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Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (*Brassica napus* L.)

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ABSTRACT

Phytoremediation of soils contaminated by heavy metals was tested by liming ($CaCO_3$) or adding biochar (1%, 5% and 10%, mass fraction) and by growing rapeseed (*Brassica napus* L.), a common bioenergy crop. Bioavailable metal concentrations (0.01 mol L^{-1} $CaCl_2$ extraction) decreased with increasing concentrations of biochar amendment. The reduction reached 71%, 87% and 92% for Cd, Zn and Pb respectively in the presence of 10% biochar. Twelve weeks after sowing, all plants cultivated on the untreated soil and on the soil amended by biochar at 1% had died, while the plants grew normally on the soil that had the other treatments. Compared to liming, treatment with 10% biochar proved equally efficient in reducing metal concentrations in shoots but the biomass production tripled as a result of the soil fertility improvement. Thus, in addition to C sequestration, the incorporation of biochar into metal-contaminated soils could make it possible to cultivate bioenergy crops without encroaching on agricultural lands. Although additional investigations are needed, we suggest that the harvested biomass might in turn be used as feedstock for pyrolysis to produce both bioenergy and new biochar, which could contribute further to the reduction of CO_2 emission.

1. Introduction

Anthropogenic activities such as metal mining, smelting and refining, have contaminated soils with heavy metals in many places throughout the world [1]. Remediation of these hazardous soils by conventional practices, including excavation and landfilling, is unfeasible on large scale because these techniques are cost-prohibitive and environmentally disruptive. In contrast, phytoremediation, the use of vegetation for *in situ* restoration of contaminated soils, is generally considered a cost-effective and environmentally friendly approach [2]. However, it is increasingly recognized that the success of phytoremediation depends on its capacity to produce valuable biomass [3]. Since metal-contaminated soils represent a significant but hitherto neglected component of the global soil resource [4], developing biofuel crops on these

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soils could provide some relief in the "fuel versus food" dilemma [5,6]. However, cultivating metal-contaminated soils is complicated because, in most instances, several growth-limiting factors for the plants, such as a high phytotoxicity of the pollutants and poor fertility conditions, are acting simultaneously [7]. Hence, soil amendments are usually necessary to render the substrate suitable for the plant establishment [8,9].

Biochar is the result of biomass pyrolysis under minimal oxygen supply [10]. Amending the soil with biochar has increasingly attracted widespread attention for two reasons. First, because of its chemical stability, biochar is ideally suited for sequestrating C in soil [11,12]. Second, biochar is often regarded as a soil conditioner because its application rapidly increases the soil fertility and plant growth by supplying and retaining nutrients while simultaneously improving the physical and biological properties of the soil [13–15]. In addition, several results show that the addition of biochar in soil might help reduce the phytoavailability of heavy metals [16–18]. For these reasons, the application of biochar has recently been suggested as a sustainable means to promote the revegetation and the restoration of degraded lands [19,20].

The application of biochar to metal-contaminated soils could thus serve two purposes: to improve the soil conditions thereby allowing energy biomass and biofuel production, and to sequester C by burying part of the produced biomass.

The objective of this study was to assess to what extent the application of different concentrations of biochar to metal-contaminated soils affected the bioavailability of Cd, Zn and Pb and the biomass production of rapeseed (*Brassica napus* L.). We selected rapeseed as the study plant because this species belonging to the Brassicacea family has received much attention due to its fast growth, elevated fully-harvestable biomass production and high energy potential while being tolerant to high metal concentrations [21–24]. Because the increase of soil pH subsequent to biochar application has been reported to be an important mechanism involved in the metal immobilization [18,25], we compared the biochar treatments with a classical alkalinizing treatment (liming using $CaCO_3$).

2. Materials and methods

2.1. Study site

The study site is located at Sclaigneaux (50°30′03″ N, 5°02′56″ E; Namur province, Belgium). Although this 55 ha site is now a natural reserve accessible to the public, from the 1850s to the 1970s it was subjected to intense Cd-, Zn-, and Pb-bearing atmospheric fallout originating from adjacent zinc and lead smelters. A total mass of 250 kg of surface soil (0–14 cm) was obtained by composite sampling of a 20 × 20 m area that was colonized by metal-tolerant plant species (*Rumex acetosa* L., *Festuca nigrescens* Lam. and *Agrostis capillaris* L.). The soil was then air-dried for two weeks, crushed and sieved to a particle size of <2 mm in diameter. Particle size analysis using the pipette method revealed that the soil was a sandy loam (USDA classification) with 640 g kg^{-1} sand, 240 g kg^{-1} silt, and 120 g kg^{-1} clay. The soil pH, elemental composition, cation exchange capacity (CEC) and exchangeable cation contents determined according to Thomas [26] are listed in Table 1.

Table 1 – pH, cation exchange capacity (CEC), exchangeable cation content and elemental composition of the soil and the biochar.

		Soil	Biochar
pH		6.57	10.24
Organic C	g kg^{-1}	190	535
N	g kg^{-1}	4.2	3.1
CEC	cmol kg^{-1}	8.01	29.47
Exchangeable Ca	mg kg^{-1}	730	1690
Exchangeable K	mg kg^{-1}	47	12,203
Exchangeable Mg	mg kg^{-1}	97	388
Exchangeable Na	mg kg^{-1}	2	500
Ca	g kg^{-1}	2.38	10.50
K	g kg^{-1}	4.27	12.20
Mg	g kg^{-1}	0.98	3.95
Na	g kg^{-1}	1.45	1.37
P	g kg^{-1}	0.53	2.91
Cd	mg kg^{-1}	24.0	0.1
Zn	mg kg^{-1}	2980	116
Pb	mg kg^{-1}	3110	n.d.[a]

a n.d., Not detected.

2.2. Soil amendments

Commercial grade biochar was obtained from Pyreg GmbH (Dörth, Germany) who uses an industrial pyrolysis reactor and miscanthus (*Miscanthus* × *giganteus*) straw as feedstock. Operating conditions include a residence time in the reactor of 30 min and an end temperature of pyrolysis of 600 °C. In our experiments, the biochar was used as supplied, without prior washing to remove soluble salts. Table 1 presents selected properties of the biochar and shows that its heavy metal content was very low compared to that of the soil. The lime used for the comparison analyses consisted of calcium carbonate ($CaCO_3$) and was of *pro analysis* grade (Merck).

2.3. Substrate preparation

Untreated soil (control), soil treated by liming (lime) and soil treated by three concentrations of biochar amendment were used for this experiment. Biochar treatments were prepared by mixing the dry soil with a mass fraction of 1% (biochar-1%), 5% (biochar-5%) and 10% (biochar-10%) of biochar. Similar to Paulose et al. [27], liming treatment was prepared by mixing the soil with 5% $CaCO_3$. Amended soils were thoroughly homogenized in large plastic containers and individually prepared immediately prior to use.

Plastic plant pots (16-cm diameter, 22-cm height) were filled with a mixture of 1800 g of soil, 600 g of washed sand (to prevent soil compaction) and 10 g of fertilizer (Osmocote® slow-release fertilizer, N:P:K 14:14:14). The pots were placed in a climate-controlled dark room and the mixtures were equilibrated during four weeks at field capacity. Each treatment had five replicates.

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2.4. Preliminary soil characterization

After the equilibration period, a composite subsample of soil (about 100 g) from each pot was collected for characterization. After air-drying, the CEC was determined [26]. The metal composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Jarrell Ash) after calcination at 450 °C followed by acid digestion (HNO_3, $HClO_4$ and HF), as described in Lambrechts et al. [28]. The available nutrients (Ca, K, Mg, P) were measured using Mehlich 3 extraction [29]. Soil 0.01 mol L^{-1} $CaCl_2$-extractable concentrations of Cd, Zn and Pb were determined according to Houba et al. [30]. Soil pH (pH-$CaCl_2$) was measured in the 0.01 mol L^{-1} $CaCl_2$ extract.

2.5. Greenhouse pot experiment

The pots were transferred to a glass greenhouse and were arranged according to a randomized design. In each pot, 20 sterilized (10 min in 2 mol L^{-1} H_2O_2) seeds of rapessed (*B. napus* L.) were sown and the surface of the pot was covered by a thin layer (1–2 mm) of quartz grains; these prevented the surface from drying-out, prevented soil destructuration by drop impact and ensured watering flow homogeneity. The trials were conducted under controlled greenhouse conditions (temperature 18–25 °C, 16-h photoperiod) with daily watering. Four weeks after sowing, excess germinated seedlings were removed (first harvest) so that only three uniform plants per pot were allowed to grow for the following eight weeks. At the end of the experiment (i.e., 12 weeks after sowing), the shoots of the surviving plants were harvested (second harvest). The total duration of the rapeseed cultivation was similar to that used in the study of Brunetti et al. [21].

When harvesting, the rapeseed shoots were cut at 1 cm above the soil surface using ceramic scissors. Plants were weighed for fresh biomass determination, then dried (60 °C; 72 h) and re-weighed for dry biomass determination. Shoot water content (SWC) was calculated by subtraction. The nutrient (Ca, K, Mg and P) and heavy metal (Cd, Zn, and Pb) contents of the plant were analyzed by ICP-AES after grinding and digesting the dried biomass in a tri-acid mixture ($HClO_4$, HNO_3 and HF) [28]. The bioconcentration factor (BCF) was calculated as the ratio between the heavy metal concentration in the plant shoot and the total heavy metal concentration in the soil [31].

2.6. Statistical analyses

Statistical analyses to compare the average results of the different treatments were performed using a one-way analysis of variance (ANOVA) followed by Fisher's test ($p < 0.05$) for multiple comparisons. Prior to ANOVA, normality of data (Shapiro–Wilk's test) and homogeneity of variances (Levene's test) were tested. Logarithmic transformation was applied to dependent variables when necessary. All statistical analyses were carried out using XLSTAT (Addinsoft, ver. 2010.5.08).

3. Results and discussion

3.1. Soil characteristics

The soil pH was clearly modified by the amendments. Table 2 shows that the pH (pH-$CaCl_2$) of the soil significantly increased with the concentration of biochar amendment, starting from 5.62 in the control to 6.70 in the biochar-10% treatment. A similar trend was observed by Fellet et al. [20] using the same concentrations of biochar application. The increase in soil pH after the application of biochar may be attributed to the alkaline nature of biochar (Table 1). As a liming agent, the application of $CaCO_3$ logically increased the soil pH.

By the end of the equilibration period, the addition of 5% and 10% biochar slightly but significantly increased the soil CEC (Table 2). This increase of soil CEC in the presence of biochar is in agreement with earlier findings [15,32,33]. According to Cheng et al. [34], the soil CEC enhancement after biochar application should become much more important with time due to the continuous oxidation of the biochar surfaces and the adsorption of organic acids by the biochar.

Significant increases in available nutrients were observed and raised with the amount of biochar added (Table 2). Potassium was the nutrient which increased the most; its available content was multiplied by 2.8, 7.5 and 15.4 after the application of 1%, 5% and 10% biochar respectively compared to the control. Similar to Laird et al. [14], we attributed the increase in available nutrient content with increasing levels of biochar predominantly to the presence of these nutrients in the biochar itself and especially in the ash it inevitably contains. According to Glaser et al. [13], ash in biochar rapidly

Table 2 – pH-$CaCl_2$, cation exchange capacity (CEC), plant-available nutrient (Mehlich 3 extractable Ca, K, Mg, P) and total metal contents. Row means ($n = 5$) with the same letter do not differ significantly at the 5% level according to the Fisher's multiple comparison test.

		Control	Biochar-1%	Biochar-5%	Biochar-10%	Lime
pH-$CaCl_2$		5.62a	5.65a	6.21b	6.70c	7.76d
CEC	cmol kg^{-1}	5.54a	5.45a	5.94b	6.16b	5.26a
Available Ca	mg kg^{-1}	512a	528a	557a	687b	3640c
Available K	mg kg^{-1}	42a	116a	317b	646c	40a
Available Mg	mg kg^{-1}	76a	83a	92b	127c	83a
Available P	mg kg^{-1}	16b	17b	21c	34d	13a
Total Cd	mg kg^{-1}	18a	19a	18a	18a	18a
Total Zn	mg kg^{-1}	2310a	2310a	2200ab	2060b	2220ab
Total Pb	mg kg^{-1}	2020a	2050a	1940ab	1870b	1960ab

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releases free bases such as K, Ca, and Mg ions into the soil solution thereby increasing the pH value of the soil and providing readily available nutrients for plant growth. The highest available Ca content was found for the lime treatment, which is obviously related to the massive input of Ca brought about by the $CaCO_3$ application. By contrast to biochar, the application of lime had no effect on the available content of both K and Mg and even decreased significantly the available P with respect to the control. According to Bolan et al. [35], the available P content decreased in limed soils due to both the precipitation of P as calcium phosphate and the higher proportion of divalent phosphate ion (HPO_4^{2-}), i.e. the P species considered to be adsorbed.

While the other treatments had no significant effects, biochar-10% significantly decreased the total concentrations of Zn and Pb in pots compared to the control. This reduction was most likely a simple dilution effect of the soil by the high addition of biochar.

3.2. Extractable (0.01 mol L^{-1} $CaCl_2$) heavy metal concentrations

Although current legislative frameworks for soil pollution are mainly based on total metal content, it is largely recognized that environmental risks inherent to the presence of heavy metals in soils are mainly dependent on their bioavailable concentrations [36]. These can be assessed by 0.01 mol L^{-1} $CaCl_2$ extraction, which is widely reported as being a proxy for bioavailability of metals in soils to plants [28,36,37].

The $CaCl_2$-extractability of Cd, Zn and Pb significantly decreased after the incorporation of biochar (Table 3). Reduction of the metal extractability increased with the concentration of biochar application. Compared to the control, incorporation of 1% biochar reduced $CaCl_2$-extractable Cd, Zn and Pb concentrations by 14%, 15% and 29%, respectively. In the presence of 5% biochar, the reduction reached 44%, 52% and 76%, while in the presence of 10% biochar, it reached 71%, 87% and 92% for Cd, Zn and Pb, respectively. Since pH is the most important parameter controlling the $CaCl_2$-extractability of metals in soils [38], the decrease in extractable metal concentrations can be attributed in a part to a significant increase in soil pH due to the addition of biochar (Table 2). This is supported by the negative relationship between pH and $CaCl_2$-extracatable metal concentrations (Fig. 1). Similarly, other studies have previously suggested that raising the pH could be one mechanism by which metal mobility was reduced by biochar [25,39]. The very high reduction of metal $CaCl_2$-extractability after liming (95%, 99% and 99% for Cd, Zn and Pb, respectively) confirms that metal immobilization in the study soil was highly sensitive to pH elevation. According to the literature, the main responsible mechanisms for metal immobilization at elevated pH are the heavy metal precipitation in the form of oxides, hydroxides, carbonates and phosphates [40] and the reduction of heavy metal solubility [41,42]. In our experiment, the increase in soil pH probably further enhanced the adsorption of metals because it increased the negative charge not only on the soil components [43,44] but also on the biochar particles because biochar predominantly possesses pH-dependent charges [45]. It is likely that the slight CEC increase after biochar application (Table 2) also contributed to the metal immobilization because the $CaCl_2$-extractability of metals is known to be negatively related to CEC [46]. Since CEC in soils amended with biochar increases with time [34], offering potentially new sites for metal sorption, further studies should be conducted to determine whether the CEC effect on metal retention intensifies in the long run.

3.3. Plant growth and metal uptake

Three weeks after sowing, visible signs of metal toxicity in the above ground parts of rapeseed (leaf chlorosis, dessication and growth retardation) were already marked for plants that grew on the untreated and the biochar-1% treated soils (Fig. 2). Such symptoms are usual for rapeseed plants submitted to metal stress and their metabolic origins have been addressed by several studies [47–49]. The very low SWC as well as the limited biomass production measured in these plants at the first harvest (Table 4) are also symptoms commonly observed in metal-stressed plants [50]. Moreover, plants remaining in the pots after the first harvest were not able to grow any longer on both the control and the biochar-1% treatment. The mortality of rapeseed seedlings due to metal toxicity is consistent with other studies [51,52]. Hernández-Allica et al. [53] found that concentrations of Cd 92 mg kg^{-1}, of Zn 10,916 mg kg^{-1}, and of Pb 328 mg kg^{-1} in rapeseed shoots caused the inhibition of the shoot growth by about 100%. In our study, the shoot concentrations of Cd and Zn in rapeseed grown on both the control and the biochar-1% treatment were very close to their respective threshold values reported by Hernández-Allica et al. [53] while Pb was much less concentrated (Fig. 3). Therefore, data suggest that in this study both Cd and Zn are toxic elements that were predominantly responsible for the death of the plants. However, these threshold values were assessed using mono-metallic and hydroponic cultures. Here, the simultaneous presence of elevated Cd, Zn and Pb concentrations in the soil most likely reinforced the soil toxicity since these metals may have strong synergetic effects on the growth of rapeseed [54].

The reduced metal bioavailability after liming and application of 5% and 10% biochar (Table 3) resulted in a

Table 3 – Extractable (0.01 mol L^{-1} $CaCl_2$) heavy metal concentration in the five substrates. Row means ($n = 5$) with the same letter do not differ significantly at the 5% level according to the Fisher's multiple comparison test.

		Control	Biochar-1%	Biochar-5%	Biochar-10%	Lime
Cd	mg kg^{-1}	3.68a	3.15b	2.05c	1.08d	0.18e
Zn	mg kg^{-1}	136a	116b	64.0c	18.2d	0.99e
Pb	mg kg^{-1}	2.41a	1.72b	0.59c	0.19d	0.01e

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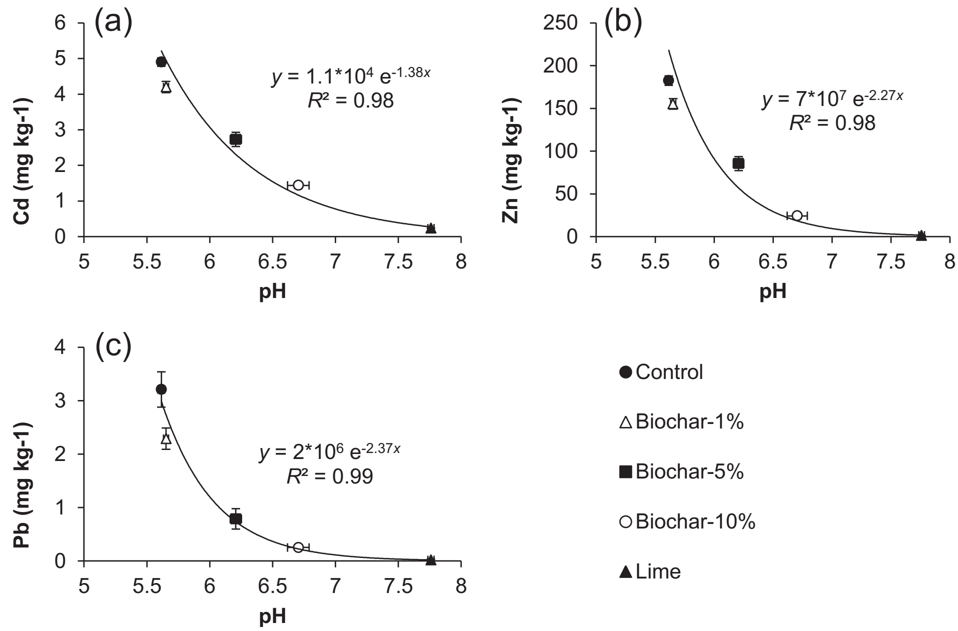

Fig. 1 – Relationships between pH (pH-CaCl2) and extractable (0.01 mol L^{-1} $CaCl_2$) concentrations of Cd (a), Zn (b), and Pb (c). Values are averages (n = 5) ± standard deviations.

significant decrease in metal concentration in shoots from the first harvest. As depicted in Fig. 3, the application of 5% and 10% biochar lowered the metal shoot concentrations at the first harvest by 47% and 75%, respectively for Cd, 65% and 91% for Zn, and 33% and 59% for Pb. Compared to the control, the addition of lime had a similar impact to that of the biochar-10% treatment (Fig. 3). This suggests that the liming effect played a significant role in the reduction of the metal bioavailability, as previously shown by results of $CaCl_2$ extraction (Fig. 2). This is consistent with other results [18] which showed that the metal uptake by plants in soils amended with biochar was rapidly reduced as a result of the increase of soil pH. By alleviating the metal phytoavailability, the biochar-5% and biochar-10% and the lime application enabled the plants to survive and grow without presenting any toxicity symptoms during the entire cultivation period (except a slight yellowing in shoots from the biochar-5% treatment). Moreover, the increase in biomass throughout the experiment (Table 4) was globally accompanied with a decrease in heavy metal concentrations in the shoots (Fig. 3). In accordance with other studies [16,18], this may reflect both a decline of metal bioavailability with time and a dilution effect as a result of increasing plant biomass.

At the end of the experiment, although both the liming and biochar-10% treatments were equally effective in reducing Cd, Zn and Pb concentrations in the shoots (Fig. 3), our results showed a significant increase in the rapeseed biomass production when biochar was applied (Table 4). The biomass of plants harvested on the biochar-10% treatment was 9.7 and 3.1 times higher than that of plants grown on the biochar-5% and lime treatments, respectively. Although all the soil treatments received slow release N:P:K fertilizer (Osmocote), the nutrients supplied by biochar and the improved soil conditions such as pH and CEC (Table 2) may have contributed to the high biomass production induced by this treatment. It can thus be inferred that higher biomass production in the presence of 10% biochar was not only due to the alleviation of metal phytotoxicity but also to the enhancement of soil fertility. This is consistent with other studies [15,55] that reported higher plant productivity when biochar was applied and attributed this enhancement to the increase in soil available nutrients. The reduction of metal bioavailability likely contributed to the increase of both K and P concentration in the shoots from the first harvest in biochar-5%, biochar-10% and lime treatments since accumulation of these nutrients in rapeseed shoots was found to decrease with increasing metal toxicity [49]. However, the application of

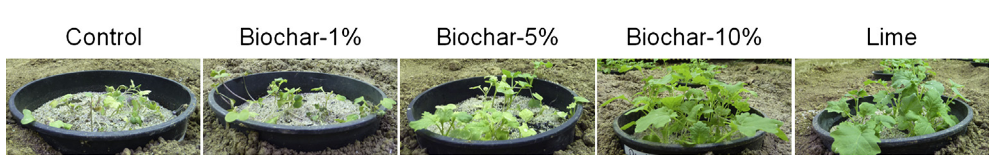

Fig. 2 – Representative image showing the differences in rapeseed (*Brassica napus* L.) growth between soil and treatments three weeks after sowing, from left to right: untreated soil (control), biochar-1%, biochar-5% biochar-10% and lime treatments. Only one of the five replicates is shown for each treatment.

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Table 4 – Dry biomass per plant, shoot water content (i.e. mass of water per kilogram of biomass; SWC) and Ca, K, Mg and P concentrations in rapeseed (*Brassica napus* L.) shoots at the first and the second harvests (4 and 12 weeks after sowing, respectively). For each harvest, column means ($n = 5$) with the same letter do not differ significantly at the 5% level according to the Fisher's multiple comparison test.

	Treatment	Biomass per plant, mg	SWC, g kg^{-1}	Ca, g kg^{-1}	K, g kg^{-1}	Mg, g kg^{-1}	P, g kg^{-1}
First harvest	Control	13a	320a	26.1b	33.6a	7.5b	2.5a
	Biochar-1%	15a	356a	29.5c	49.6b	9.0c	2.9a
	Biochar-5%	19a	841b	28.7bc	81.8d	9.1c	3.5b
	Biochar-10%	49b	903b	19.8a	89.3e	7.1b	3.8b
	Lime	51b	893b	33.4d	66.8c	4.6a	3.8b
Second harvest	Biochar-5%	419a	916a	28.0a	54.0b	6.9b	3.2a
	Biochar-10%	4080c	881a	25.1a	46.5b	4.8a	3.7ab
	Lime	1312b	900a	26.9a	43.1a	4.3a	4.3b

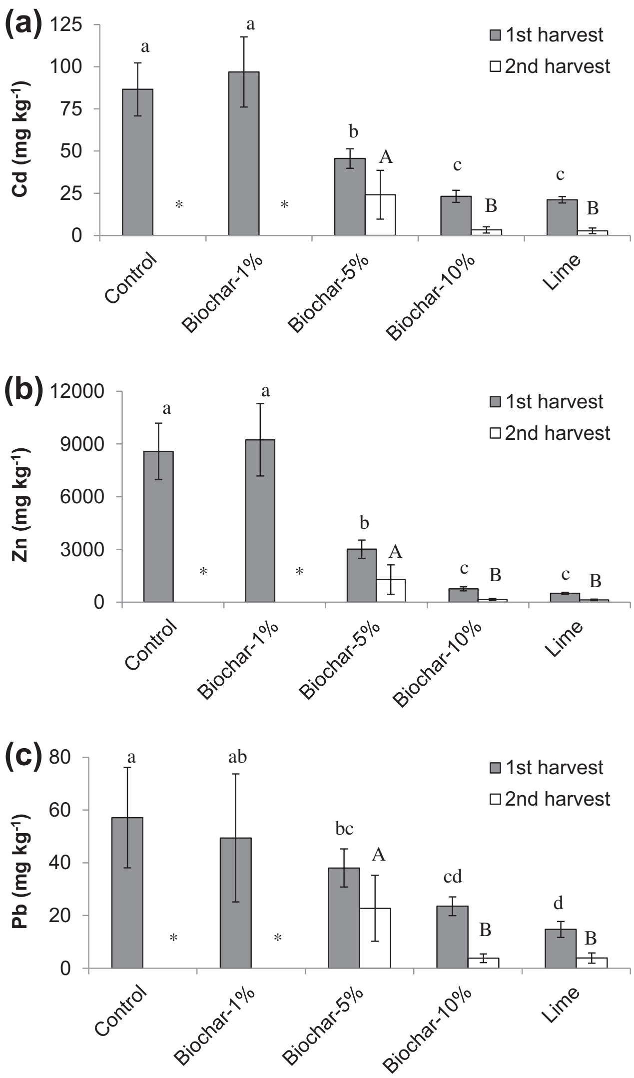

Fig. 3 – Cd (a), Zn (b) and Pb (c) concentrations in rapeseed (*Brassica napus* L.) shoots at the first and the second harvests (4 and 12 weeks after sowing, respectively). Values are average ($n = 5$) ± standard deviation. Columns with the same letter do not differ significantly at the 5% level according to the Fisher's multiple comparison test. *No data are available for plants on the control and the biochar-1% treated soils at the second harvest because all plants had died.

biochar-5% and biochar-10% significantly increased the K concentration in shoots from the first harvest in comparison with the lime treatment (Table 4). This marked increase with increasing levels of biochar (Table 4) reflects the great improvement in soil K availability after biochar application (Table 2). Such a relationship was nevertheless less evident for the other nutrients. At the second harvest, the absence of any significant increase in nutrient concentrations in shoots in the presence of 10% biochar was probably due to a dilution effect caused by the much higher rapeseed biomass (Table 4).

3.4. *Bioconcentration factor (BCF) and impact on phytoremediation strategies*

For rapeseed grown on metal-contaminated soils, Fornes et al. [56], Brunetti et al. [21] and Romih et al. [23] reported BCF values ranging from 0.05 to 1.01 for Cd, 0.05 to 1.17 for Zn and 0.002 to 0.05 for Pb. Compared to these values, rapeseed grown on the control and 1% biochar-amended soils exhibited largely higher BCFs for Cd and Zn (Table 5), indicating that the uptake of Cd and Zn by the plants was unrestricted. On the contrary, in the biochar-5%, biochar-10% and lime treatments, metal uptake was restricted, even during the first harvest. The BCFs for Cd, Zn and Pb were in the range of, or lower than, the above-reported values, except for the BCF measured for Cd (both harvests) and Zn (first harvest) in plants grown on the biochar-5% treated soil (Table 5). According to McGrath and Zhao [31], phytoextraction is not feasible when plants have a

Table 5 – Bioconcentration factor (BCF = shoot metal concentration/soil total metal concentration) of Cd, Zn and Pb in rapeseed (*Brassica napus* L.) at the first and the second harvests (4 and 12 weeks after sowing, respectively).

	Treatment	Cd	Zn	Pb
First Harvest	Control	4.81	3.72	0.028
	Biochar-1%	5.10	4.00	0.024
	Biochar-5%	2.53	1.37	0.020
	Biochar-10%	1.29	0.37	0.012
	Lime	1.17	0.22	0.008
Second Harvest	Biochar-5%	1.66	0.73	0.020
	Biochar-10%	0.18	0.07	0.002
	Lime	0.15	0.06	0.002

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BCF value lower than 1, regardless of how large the achievable biomass is. Our study shows that combining biochar soil incorporation with rapeseed cultivation for phytoextraction purposes would not be realistic since plants with a BCF value higher than 1 did not survive while the surviving plants exhibited BCF values lower than 1 (Table 5). Phytoextracting heavy metals to reach acceptable metal levels in the soil would consequently require an excessively long amount of time. However, the large decrease in heavy metal bioavailability and shoot concentration we observed as well as the increase in valuable biomass production make the combination of biochar incorporation into the soil and rapeseed cultivation both environmentally and economically suitable as a phytostabilization strategy [3].

3.5. *Practical implications*

Recently, Witters et al. [22,57] provided evidence that phytoremediation, when used to produce bioenergy crops including rapeseed, could positively abate atmospheric CO_2 while being economically efficient. Energy can be obtained from such crops using pyrolysis [58,59]. This technique generates biochar which can be incorporated into the soil to reduce greenhouse gas emissions [60,61]. Investigating the potential use of 10 by-products from different bioenergy chains as soil amendments, Cayuela et al. [62] concluded that biochar was the ideal by-product for mitigating climate change because it contains highly stable C and does not promote N_2O formation and emission. Pyrolysing biomass harvested on metal-contaminated soils for production of both bioenergy and biochar followed by biochar incorporation into the soils could be therefore a suitable option for contributing to climate change mitigation. This would be feasible provided that feedstock biomass does not contain excessive metal levels. Indeed, Liu [63] demonstrated that, although the pyrolysis of heavy metal-contaminated biomass produces both noncondensable fractions and bio-oil with a very low amount of heavy metals, ensuring their application in many fields without secondary pollution, the major part of metals is retained in the biochar. As a result, biochar enriched in heavy metals would not be suitable for soil application and would require burial in a secure landfill [64]. In our study, rapeseed grown on biochar-10% treatment presented Zn and Pb concentrations of 147 mg kg^{-1} and 3.80 mg kg^{-1} respectively, which is within or below the “normal” range of metal concentration commonly found in shoots of various plant species (25–150 mg kg^{-1} and 5–10 mg kg^{-1} respectively [65]) while Cd concentration (3.29 mg kg^{-1}) was above the “normal” range of Cd concentration (0.01–0.2 mg kg^{-1}) but still lower than the excessive or toxic range of concentrations (5–30 mg kg^{-1} [65]). Although these data indicate that rapeseed grown in the presence of 10% biochar did not present excessive metal concentration and could therefore possibly be used to produce new biochar, clear guidelines for biochar production from various feedstock are nevertheless essential to ensure that biochar compositions meet acceptable standards [66].

An additional advantage of biochar incorporation is the improvement of soil fertility parameters such as nutrient contents, pH and CEC (Table 2) and water retention capacity [20] thereby lessening the need for fertilizer and irrigating water. Moreover, the agronomic benefits of biochar last longer than those offered by any other form of organic matter (e.g. manure or compost) commonly applied to land due to its greater efficiency in retaining nutrients and keeping them available as well as its favorably long persistence in soil [67].

4. Conclusion

The incorporation of biochar into metal-contaminated soils decreased the availability of Cd, Zn and Pb and improved the production of rapeseed (*B. napus* L.). This has implications for the use of contaminated soils for growing bioenergy crops combined with simultaneously sequestering C in the soil. Compared to liming, the application of 10% biochar presented similar efficacy in decreasing the heavy metal concentration in rapeseed shoots but tripled biomass production. Since the biomass that was harvested in the presence of 10% biochar did not present excessive metal concentrations in comparison with the normal range of various plants, it might be pyrolyzed to provide both bioenergy (e.g. biofuels) and new non-polluting biochar. Our study shows that contaminated land that is unsuitable for growing food crops can be used in a scheme that combines soil reclamation through phytoremediation, biochar utilization and bioenergy production. Further studies including life cycle assessment and evaluation of external costs are needed to quantify the societal, economic and environmental pros and cons associated with this combination strategy.

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