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Characteristics of different types of biochar and effects on the toxicity of heavy metals to germinating sorghum seeds

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ABSTRACT

Soils contaminated with heavy metals are often notably nutrient poor and unsuitable for plant growth. The addition of biochar can significantly improve soil properties. In this study, the contents of organic compounds and inorganic elements in biochar and the effect of biochar on plant germination were examined. The PAH content of biochar from four different sources was examined, and naphthalene, phenanthrene, fluoranthene and pyrene were identified as primary compounds. The most abundant inorganic elements were potassium, calcium, magnesium, sodium, aluminium, iron and manganese, with strontium and barium also being significantly elevated. The pH of biochar from all sources was strongly alkaline. The sorption characteristics for heavy metals (Cd, Cu and Pb) were also tested for the different types of biochar. Adsorption data were well-described by a Langmuir isotherm with maximum Cd (II), Cu (II) and Pb (II) adsorption capacities of 20.16, 7.83 and 70.92 mg/g for bamboo-derived biochar; 18.80, 13.85 and 200 mg/g for rice husk-derived biochar; 11.63, 20.08 and 123.46 mg/g for ash tree-derived biochar; and 15.11, 10.86 and 196.08 mg/g for beech tree-derived biochar, respectively. The effect of biochar on the toxicity of heavy metals was measured by the inhibition of sorghum seed germination. With biochar, the toxicity of cadmium, copper and lead was reduced. Bamboo-derived biochar was less efficient in reducing the toxicity of cadmium and copper compared with the other types of biochar. For lead, the rice husk-derived biochar was the least efficient in reducing the toxicity.

1. Introduction

For humans and the environment, heavy metals are a significant stress factor. Therefore, reducing the concentrations of toxic metals to a natural level is important. Phytoremediation is a method that relies on the accumulation of metals in plants and their associated microorganisms to remove heavy metals from the environment (Pilon-Smits, 2005). The advantage of this method is that interference with the environment is minimal; however, the effectiveness of phytoremediation is limited when the concentrations of contaminants are high and the characteristics of contaminated soils are poor for plant growth.

Biochar increases the effectiveness of phytoremediation by reducing the mobility (Beesley et al., 2011) and the phytotoxicity (Beesley et al., 2010) of certain organic and inorganic pollutants in soils. Biochar is a product of biomass conversion under a sufficiently high temperature (300–600 °C) and limited air or without air (Lehmann and Joseph, 2009). Through pyrolysis, the chemical properties of carbon fixed in biomass are changed, and as a result, biochar is more resistant to microbial decomposition (Lehmann and Joseph, 2009). The residence time in soils for carbon bound in biochar is many centuries to millennia (Steinbeiss et al., 2009). Because of the long residence time in soil, biochar could be used for carbon capture and storage, leading to a reduction of CO_2 concentration in the atmosphere and slowed climate change (Lehmann and Joseph, 2009). However, the primary soil application of biochar is to improve soil fertility and increase crop yields (Lehmann and Joseph, 2009; Steinbeiss et al., 2009). The application of biochar to improve soil fertility is not new and was used in some ancient cultures (particularly in the humid tropics); in these cultures, biochar was deliberately added to the soil, which created black soil that was not exhausted within a few years of deforestation. Many of these soils, Terra Preta (black soil), are found in the Amazon, with ages that exceed a thousand years (Ennis, 2012). Biochar, because of the porosity, increases soil moisture retention and positively influences aeration. In addition to an increase in water holding capacity, biochar fixes nutrients or fertilizers added to soils (N, P, and K), thereby decreasing the leaching and erosion of nutrients and the consequent eutrophication of local waters. Moreover, biochar forms complexes with minerals, including those that create humus. With a huge internal surface, biochar provides a substrate for abundant microbial colonization (Steinbeiss et al., 2009) and also serves as a refuge for recolonization by microorganisms. All the nutrients contained in the original biomass remain in biochar and are

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slowly released, and unlike ash, which retains only alkali (i.e., K, Ca, and Mg), biochar also contains phosphorus and sulphur. For nitrogen, biochar contains half that in the original biomass. Because of these properties, biochar is also used to mitigate the effects of pollutants through sorption and sequestration (Bornemann et al., 2007; Chen and Yuan, 2011; Soudek et al., 2014) and to remediate contaminated soils and sediments (Beesley et al., 2010). However, information on the application of biochar to improve the efficiency of phytoextraction and phytostabilisation is currently very limited.

Therefore, the aims of this study were to characterize the biochar from different sources and to evaluate the effect of these biochar on metal toxicity, as measured by the germination of sorghum (*Sorghum bicolor* L.) seeds.

2. Materials and methods

2.1. Plant material and chemicals

Seeds (SEED SERVICE s.r.o., Czech Republic) of three cultivars of *S. bicolor* L. (Expres, Honey Graze BMR and Nutri Honey) were used in the germination test. Heavy metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}) were obtained from the salts $Cd(NO_3)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Pb(NO_3)_2$. The source of the biochar was ash tree (OFFICIO P.S. Ltd., Czech Republic), beech tree (EKOGRILL Ltd., Czech Republic), rice husks or bamboo (Dr Jing Song, Nanjing, China). The substances used in the germination test were dissolved in double-distilled water containing 2 mM $CaCl_2 \cdot 2H_2O$, 0.5 mM $MgSO_4 \cdot 7H_2O$, 0.8 mM $NaHCO_3$, and 0.08 mM KCl (according to ČSN EN ISO 7346) (the chemicals were all from Penta [http://www.pentachemicals.eu]). The pH was adjusted to 7.6 with the addition of 0.1 M NaOH. For the adsorption experiments, double-distilled water was also used.

2.2. Heavy metal determination by ICP-MS

Element concentrations in solutions were determined with quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, X Series 2; Thermo Scientific, Thermo Fisher Scientific, USA) under the conditions given in Table 1. To ensure the quality of the analytical data, the procedure was verified using standard reference materials, i.e., NIST 1640 (Trace Elements in Natural Water) and acid digests of NIST 2711 (Montana Soil). The differences between the measured and standard values did not exceed 5% relative standard deviation (RSD). Reagent blanks and unexposed filters mineralized in the identical acid mixture were used at the start of batch of analyses.

Table 1
Operating conditions used for ICP-MS measurements of elements.

Instrument	X Series 2, Thermoscientific
Plasma RF power	1400 W
Reflected power	<1 W
Plasma gas flow rate	13.5 L min^{-1} (Ar)
Auxiliary gas flow rate	0.95 L min^{-1} (Ar)
Nebulizer gas flow rate	0.75 L min^{-1} (Ar)
Cones	Nickel
Sensitivity (solutions)	~3 × 10^4 cps per ng ln mL^{-1}
Nebuliser	Meinhard type
Measurement mode	Peak jumping
Points per peak	1
Dwelltime	10.0 ms
Acquisition time	3 × 67 s
Detector voltage	2986 V (pulse count) −1680 V (analogous)
Measured isotopes	^{7}Li, ^{9}Be, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{44}Ca, ^{45}Sc, ^{47}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{75}As, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{95}Mo, ^{103}Rh, ^{105}Pd, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{182}W, ^{185}Re, ^{195}Pt, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
Internal standards	^{74}Ge, ^{103}Rh, ^{187}Re

2.3. Heavy metal determination by AAS

Standards of Cd, Cu and Pb (Analytika Ltd., Czech Republic) were used as reference analytes for the quantitative estimation of heavy metals and to ensure accurate calibration and quality assurance for each analyte. Standard stock solutions (1.0 g/L) were diluted to obtain working standard solutions that ranged from 0.2 to 4 μg/mL for Cd, from 0.5 to 4 μg/mL for Cu and from 2 to 40 μg/mL for Pb; solutions were stored at 4 °C. In all solutions, acidity was maintained with 0.1% nitric acid. A calibration curve was plotted between measured absorbance and concentration (μg/mL). All samples were analyzed in triplicate using a flame atomic absorption spectrophotometer (SensAA, GBS, Australia) with GBS Avanta software version 2.02.

2.4. Sample preparation

Approximately 0.25 g of dry biochar was predigested in 5 mL of a mixture of $HNO_3/HClO_4$ at a ratio of 7:1 (v/v) overnight at room temperature. Then, 3 mL of the acid mixture was added to clean the walls of tube, and the contents of the closed Teflon vessel were digested in a gradient to 100% power after 15 min and at 100% power for an additional 25 min. Digestion was performed in a Multiwave reaction system (Multi-wave PRO, Anthon Paar GmbH, Austria). The cooling required an additional 20 min. The volume of samples was filled to 10 mL and they were analyzed.

2.5. Biochar sample preparation

In order to keep the biochar particles size uniformity, eliminate the interference of other substances and microbial interference in biochars, the original samples were treated as follows: the particle size of the biochar was 0.4–0.8 mm after grinding. The microbial interference was excluded by 30 min UV irradiation.

2.6. pH measurement

The pH was determined on a 1:5 biochar/0.01 M $CaCl_2$ or biochar/distillate water suspension after 30 min of settling. Values of pH were determined using an UltraBasic pH meter (Denver Instrument Company, CO, USA).

2.7. Total carbon and nitrogen determination

For carbon and nitrogen analysis the Skalar Primacs SCN analyzer (Skalar Analytical, Breda, The Netherlands) was used. Total carbon was determined by heating the sample in the presence of a cobalt oxide catalyst at 1050 °C in pure oxygen and IR determination of evolved CO_2 at 4.2 μm. Total nitrogen was determined by analysis, which uses the Dumas method of combusting all nitrogen to NO_x.

2.8. PAH extraction and determination

Biochar (4 g) and anhydrous sodium sulphate (1 g) were placed in Erlenmeyer flasks and extracted with 40 mL of dichloromethane at 25 °C for 24 h.

The dichloromethane solution was evaporated to near dryness using a rotary evaporator (400 mbar, 70 rpm, water bath temperature 35 °C) and then dissolved in 2 mL of cyclohexane. Then, 1 mL of the cyclohexane was cleaned by silica gel column and eluted with acetone/hexane (1:1, v/v). Approximately 4 mL of eluent was collected and subsequently evaporated to dryness under nitrogen gas. The PAHs were dissolved in 1 mL of dichloromethane before HPLC analysis.

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