Plant availability of arsenic and cadmium as influenced by biochar application to soil

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Abstract
Biochar has gained significant importance due to its ability to increase long-term soil carbon pool and crop productivity. A pot experiment was conducted to investigate the influence of biochar on the availability of arsenic (As) and cadmium (Cd) to maize. An activated wood biochar was applied at three rates (0, 5 and 15 g/kg) in factorial combinations with three rates (0, 10 and 50 mg/kg) each of As and Cd separately to a sandy soil. After 10 weeks of growth, crop was harvested and dry matter yield and concentration of As and Cd were determined. The soil was analysed for extractable trace elements after the plant harvest. The results showed that the addition of wood biochar to soil did not have any significant influence on the dry matter yield of maize shoot, even at the highest application rate. However, application of As and Cd significantly reduced the dry matter yield by 93 and 27%, respectively. Biochar application decreased the concentration of both As and Cd in maize shoots. However, the concentrations of extractable As increased with biochar treatment and the effect of biochar on DTPA extractable Cd in soil was inconsistent. The results show that biochar application can significantly reduce the bioavailability of As and Cd to plants and suggest that biochar application may have potential for remediating contaminated soils.

Key Words
Trace elements, charcoal, adsorption, bioavailability, heavy metals.

Introduction
Biochar is a product of thermal decomposition of biomass produced by the process called pyrolysis. Biochar has been found to be biochemically recalcitrant as compared to un-charred organic matter and possesses considerable potential to enhance long-term soil carbon pool (Lehmann *et al.* 2006). Biochar has been shown to improve soil structure and water retention, enhance nutrient availability and retention, ameliorate acidity, and reduce aluminium toxicity to plant roots and soil microbiota (Glaser *et al.* 2002). Research has demonstrated that biochar application to soil can substantially raise the productivity of field crops (Chan *et al.* 2007; Lehmann *et al.* 2003; Rondon *et al.* 2007; Rondon *et al.* 2006). Biochar possesses organic functional groups on its surfaces and the negatively charged organic functional groups increase over time during its oxidation in soil (Cheng *et al.* 2008). The formation of surface functional groups and adsorption sites on biochar could influence its cation exchange capacity (CEC) (Cheng *et al.* 2006; Liang *et al.* 2006) and consequently the capacity of biochar-amended soils to form complexes with metal ions. This research was conducted to investigate the influence of an activated wood biochar on the availability and uptake of As and Cd by maize.

Materials and methods
A glasshouse experiment was conducted using three levels of biochar (i.e.; 0, 5 and 15 g/kg soil) combined factorially with three rates (i.e.; 0, 10 and 50 mg/kg soil) each of As and Cd separately. The required amount of biochar was thoroughly mixed with 1 kg soil. Each of the pots was fertilized with a basal dose of N, P and K at 100, 40 and 50 mg/kg, respectively. Hybrid maize (cv 31H50) were sown in each pot, and the germinated plants were later thinned to keep three plants per pot. After 10 weeks of growth, the aboveground biomass of the maize plants was harvested. The dry matter yield was recorded and the dried samples were digested in a mixture of nitric and percholoric acids. The digests were analysed for As and Cd with a Varian Vista AX CCD inductively coupled plasma atomic emission spectrometer. After the harvest of plants, soil was air dried, well mixed and passed through a 2-mm sieve. Soil pH and electrical conductivity (EC) were measured. The available Cd in soil was extracted by the DTPA extractant (Lindsay and Norvell 1978) and solutions were analysed for available Cd with a Varian 220FS flame atomic absorption spectrometer. Available soil As was determined by the phosphate extraction method (Alam *et al.* 2001) and the extracts were analysed for As with a Varian 220Z hydride generation atomic absorption spectrometer. All data were analysed by the generalized linear model analysis of variance using Genstat v10 (VSN International Ltd, UK, 2007).

Results and discussion

The shoot dry matter yield of maize was not significantly affected by biochar application at different rates (0, 5 and 15 g/kg) in the absence of trace elements (Figure 1); these results are consistent with the results of a study by Hartley et al (2009), where biochar application did not show any significant effect on the dry matter yield of *Miscanthus*. Since the nutrient-poor sandy soil used in this study received adequate amounts of essential nutrients through basal fertilizers in all treatments, a positive response in biomass yield to nutrient addition through biochar application was not expected. Furthermore, the response of dry matter yield to biochar application may be more pronounced at levels higher than used in the present study. Arsenic was found to have the more significant adverse effect on the dry matter yield of maize (Figure 1).

(a) (b)

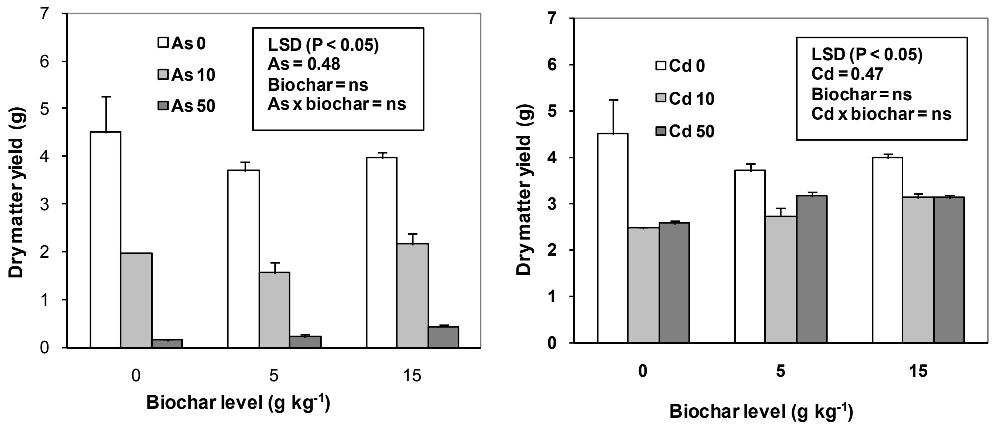

Figure 1. Maize shoot yield as influenced by biochar application to soil in combination with (a) As and (b) Cd.

Addition of biochar to soil was found to reduce shoot concentration of As (Table 1), possibly due to strong binding of As on the surface functional groups of biochar, making it less available to the plants. Cao and Ma (2004) found that addition of compost reduced As accumulation in carrot and lettuce, which they attributed to strong adsorption of As by organic matter. It is well established that trace elements can readily bound to organic matter in soil; however, organic amendments may enhance trace element mobility and bioavailability if the complexes are formed with soluble components of the amendments (Kumpiene *et al.* 2008), or by increasing supply of organic anions that may compete with certain trace elements for adsorption sites in soil (Dobran and Zagury 2006). The increase in extractable As in biochar-amended soil, as observed at the highest rate of biochar application (Table 1), may be attributed to the fact that biochar possesses and develops negatively-charged functional groups (Cheng *et al.* 2006), which may limit adsorption sites for As and hence contribute to the slight increase in extractable As in soil where biochar was added at the highest level. It is also possible that As accumulated in maize roots, which were not removed from soil, may have been extracted by the extractant used to measure available As.

Significant reduction in the concentration of Cd in maize shoots in biochar-amended soil (Table 1) can be attributed to the formation of stable metal-organic complexes (Kumpiene *et al.* 2008) and adsorption of the trace elements to organic matter (Elliott *et al.* 1986). The increase in pH caused by biochar application may also have enhanced the Cd adsorption to biochar. The development of carboxylic-C and aromatic-OH functional groups on biochar surfaces during their oxidation (Liang *et al.* 2006) could also increase CEC of soil (Cheng *et al.* 2006) and possibly increased Cd exchange capacity of soil. The increased concentration of extractable Cd in soil after plant harvest, in 10 and 50 mg/kg Cd treatments combined with at 5 g/kg biochar application, may be attributed to reduced plant Cd uptake in these treatments and thus more available Cd being left in soil. However, the decrease in concentration of soil Cd at the highest rate of biochar application can be attributed to increase in biochar bound Cd, which is not available to plants and is also not extractable by DTPA. Another explanation for the decreased concentration of available Cd at the highest biochar level could be due to its precipitation at high pH (Kabata-Pendias 2000), since at this rate biochar addition significantly increased soil pH compared with the other treatments.

Table 1. Arsenic and Cd in maize shoot in response to biochar, As and Cd application to soil. Phosphate extractable As and DTPA extractable Cd in soil after the pot experiment are also given. LSD values for trace element, biochar, and their interaction effects are presented at P<0.05.

Biochar (g/kg)	Trace element (mg/kg)	Shoot concentration (mg/kg)		Phosphate extractable (mg/kg)	DTPA extractable (mg/kg)
		As	Cd	As	Cd
0	0	0.15 ± 0.02	0.20 ± 0.04	0.12 ± 0.03	0.28 ± 0.04
5	0	0.11 ± 0.01	0.22 ± 0.01	0.24 ± 0.01	0.36 ± 0.02
15	0	0.24 ± 0.01	0.22 ± 0.02	0.22 ± 0.03	0.42 ± 0.03
0	10	4.38 ± 0.30	6.78 ± 0.26	2.80 ± 0.07	6.07 ± 0.39
5	10	6.48 ± 1.43	5.00 ± 0.36	2.54 ± 0.21	7.30 ± 0.12
15	10	3.36 ± 0.63	4.59 ± 0.37	2.79 ± 0.17	6.78 ± 0.12
0	50	29.11 ± 1.74	31.26 ± 0.94	12.66 ± 0.29	28.77 ± 0.56
5	50	26.47 ± 1.94	23.24 ± 0.92	12.77 ± 0.36	34.44 ± 0.46
15	50	18.87 ± 2.75	12.80 ± 0.99	14.86 ± 1.01	27.79 ± 1.76
LSD	Biochar	2.4	1	0.7	1.1
(P < 0.05)	Trace element	2.4	1	0.7	1.1
	Biochar × trace element	4.1	1.7	1.1	1.9

Conclusions

This study has shown that the application of wood biochar to soil possesses the potential to reduce the availability of As and Cd to plants. The concentration of As and Cd in maize shoots decreased with the application of biochar to soil. Biochar application increased extractable As, whereas biochar application had inconsistent effects on extractable Cd. This study highlights the need for detailed mechanistic investigation of biochar-trace element interactions in order to generalize conclusions regarding whether biochar application can reduce trace element availability to plants. Field experiments evaluating long-term benefits of soil biochar addition using higher application rates and different types of biochar in relation to the bioavailability of toxic trace elements in contaminated soils are required.

Acknowledgements

Tshewang wishes to acknowledge the Sustainable Land Management Project, National Soil Services Centre, Ministry of Agriculture, Thimphu, Bhutan for the financial assistance through a postgraduate scholarship. The authors would like to thank the BEST Energies, NSW, Australia, for the biochar supplied for the experiment.

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