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Use of a hyperaccumulator and biochar to remediate an acid soil highly contaminated with trace metals and/or oxytetracycline

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HIGHLIGHTS

- Use of biochar and a hyperaccumulator combined to remediate a Cd/Zn polluted acid soil.
- Biochar enhanced Cd and Zn accumulation by hyperaccumulator shoots > three times.
- Inclusion of hyperaccumulator caused lower soil available Cd and Zn than biochar alone.
- Biochar decreased plant OTC uptake, but OTC had no effect on metal phytoextraction.

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ABSTRACT

Biochars and hyperaccumulators have been widely used for the remediation of trace metal contaminated soils through immobilization and phytoextraction. These two options have rarely been used simultaneously despite their potential to achieve a greater decline in trace metal availability and higher removal efficiency in polluted soils. This study investigated the combined effects of biochar and the cadmium/zinc (Cd/Zn) hyperaccumulator *Sedum plumbizincicola* in a pot experiment and examined the effect of an antibiotic (oxytetracycline, OTC) in an acid soil spiked with Cd/Zn alone and with OTC. Biochar amendment alone significantly decreased soil $CaCl_2$-extractable Cd and Zn by 22.7 and 43.1%, respectively. Growing *S. plumbizincicola* alone resulted in 11.3% Cd and 3.88% Zn removal after ten weeks of phytoextraction. Growing *S. plumbizincicola* with biochar resulted in higher decreases in extractable Cd and Zn by 60.0% and 53.2%, respectively, and more than three times Cd and Zn removal efficiencies compared to growing *S. plumbizincicola* without biochar. The results indicate that biochar addition promoted plant growth and increased shoot trace metal concentrations, consequently increasing the removal efficiency and that soil trace metal removal by the hyperaccumulator further reduced the extractable trace metals in addition to immobilization by biochar. Biochar amendment decreased plant OTC concentrations. However, OTC showed no effect on trace metal phytoextraction. Results indicate that the simultaneous use of biochar and the hyperaccumulator can give high Cd/Zn phytoextraction efficiency in terms of both soil total and available trace metal concentrations in acid soils highly contaminated with trace metals or trace metals and OTC.

1. Introduction

Anthropological activities such mining and smelting, wastewater irrigation, and excessive application of fertilizers for crop production have resulted in soil contamination due to the release of large amounts of trace metals. Excessive trace metal accumulation in soils is hazardous to environmental safety and human health (Salmani-Ghabeshi et al., 2016). The strategies implemented for the remediation of trace metal-polluted soils, especially agricultural soils, generally remove the trace metals from the soils or immobilize the soil soluble trace metal fractions to reduce their uptake by plants (Mahar et al., 2015; Ali et al., 2013). Phytoextraction is a bioremediation technique that can use hyperaccumulator plant species to extract trace metal(loid)s from soils and decrease their bioavailable concentrations to non-toxic levels. Phytoextraction, due to its cost-effective and eco-friendly nature as well as to *in situ*

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application, has aroused global interest for its use to remediate soils contaminated with trace metals (McGrath et al., 2006; Wu et al., 2012; Li et al., 2014a). Biochar is analogous to black carbon and can be derived from the pyrolysis of organic materials. Biochars, due to their alkaline substances and surface functional groups, have been widely investigated as amendments for the stabilization of soil trace metals to restrict crop trace metal uptake and to enhance food safety (Xu et al., 2016; Wang et al., 2016; Moreno-Jimenez et al., 2016).

Amendment with biochars has shown stimulatory effects on plant growth as reported in some studies by increasing soil nutrient contents and soil pH and also by modifying soil physical structure and biological properties (MacDonald et al., 2014; Wang et al., 2016). Therefore, biochars have the potential to enhance phytoextraction efficiency by promoting plant growth. Phytoextraction might progressively remove the phytoavailable trace metal fraction in the soil and thus decrease total soil trace metals (Li et al., 2014b, 2016) in addition to the immobilization of trace metal by biochars. The simultaneous use of biochar and phytoextraction can substantially increase trace metal phytoremediation efficiency (Paz-Ferreiro et al., 2014). Attempts have been made to investigate the simultaneous use of biochar and trace metal hyperaccumulators or accumulators, but their results have been inconsistent (Lu et al., 2014a; b; Hu et al., 2014; Fellet et al., 2014; Rees et al., 2015). The contrasting results of plant trace metal uptake (no effect, positive and negative effects) are generally associated with a decrease in soil trace metal availability and promotion of plant growth as a consequence of biochar amendment. However, the net effect largely relies on the key factors controlling plant trace metal uptake under specific experimental conditions. We hypothesized that if biochars increase hyperaccumulator growth but do not decrease trace metal availability to the hyperaccumulator (although the trace metal fraction extractable by a chemical extractant in the soil may decrease), the remediation efficiency will be enhanced. This may occur in acid soils and soils highly polluted with trace metals due to the high availabilities of trace metals in such soils.

The overuse and misuse of antibiotics in clinical and veterinary medicine, aquaculture, and agriculture have led to higher accumulation of antibiotic residues in soils. Application of wastewater sludges, sewage biosolids, and livestock manures to increase the nutrient status of agricultural soils are major sources of antibiotic inputs to soils together with trace metals. Previous studies indicate that biochars can immobilize antibiotics through adsorption (Jia et al., 2016), and thus can be used to lower the availability of antibiotics to plants (Rajapaksha et al., 2014). The role of antibiotics in enhancing Cd phytoextraction has previously been investigated (Ma et al., 2016). However, the effects of antibiotics on trace metal phytoextraction in the presence of biochar in soils simultaneously polluted with trace metals and antibiotics remain unclear and require further investigation.

Sedum plumbizincicola is a recently discovered Cd/Zn hyperaccumulator (Wu et al., 2013) and has a remarkable ability to extract Cd and Zn from contaminated soils. In the present study an acid agricultural soil was collected from the field and spiked with Cd and Zn alone and/or with an antibiotic (oxytetracycline, OTC). The biochar amendment and *S. plumbizincicola* were investigated to evaluate the combined effects of biochar and the hyperaccumulator on the remediation efficiency of the acid soil contaminated with Cd, Zn and OTC, and the effects of OTC on Cd and Zn phytoextraction by *S. plumbizincicola* in the presence of biochar in a glasshouse pot experiment.

2. Materials and methods

2.1. Soil characterization

The Typic Agri-Udic Ferrosol soil was collected from the top 15 cm of the soil profile in a peanut field (31°05′ 35″ N, 119°07′ 52″ E) situated in Xuanchen city, Anhui Province, east China. The soil collected was air-dried at room temperature and thoroughly mixed after passing through a 2-mm nylon sieve. The soil contained small amounts of Cd (0.1 mg kg^{-1}) and Zn (43 mg kg^{-1}) but no OTC was detected. The dried soil was then prepared for the experiment by spiking with Cd, Zn and OTC. Briefly, portions of unpolluted soil (control) were spiked with Cd and Zn (as the nitrates), adjusted to and maintained at 70% of maximum soil water holding capacity (WHC), and equilibrated for 8 weeks at room temperature. The soil spiked with Cd and Zn was air-dried and sieved again using a 2-mm nylon sieve. The control soil (non-spiked) and trace metal (Cd and Zn)-spiked soil were then spiked with OTC using a stock solution dissolved in methanol. The soil was thoroughly mixed after volatilization of methanol in a fume cupboard. Total Cd, Zn and OTC contents determined in the spiked soil were (on average) 5.06, 924, and 6.73 mg kg^{-1}, respectively, on a dry weight (DW) basis. Four soil treatments [unpolluted control soil, trace metal-spiked soil (M), OTC-spiked soil (A), and soil spiked with both trace metals and OTC (M + A)] were obtained for the pot experiment.

2.2. Pot experiment

The biochar used was derived from corn straw pyrolyzed at 500 °C in the absence of oxygen as described by Jia et al. (2016). There were eight soil treatments: i) control soil (CK); ii) control soil with 5% biochar (BC); iii) trace metal-spiked soil (M); iv) trace

Table 1
Selected physicochemical properties of the soil before the pot experiment.

Property	CK	BC	M	M + BC	A	A + BC	M + A	M + A + BC
pH	3.63 ± 0.04	4.22 ± 0.16[a]	3.57 ± 0.01	4.27 ± 0.01[a]	3.61 ± 0.03	4.29 ± 0.08[a]	3.61 ± 0.01	4.38 ± 0.07[a]
Organic carbon (g kg^{-1})	7.32 ± 0.29	22.5 ± 0.3[a]	7.09 ± 0.10	25.1 ± 1.3[a]	6.64 ± 0.46	27.1 ± 1.06[a]	7.16 ± 0.23	23.3 ± 0.4[a]
CEC (cmol (+) kg^{-1})	12.7 ± 0.8	12.8 ± 0.3	13.5 ± 0.4	13.4 ± 0.5	12.3 ± 0.2	13.8 ± 0.1[a]	13.2 ± 0.4	12.7 ± 0.4
Total N (g kg^{-1})	0.76 ± 0.02	1.08 ± 0.02[a]	0.92 ± 0.04	1.23 ± 0.05[a]	0.83 ± 0.15	1.18 ± 0.04[a]	0.89 ± 0.04	1.17 ± 0.06[a]
Total P (g kg^{-1})	0.42 ± 0.01	0.53 ± 0.03[a]	0.37 ± 0.01	0.43 ± 0[a]	0.44 ± 0.05	0.47 ± 0.02	0.37 ± 0.04	0.43 ± 0.03
Total K (g kg^{-1})	11.8 ± 0.4	12.6 ± 0.3[a]	12.4 ± 0.1	13.7 ± 0.2[a]	12.5 ± 0.1	13.3 ± 0.3[a]	12.4 ± 0.2	13.4 ± 0[a]
Available N (mg kg^{-1})	69.8 ± 6.7	62.5 ± 6.4	106 ± 1.57	91.9 ± 0.0[a]	71.6 ± 2.5	69.8 ± 3.6	104 ± 31	91.9 ± 5.2
Available P (mg kg^{-1})	29.4 ± 0.8	52.4 ± 5.4[a]	36.8 ± 12.6	36.3 ± 0.3	40.8 ± 16.3	50.4 ± 5.4	23.7 ± 4.0	36.7 ± 2.6[a]
Available K (mg kg^{-1})	144 ± 10	1062 ± 94[a]	159 ± 2	1375 ± 44[a]	165 ± 11	1312 ± 177[a]	158 ± 19	1344 ± 17[a]
Total Cd (mg kg^{-1})	0.14 ± 0.02	0.16 ± 0.03	5.06 ± 0.09	4.86 ± 0.22	0.14 ± 0.03	0.14 ± 0	5.09 ± 0.29	4.82 ± 0.42
Total Zn (mg kg^{-1})	43.4 ± 1.4	45.1 ± 1.8	924 ± 13	892 ± 37	45.6 ± 0.3	44.6 ± 5.1	924 ± 10	884 ± 20[a]
Available Cd	0.03 ± 0.01	0.04 ± 0.01	4.32 ± 0.01	3.28 ± 0.14[a]	0.03 ± 0.00	0.03 ± 0.01	4.28 ± 0.13	3.30 ± 0.26[a]
Available Zn	1.35 ± 0.30	0.91 ± 0.21	457 ± 13	267 ± 7[a]	1.45 ± 0.32	0.92 ± 0.30	461 ± 12	288 ± 25[a]

[a] a significant difference in the property between the soil and the corresponding soil with biochar addition by independent-samples *t*-test; N, nitrogen; P, phosphorus; K, potassium; CK, unamended control soil; "A", addition of antibiotic (oxytetracycline, OTC); "BC", addition of biochar; "M", addition of Cd and Zn.