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Research article

Utilization of biochar and activated carbon to reduce Cd, Pb and Zn phytoavailability and phytotoxicity for plants

Kateřina Břendová [a, *], Veronika Zemanová [b], Daniela Pavlíková [a], Pavel Tlustoš [a]

[a] Department of Agroenvironmental Chemistry and Plant Nutrition, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 21 Prague 6, Czech Republic
[b] Isotope Laboratory, Institute of Experimental Botany, Academy of Sciences of the Czech Republic, Vídeňská 1083, 142 20 Prague, Czech Republic

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ABSTRACT

In the present study, the content of risk elements and content of free amino acids were studied in spinach (*Spinacia oleracea* L.) and mustard (*Sinapis alba* L.) subsequently grown on uncontaminated and contaminated soils (5 mg Cd/kg, 1000 mg Pb/kg and 400 mg Zn/kg) with the addition of activated carbon (from coconut shells) or biochar (derived from local wood residues planted for phytoextaction) in different seasons (spring, summer and autumn). The results showed that activated carbon and biochar increased biomass production on contaminated site. Application of amendments decreased Cd and Zn uptake by spinach plants. Mustard significantly increased Pb accumulation in the biomass as well in subsequently grown autumn spinach. Glutamic acid and glutamine were major free amino acids in leaves of all plants (15–34% and 3–45%) from total content. Application of activated carbon and biochar increased content of glutamic acid in all plants on uncontaminated and contaminated soils. Activated carbon and biochar treatments also induced an increase of aspartic acid in spinach plants. Biochar produced from biomass originated from phytoextraction technologies promoted higher spinach biomass yield comparing unamended control and showed a tendency to reduce accumulation of cadmium and zinc and thus it is promising soil amendment.

1. Introduction

Under the European Union (EU) Thematic Strategy for Soil Protection, the European Commission identified soil contamination; occurrence of 342 000 polluted sites was reported, most commonly polluted with heavy metals and mineral oil (Panagos et al., 2013). Key factor of elements toxicity or deficiency for plants is their plant-available concentration in soil (Alloway, 2012; Puga et al., 2015). Considering the reduction of hazardous elements bioavailability, the promising *in-situ* remediation method is the fixation of such elements by additives applied to the soil (Guo et al., 2006). These materials predominantly form complexes, precipitates with risk elements, and thus reduce their mobility (Basta and McGowen, 2004; Kumpiene et al., 2008).

Among a wide scale of available soil stabilization materials, inorganic and organic substances based on coal-like materials or combustion by-products have been investigated, e.g. coal or biofuel fly ashes (Clark et al., 2001) or lignite (Uzinger and Anton, 2008). In recent years the investigation was focused on biochar, stable carbon-rich charred biomass and its utilization as a soil additive (Qayyum et al., 2014).

Biochar (BC) has been evidenced to act as an efficient sorbent of various contaminants, organic and inorganic, because of its huge surface area and specific structure (Tang et al., 2013). Its sorption capacity is given by both its property and characteristics of bind element (Uchimiya et al., 2011). Mechanisms of risk element immobilization by biochar are different: i) development of hydroxides, carbonates, or phosphates, ii) precipitation (thanks to high pH of biochars, especially occurs for Pb immobilization; Wang et al., 2015), iii) electrostatic interaction between cations and functional groups (described as main mechanism for As sorption, Wang et al., 2015), iv) surface chemisorption between d-electrons of metals and π-electrons of biochar (Cao et al., 2009). Indirectly, biochar can caused risk element immobilization by increasing of pH, which increases negative charge of surface and thus increase soil affinity to cations of risk elements (Jiang et al., 2012).

Increased growth of ryegrass on contaminated acidic soil was observed, while metal uptake into shoots was reduced after biochar

* Corresponding author.
E-mail address: brendova@af.czu.cz (K. Břendová).

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application. However, decreasing growth occurs on alkaline contaminated soil where biochar dose excessing 0.5% was applied (Rees et al., 2015).

Plant response to biochar application was observed by Macdonald et al. (2014). They observed strong relationship between biochar effect on plant yield and soil type where biochar was applied. The significant plant response was observed after biochar application into acidic soils in comparison to alkaline ones, but high contrasts occur between different acidic soil types. Negative effect of biochar on plant growth was observed in acidic Arenosol, while high biomass yield was achieved in acidic Ferrosol.

Gregory et al. (2014) observed increasing ryegrass shoot growth after application of 1 and 2% of wood biochar into acidic soil. They also showed higher arsenic extraction by ryegrass shoots at amended treatments. Authors mentioned that more studies are needed to understand the mechanisms through which these benefits are provided.

The disposal of contaminated biomass is of major concern for phytoexreaction, therefore pyrolysis of it can be suitable technique. Application of biochar from contaminated biomass into soil was described by Jones and Quilliam (2014) and Evangelou et al. (2015).

Activated carbon (AC) is the most commonly used sorbent and is characterized by enhanced surface area due to thermal or chemical activation. This material successfully adsorbs especially organic substances (Bucheli and Gustafsson, 2000). Study of Kadirvelu et al. (2001) confirmed the ability of AC to bind heavy metals. There is lack of studies comparing biochar and AC sorption ability; however Hale et al. (2011), observed comparable abilities of these materials to adsorb organic substances.

There are studies describing BC or AC ability to reduce bioavailability of risk elements, but we were not able to find answers to the following questions:

Will be the effect of BC produced from local contaminated wood, without any surface activation comparable to purchased AC in term of reduction of risk elements bioavailability?

Can we observe any changes in metabolites reflecting external influences in plants, which are grown on soil amended by BC or AC?

Will the plants respond to BC or AC application also on uncontaminated soil?

Hypothesis and objectives of our study:

Hypothesis

1) Biochar produced from local wood residue will have similar ability to immobilize risk elements compare to activated carbon.
2) Plants grown in soil amended with biochar and activated carbon change some metabolites in plants.
3) The carbonaceous amendments will improve plant growth on contaminated soil in higher extend comparing uncontaminated one.

First aim of our study was to compare the ability of purchased AC produced from coconut shells with BC produced from local wood residues of phytoextraction technology to reduce accumulation of risk elements by spinach and mustard plants. The plants will be planted in rotation spring spinach-mustard-autumn spinach to observe amendments influence in longer term.

Secondly, the target was to show the direct and subsequent molecular plant response to BC or AC application into soil.

The third aim was to compare the effectiveness of applied BC or AC on contaminated and uncontaminated soils.

2. Materials and methods

2.1. Biochar and activated carbon characterization

Biochar was derived from willow biomass by pyrolysis. Willows were harvested on medium contaminated side of old smelter area of Příbram locality - short-rotation coppice plantations (49°42′24″ N, 13°58′32″ E; Zárubová et al., 2015). The process was conducted in a muffle furnace in the inert nitrogen atmosphere (nitrogen flow 1 m^3/h), at atmospheric pressure and retention time of 30 min. The process followed final temperature of 500 °C. It was characterized by: ash content = 13%, pH_{CaCl2} = 6.9, CEC = 176 $mmol_+$/kg, SSA_{BET} = 324 m^2/g, particle fraction = 5 × 6 × 0.5 mm.

Activated carbon was purchased from Erspol., Ltd. (Czech Republic) and was derived from coconut shells was characterized by: ash content = 12%, pH_{CaCl2} = 8.9, CEC = 73 $mmol_+$/kg, SSA_{BET} = 486 m^2/g (activated by water steam), particle fraction = 4 × 2 × 2 mm.

Content of C was determined by using the apparatus Flash EA 1112 in the CHNS/O configuration (Thermo Fisher Scientific, USA). The element content both in BC and AC were determined by neutron activation analysis with k0 standardization (k0-INAA) using short (1 min) and long irradiation (3 h) of neutrons in the reactor LVR-15 with the heat flux density of epithermal and fast neutrons (Kubešová and Kučera, 2010). Element contents of amendments are given in Table 1. The biochar is characterized by higher content of Cd, Pb, and Zn in comparison to AC.

2.2. Soil characterization

Soil was sampled from top layer (0–30 cm) of arable land in Prague - Suchdol (Czech Republic; 50°8′8″ N, 14°22′43″ E). The type of soil was modal Chernozem: pH_{KCl} = 7.2, CEC = 258 $mmol_+$/kg, $C_{org.}$ = 1.83%, contents of Cd = 0.3 mg/kg, Pb = 37.2 mg/kg and Zn = 113 mg/kg. Soil was air-dried and homogenized.

For determination of the total content of risk elements in soils 0.5 g of soil sample was decomposed in a closed system with microwave heating in the device Ethos 1 (MLS GmbH, Germany) in a mixture of 8 ml HNO_3, 5 ml HCl and 2 ml HF. The element contents in the soil digests and extracts were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 720, Agilent Technologies Inc., USA).

2.3. Experimental design

The experiment was established at greenhouse controlled conditions. Each pot was filled with 2.5 kg of soil. Spinach (*Spinacia oleracea* L. cv. Matador) and mustard (*Sinapis alba* L.) were chosen as experimental plants, while the crop rotation was spinach - mustard - spinach. Both plants are common edible crops and good accumulators, thus the prevention of risk elements uptake is necessary. The spinach (spinach 1 = S1) was sown in March and harvested after 64 days. Mustard (M) was sown in May and harvested after 35 days. Late spinach (spinach 2 = S2) was sown in

Table 1
Total element contents of activated carbon and biochar.

	K	Ca	Mg	Fe	Cd	Pb	Zn	C	N
	g/kg				mg/kg			(% w/w)	(% w/w)
AC[a]	0.5	2.9	2.2	4.1	<0.1	nd[b]	8.3	93	0.2
BC[a]	16.1	28	-	2.8	27	282[b]	950	64	1.1

[a] Determined by INAA.
[b] Determined by X-ray fluorescence; nd: levels below detection limit.