

Effects of Three Soil Amendments on Cr (III) Bioavailability in Cr (III)-contaminated Soil

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Abstract: The effect of soil amendments on the bioavailability of heavy metals has been progressively examined both in the field and under laboratory conditions. To evaluate the effect of three soil amendments, i.e., chicken manure (CM), peat (PE) and vermiculite (VE) on Cr bioavailability, we planted *Lolium perenne* (*L. perenne*) and *Pharbitis purpurea* (*P. purpurea*) in soils contaminated with 1000 mg•kg⁻¹ Cr (III) in the laboratory. The results showed that all three amendments decreased the bioavailability of Cr (III). Cr (III) accumulation in *L. perenne* was most significantly reduced by CM, leading to a Cr (III) concentration that was only 54.1% of that of the control. CM alleviated Cr (III) stress on the plants, most obviously. Therefore, CM have the potential to serve as efficient soil amendments for Cr-contaminated soil.

1 INTRODUCTION

Chromium (Cr) contamination in soil is a global problem that can enter plants and animals through the food chain and ultimately affect human health (Gangwar 2011). Therefore, it is urgent to study the treatment of Cr-contaminated soil. Cr has several valence states, but Cr (III) is the most abundant valence state of Cr in soil (Ashraf 2011). Therefore, studying Cr (III)-contaminated soil is of significance.

The use of soil amendments to treat heavy metal-contaminated soils is currently a popular and environmentally friendly method (Huang 2018, Liang 2014). Among them, natural soil conditioners with cheap price and wide sources have greater prospect and potential (Abd 2015, Habashy 2011). In previous studies, various natural amendments such as red mud, lime, and compost were used to treat heavy metal-contaminated soils (Reijonen 2016, Zhou 2017). Additionally, natural amendments can greatly affect Cr (III) concentration and Cr (III) bioavailability in soil (Ke 2012, Taghipour 2016). The heavy metals bioavailability is better controlled by organic amendments in soil. Diverse types of organic materials, such as compost from the food industry, municipal waste solids, and manure and agriculture residues, can be used to remediate the soils contaminated with metals (Qi

2018). It has been reported that organic materials can decrease the metal availability by improving the soil pH and via the complexation of the reactive groups in organic materials (Abbas 2017). In addition, the functional groups of organic amendments provide excellent adsorption sites for binding metals. Therefore, it is necessary to study the effect of different organic and inorganic amendments in Cr-contaminated soil.

Extracting Cr from the soil via roots and translocating plants is complex. The uptake of Cr by plants and its bioavailability in the soil can be influenced by several factors, including the plant type, its concentration in the soil, the soil organic matter, the pH and the cation exchange capacity (CEC) (Khan 2018). Different types of plants have differing bioaccumulation capacities with respect to Cr.

The purpose of this study is to (1) study the effects of the three soil amendments on the bioavailability of Cr (III) in soil; (2) explore the differences in uptake, transport and accumulation of Cr (III) in plants with the three soil amendments.

2 MATERIALS AND METHODS

2.1 Soil and Amendments

Soil samples were collected from the 0-20 cm interval of Chromium Salt Factory in Upper Loushan River, Licang District, Qingdao, China (36.21°N, 120.39°E). To homogenize the samples, each sample was completely mixed; then, each sample was air dried and passed through a 2-mm sieve. The three soil amendments examined included chicken manure (CM), peat (PE) and vermiculite (VE) in this study. Before addition to the soil, the amendments were ground and passed through a 2-mm mesh. The basic chemical properties of the experimental soil and amendments are presented in Tables 1 and 2.

Table 1. The basic chemical properties of the soils.

Project	pH value	Organic matter content /g·kg ⁻¹	CEC /cmol·kg ⁻¹	Cr(III) /mg·kg ⁻¹	Cr(T) /mg·kg ⁻¹
Soil	7.32	10.47	16.48	9.06	9.58

Table 2. The basic chemical properties of the three amendments.

Amendments	pH value	Organic matter content /g·kg ⁻¹	total nitrogen /%	Cr(T) /mg·kg ⁻¹
CM	7.87	45.3	20.4	-
PE	6.10	62.4	15.8	-
VE	7.40	-	-	-

-: indicates not detected.

2.2 Pot Experiment

The experiments in this study were conducted by potting *Lolium perenne* (*L. perenne*) and *Pharbitis purpurea* (*P. purpurea*) with CM and PE (organic amendments), and an inorganic amendment (VE) in Cr (III)-contaminated soils. *L. perenne* and *P. purpurea* are more tolerant to Cr when exposed to Cr (III) levels no greater than 1000 mg·kg⁻¹ (Chen 2017). Therefore, the concentrations of Cr (III) in the soil samples were set at 1000 mg·kg⁻¹ in this study. Cr was added uniformly in the form of a CrCl₃·6H₂O solution and then equilibrated at 25 °C for one week in the laboratory.

The three amendments were added to the soil at a 20 mg·kg⁻¹ application concentration and thoroughly mixed. Choose plastic pots of suitable size, each containing 1 kg soil (dry weight, dw). Each treatment and one control (no treatment) were

prepared in triplicate. Two copies were prepared for the treatment group, one for *L. perenne* and another one for *P. purpurea*. Irrigated deionized water was added to the pots equally when needed.

Seeds of *L. perenne* and *P. purpurea* were obtained from Shangpin Landscaping Engineering Company, Hefei. The seeds were washed with H₂O₂ and then with deionized water. Then, the seeds were sown in the selected pots. The pots were kept in a greenhouse with a controlled environment. After germination, there were equal numbers of uniform and healthy seedlings in each pot. All pots were adjusted daily to a water content of 75% and a field capacity (FC) of 100% by weight.

2.3 Analysis

Ten grams of treated soil was sampled after 7, 21, and 35 days; then, the soil was air dried, gently homogenized with a mortar and analyzed to determine its chemical parameters. Ten grams soil samples were taken after one week, three weeks and five weeks, then air-dried. After gently homogenized with a mortar, it was used for the analysis of its physical and chemical properties. The plants were harvested after 30 days of growth. After rinsing, plant roots and shoots were dried and ground.

Flame atomic absorption spectrometry was used to digest and analyze total Cr and Cr (III) in the soil samples (with detection limits of 5 mg/kg and 2 mg/kg). Determination of Cr concentration after digestion with 0.5 g powder sample using H₂SO₄-H₂O₂ according to a literature method (Parkinson 1975).

The chemical fraction of Cr in the soil was assessed according to the BCR protocol, which is a sequential extraction program involving four steps (Sahuquillo 1999).

2.4 Bioconcentration Factor and Translocation Factor

The bioconcentration factor (*BCF*) and translocation factor (*TF*) are key indexes used to assess the ability of a plant species to remediate metal-contaminated soil. The *BCF* and *TF* for Cr in the studied plants were determined according to a literature method (Sidhu 2016). The *BCF* and *TF* of the plants were calculated using equations (1) and (2):

$$BCF = C_p / C_s \quad (1)$$

where C_s is the Cr(III) concentration in soil (mg·kg⁻¹) and C_p is the concentration in plants (mg·kg⁻¹), and

$$TF = C_s / C_r \tag{2}$$

where C_r and C_s are the Cr(III) concentrations in roots and shoots of the plants ($\text{mg}\cdot\text{kg}^{-1}$).

2.5 Statistical Analysis

The Statistical Product and Service Solutions software package was used in the statistical analysis. One-way analysis of variance (ANOVA) using Duncan's multiple range test ($P = 0.05$) was conducted to determine the statistical significance of the differences among samples. The correlations were analyzed by Pearson's test (two tailed) using SPSS 20.0 ($P < 0.05$).

3 RESULTS AND DISCUSSION

3.1 Cr Fraction in Soil

Although the heavy metals concentration is an important indicator to express the degree of soil pollution, the toxicity of heavy metals is associated with their chemical fraction and bioavailability (Meng 2017). According to the difficulty of extracting the different Cr chemical fractions, the harm and degree of toxicity of Cr to the environment are expressed as acid-soluble > reducible > oxidizable > residual fractions. Namely $B1 > B2 > B3 > B4$. The sum of B1, B2 and B3 represents the bioavailability content, which poses a potential threat to organisms (Qiao 2003). Figure 1 shows the proportion changes of the Cr (III) fractions after application of the amendments in Cr-contaminated soil. In each group, B4 was dominant in the initial stage (7 days) of the incubation experiment, with the proportions in the Cr (III) fraction ranging from 79.3% to 71.6%. The three soil amendments had little effect on the fraction of Cr (III), which changed slowly over time. Only CM reduced the proportions of B1 + B2 to 66.7% of that of CK in the later stage (35 days). The contents of Cr (III) in the soil were influenced by the organic matter contents of CM and PE. VE played a similar role in soil containing Cr (III) but showed less of an effect than CM and PE. The organic matter content in the amendments plays a certain role in reducing the bioavailability of heavy metals in soil.

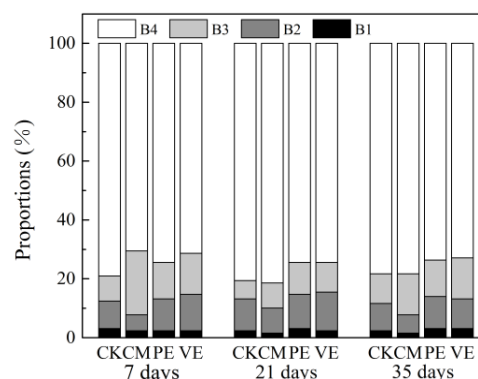


Figure 1: Effect of amendments on the fraction of Cr(III) in the soil.

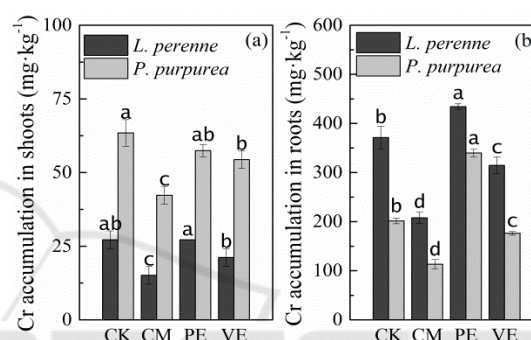


Figure 2: Effect of amendments on Cr(III) accumulation in two plants.

3.2 Cr Accumulation in Plants

The accumulation of Cr (III) in the shoots and roots of *L. perenne* and *P. purpurea* is shown in Figure 2. In the plant shoots, CM had the most significant reduction of Cr (III) in the shoots of *L. perenne* and *P. purpurea*, with values of only 55.6% and 68.0% of those of CK, respectively (Figure 2a). There was no significant change in Cr (III) accumulation in the two plants between the PE and CK groups.

The effect of the amendments on the Cr (III) accumulation in the roots of the two plants is shown in Figure 2b. The rank order of the three amendments in terms of reduced Cr (III) accumulation in the roots of the two plants was $CM > VE > CK > PE$. The decrease in the Cr(III) concentration upon CM treatment was the most significant and was less than 60% of that of CK ($P < 0.05$). PE treatments promoted the accumulation of Cr(III) in the plant roots; the Cr(III) accumulation in the roots of *L. perenne* and *P. purpurea* was 1.2 and 1.1 times higher than that of CK.

3.3 Cr Uptake and Transport in Plants

Under Cr (III) stress, the effects of the three amendments on the uptake and transport in *L. perenne* and *P. purpurea* are shown in Table 3. The transport of Cr (III) to the plant shoots was reduced. PE had the best inhibitory effect on Cr (III) with *P. purpurea*, and the *TF* decreased by 47.1%. The application of the amendments did not significantly enhance the *BCF* of the shoots of the two plants. In contrast, PE had a significantly positive effect on Cr(III) enrichment in the roots of *L. perenne* and *P. purpurea*, and the *BCF* of Cr (III) reached 1.2 and 1.7 times higher than that of CK, respectively.

Table 3. Effects of amendments on Cr (III) *TF* and *BCF* for two plants under Cr (III) stress.

amendments	<i>P. purpurea</i>		
	<i>TF</i>	<i>BCF</i> of shoots	<i>BCF</i> of roots
CK	0.32	0.06	0.20
CM	0.37	0.04	0.11
PE	0.17	0.06	0.34
VE	0.31	0.05	0.18

amendments	<i>L. perenne</i>		
	<i>TF</i>	<i>BCF</i> of shoots	<i>BCF</i> of roots
CK	0.07	0.03	0.37
CM	0.07	0.02	0.21
PE	0.06	0.03	0.43
VE	0.07	0.02	0.31

3.4 Pearson Correlation Analysis of Cr in Soil and Plants

As described in the above data, the amendments significantly reduced the B1 and B3 proportions of Cr (III) in the soil but had little effect on the B2 proportion. To explore the correlation between the change in the Cr (III) proportion in the soil and the Cr (III) accumulation in the plants after application of the three amendments, Pearson's correlation analysis of the Cr proportion and Cr (III) accumulation was performed, and the results are shown in Table 4. As seen from the table, the single-factor results showed Cr (III) accumulation in the plants in the order of B1 > B3 > B2. Usually, B1+B2+B3 represents the bioavailable heavy metals in soil(Wang 1997), but in this study, B1+B3 had a similar or even greater effect than B1+B2+B3. In addition, the role of B2 was minimal.

Table 4. Pearson correlation analysis for soil Cr forms and plant Cr contents.

Cr fraction	<i>L. perenne</i>		
	Cr content in shoots	Cr content in roots	Cr content in plant
B1	0.722*	0.704	0.715*
B2	0.218	0.377	0.320
B3	0.518	0.512	0.517
B1+B2	0.693	0.705	0.705
B1+B3	0.933**	0.914**	0.926**
B2+B3	0.594	0.629	0.620
B1+B2+B3	0.924**	0.931**	0.934**

Cr fraction	<i>P. purpurea</i>		
	Cr content in shoots	Cr content in roots	Cr content in plant
B1	0.750*	0.440	0.569
B2	0.205	0.240	0.235
B3	0.492	0.755*	0.682
B1+B2	0.717*	0.442	0.558
B1+B3	0.940**	0.848**	0.909**
B2+B3	0.563	0.804*	0.768*
B1+B2+B3	0.929**	0.847**	0.905**

The results showed that the amount of available heavy metals in the soil directly reflected the absorption of heavy metals by the plants. The decrease in Cr (III) accumulation in the plants was the most obvious in the CM group, followed by the VE group; meanwhile, the PE group promoted the accumulation of Cr in the plant roots and had the same level as that in the shoots of the plants in the CK group. Therefore, the amendments can reduce the Cr content in the plants by changing the soil Cr proportion, and the rank order was CM > VE > PE. In the Cr-contaminated soil, we found that the content of organic matter in the soil is not the most important factor affecting the heavy metal bioavailability, which is slightly different from the study of(Xiao 2017). This difference may be because CM and VE can increase the soil pH, which enhances the chelating ability of the soil to heavy metal(Reijonen 2016). The bioavailability of heavy metals can be reduced by stabilization processes, including surface complexation, cation exchange, precipitation, and physical adsorption (Li 2017).

4 CONCLUSIONS

In this study, we found that the three amendments has the improvement for the Cr (III)-contaminated soil. In this complicated experimental system, The positive correlation between the chemically extractable Cr and the Cr taken up by the plants

indicates that chemical extractability is a reliable indicator to predict the bioavailability of Cr in amended soil. Among the three amendments, CM has the strongest effect on reducing the bioavailability of Cr (III).

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