow-red soil, but the effectiveness is dependent upon application rate and their mixture.

Materials and methods

The acidic yellow-red soil was collected at the 0-20 cm depth from the Southern region of Hubei province, air dried and ground to pass a 2--mm sieve. Selected properties of the soil were 5.13 pH (1: 1H_2O), 8.5 g kg^{-1} organic C, 5.75 mg kg^{-1} M3 extractable P, and 1.27 mg kg^{-1} total Cd.

The flowering fresh alfalfa and air-dried rice straw samples were cut into 1~1.5 cm prior to use. Selected properties of the alfalfa and rice straw were 2.38% and 1.08% total N, 0.26 % and 0.20 % total P, as well as 45.0 % and 76.7 % total C, respectively with no Cd.

The incubation experiment consisted of CK (without organic materials amendment) and 8 organic material treatments including A1, A2, S1, S2, A1+S1, A1+S2, A2+S1 and A2+S2, in which A1 and A2 represented 22.5 t/ha and 45.0 t/ha of fresh alfalfa amendment, respectively, S1 and S2 represented 4.5 t/ha and 9.0 t/ha of air-dried rice straw amendment, respectively. For each treatment/control, organic material as designed was mixed with 1kg soil (oven-dry basis) thoroughly and packed into a 2-L plastic container, then 4 mg Cd (as $CdCl_2$ solution) was added into soil and stirred evenly. The mixture was incubated in a temperature-controlled chamber at 25 ℃. There were three replicates for each treatment and all the containers were randomly arranged with a split factorial design. DI water was added as needed to keep the soil water between 1 cm higher than the soil surface and 100% water-holding capacity. At the intervals of 20, 40, 60, 80, 100 and 120 d of incubation, subsamples in three replicates were taken for measurements of soil pH, organic C and M3 extractable P and Cd, and soil Cd fractionation was determined at 40, 80 and 120 d of incubation.

Results

1. Soil Cd fractionation

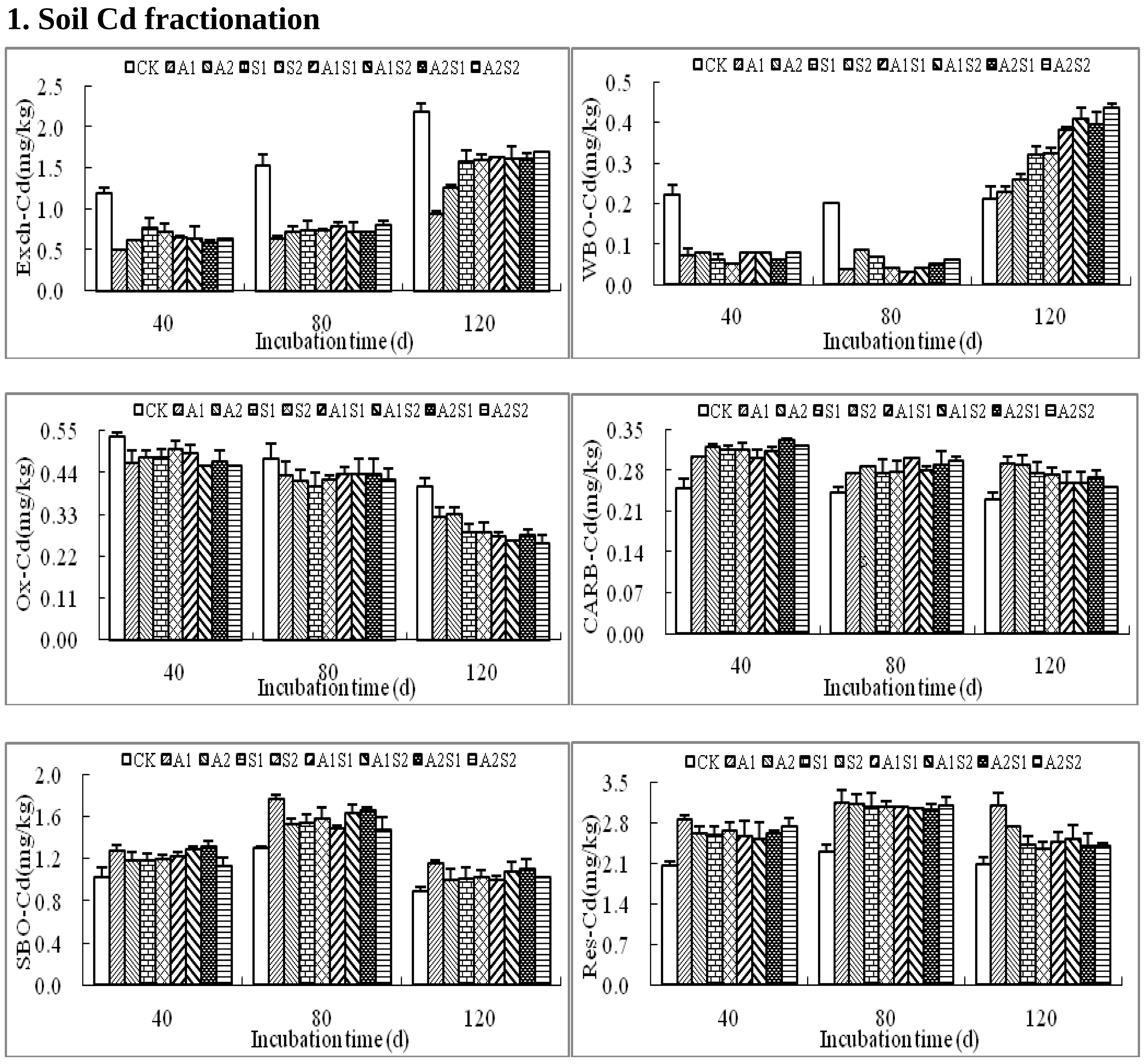

Fig.1 Cd fractions in acidic yellow-red soil as affected by organic materials addition and incubation time. Error bars represent standard error

Cadmium in the acidic yellow-red soil was mainly transformed into residue bound Cd (Res-Cd) fraction regardless of organic material additions, followed by strongly bound organic Cd (SBO-Cd) and exchangeable Cd (Exch-Cd) fraction, with a small portion being associated with carbonate bound Cd (CARB-Cd) and weakly bound organic Cd (WBO-Cd) fraction (Fig. 1). Exch-Cd increased with incubation time, up to 120 d of incubation. Compared with CK, addition of alfalfa and/or rice straw remarkably reduced Exch-Cd regardless of incubation time, but A1 treatment with 22.5 t/ha of fresh alfalfa amendment showed the lowest Exch-Cd, especially at 120 d of incubation.

Only a small portion of Cd was associated with CARB-Cd and WBO-Cd fraction. Compared with CK, addition of alfalfa and/or rice straw increased CARB-Cd, but decreased WBO-Cd significantly at 40 and 80 d of incubation, and then increased WBO-Cd obviously at 120 d of incubation except for A1 and A2 treatments.

Ox-Cd decreased significantly at 120 d of incubation compared with 40 and 80 d of incubation. Moreover, addition of alfalfa and/or rice straw reduced Ox-Cd significantly at 120 d of incubation compared with CK.

Soil SBO-Cd increased and then decreased with incubation time, with the highest concentration at 80 d of incubation and the lowest concentration at 120 d of incubation. Furthermore, addition of alfalfa and/or rice straw increased SBO-Cd compared with CK, and A1 and A2S1 treatments showed a greater effect than any other treatment (Fig. 1).

Res-Cd increased and then decreased with incubation time except for CK and A1 treatments which showed little change. Compared with CK, addition of alfalfa and/or rice straw increased Res-Cd remarkably regardless of incubation time, but A1 treatment showed the highest Res-Cd, especially at 120 d of incubation (Fig. 1).

2. Distribution of Cd with different activity

Percentage of different activity Cd as affected by organic material amendment and incubation time

Cd activity	Incubation time (d)	CK	A1	A2	S1	S2	A1S1	A1S2	A2S1	A2S2
High activity Cd (%)	40	22.2 a D	8.8e D	12.1cd E	14.1b E	13.1bc E	12.1bcd E	12.0bc E	10.7d E	11.7cd E
	80	25.0a D	9.9c D	11.5bc E	11.9b F	12.0b E	12.7b E	11.7b E	11.7b E	13.0b E
	120	36.1a C	15.2d B	20.8c C	26.7b C	27.3b C	26.9b C	26.4b C	26.8b C	28.0b C
Medium activity Cd (%)	40	18.9a E	15.5b B	16.6ab D	16.2b D	16.0b D	16.5ab D	16.1b D	16.1b D	16.1b D
	80	15.3a F	11.9b C	12.7b E	12.0b F	12.1b E	12.6b E	12.1b E	12.3b E	12.6b E
	120	14.4a F	13.9a B	15.2a D	14.9a DE	15.1a D	15.2a D	15.2a D	15.5a D	15.6a D
Low activity Cd (%)	40	58.3b A	75.6a A	71.2a AB	69.7a A	70.9a A	71.4a A	71.9a A	73.2a A	72.2a A
	80	59.7b A	78.2a A	75.8a A	76.0a A	75.9a A	74.7a A	76.2a A	76.0a A	74.3a A
	120	49.5d B	70.9a A	64.0ab B	58.4bc B	57.6bc B	57.9bc B	58.6bc B	57.7bc B	56.4c B

Note: Values in the table are means of three replicates. Different lowercase letters indicate significant differences within the same row, and the different capital letters indicate significant differences within the same column ($P < 0.05$)

In soil, heavy metals commonly exist as water soluble, exchangeable, carbonate bound form, iron and manganese oxide bound form, strongly and weakly bound organic fraction and residue bound fraction. Water soluble and exchangeable Cd fractions are of high activity due to their high mobility and availability to plants. On the contrary, strongly bound organic fraction and residue Cd are of low activity because of their stability in soil. Carbonate bound, iron and manganese oxide bound and weakly bound organic fractions are of medium activity.

In this study, low activity Cd was dominant regardless of incubation time and organic material amendment, but it decreased significantly at 120 d of incubation compared with 40 and 80 d of incubation except for A1 treatment. High activity Cd increased remarkably at 120 d of incubation compared with 40 and 80 d of incubation. Furthermore, compared with CK, addition of alfalfa and/or rice straw increased the low activity Cd, but decreased the high activity Cd obviously regardless of incubation time, and A1 treatment was most effective.

Discussion

Soil characteristics are the important factors controlling the distributions of heavy metals in soil (Lu et al. 2015; Zhao et al., 2015). Soil pH affects the migration and transformation of heavy metals (Bradl, 2004), and low pH can result in high levels of Cd accumulation in rice (Kögel-Knabner et al., 2010). In this study, subsamples were taken every 20 d for measurements of soil pH and organic matter. The results indicated that compared with CK, addition of alfalfa and rice straw alone or together increased soil pH by 0.14 to 0.38, depending upon incubation time. Moreover, soil pH with alfalfa amendment alone was obviously higher than that with rice straw addition within 120 d of incubation, and also significantly higher than those with the mixture of alfalfa and rice straw (data not shown). So, addition of alfalfa and/or rice straw decreased the high activity Cd pools, but increased the low activity Cd pools, including strongly bound organic Cd and residue bound Cd fraction, and A1 treatment with 22.5 t/hm^2 of alfalfa amendment was more effective than other treatments.

Conclusions

1. Alfalfa and rice straw can be used alone or together to reduce water soluble and exchangeable Cd in soil.
2. 22.5 t/hm^2 of fresh alfalfa (which is of normal biomass yield in practice) is more effective than rice straw and their mixture in the immobilization of Cd in the acidic yellow-red soil under flooded condition.