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RESEARCH ARTICLE

Trace element biogeochemistry in the soil-water-plant system of a temperate agricultural soil amended with different biochars

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Abstract Various biochar (BC) types have been investigated as soil amendment; however, information on their effects on trace element (TE) biogeochemistry in the soil-water-plant system is still scarce. In the present study, we determined aqua-regia (AR) and water-extractable TEs of four BC types (woodchips (WC), wheat straw (WS), vineyard pruning (VP), pyrolyzed at 525 °C, of which VP was also pyrolyzed at 400 °C) and studied their effects on TE concentrations in leachates and mustard (*Sinapis alba* L.) tissue in a greenhouse pot experiment. We used an acidic, sandy agricultural soil and a BC application rate of 3 % (*w*/*w*). Our results show that contents and extractability of TEs in the BCs and effectuated changes of TE biogeochemistry in the soil-water-plant system strongly varied among the different BC types. High AR-digestable Cu was found in VP and high B contents in WC. WS had the highest impact on TEs in leachates showing increased concentrations of As, Cd, Mo, and Se, whereas WC application resulted in enhanced leaching of B. All BC types increased Mo and decreased Cu concentrations in the plant tissue; however, they showed diverging effects on Cu in the leachates with decreased concentrations for WC and WS, but increased concentrations for both VPs. Our results demonstrate that BCs may release TEs into the soil-water-plant system. A BC-induced liming effect in acidic soils may lead to decreased plant uptake of cationic TEs, including Pb and Cd, but may enhance the mobility of anionic TEs like Mo and As. We also found that BCs with high salt contents (e.g., straw-based BCs) may lead to increased mobility of both anionic and cationic TEs in the short term.

Keywords Biochar · Heavy metals · Trace elements · Leaching · Sorption · Plant uptake

Symbols and Abbreviations

BC	Biochar
WC	Woodchip-derived biochar
WS	Wheat straw-derived biochar
VP400	Vineyard pruning-derived biochar (pyrolysis temperature 400 °C)
VP525	Vineyard pruning-derived biochar (pyrolysis temperature 525 °C)
TE	Trace element
EC	Electrical conductivity
CEC	Cation exchange capacity
SSA	Specific surface area
EBC	European Biochar Certificate

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Introduction

Biochar (BC) is the solid product of pyrolysis, which is the thermal decomposition of biomass under low-oxic conditions (Sohi et al. 2009). BC is increasingly promoted as a new soil additive because of a multitude of expected positive effects. These include the potential to sequester carbon (C) while increasing soil fertility, promoting plant growth, and remediating contaminated soils (Kuhlbusch and Crutzen 1995; Lehmann and Joseph 2009; Beesley et al. 2011; Houben et al. 2013a). However, BC may simultaneously induce unwanted effects for the soil-water-plant system including enhanced solubility and bioavailability of potentially toxic trace elements (TEs).

TE solubility and bioavailability are closely linked to soil pH (Adriano 2001) that was often found to increase upon BC application (Major 2010; Rondon et al. 2007; Van Zwieten et al. 2007) and positively affect soil sorption potential of cationic TEs (Tang et al. 2013). Several studies showed that BC application to soil immobilized Cu, Cd, Zn, and Pb (Houben et al. 2013b; Jiang and Xu 2013; Kim et al. 2013; Li et al. 2013). This makes BC a useful tool for soil remediation. However, it must be emphasized that the BC remediation potential may only be true for cationic TEs. Up to now, there are only few studies on anionic TE biogeochemistry in BC-amended soils. For instance, Beesley et al. (2013) found that BC application to soil increased As concentration in the pore water, which is toxic even at low concentrations (Oves et al. 2012). In addition to an impairment of the groundwater with high levels of anionic TEs, excessive plant concentrations of anionic micronutrients such Mo may reach toxic levels as a result of the pH increase by BC additions, whereas a concomitant decreased plant transfer of cationic micronutrients due to increased retention may lead to micronutrient deficiency in plants (Agrawal et al. 2011; Alloway 1995; Alloway 2013a; Alloway 2013b).

The properties of BC can be influenced by adjusting the pyrolysis conditions such as the highest treatment temperature (HTT; Downie et al. 2009), which is then reflected in feedstock-dependent effects on the soil (Dai et al. 2013; Lei and Zhang 2013). Important characteristics of BC include a high pH, porosity, specific surface area (SSA), and cation exchange capacity (CEC) while also directly adding nutrients to the soil (Bagreev et al. 2001; Chan and Xu 2009; Lua et al. 2004; Singh et al. 2010). The pyrolysis process may concentrate TEs in the BCs compared to the original feedstock with feedstock-dependent differences (Bridle and Pritchard 2004; Oleszczuk et al. 2013; Meng et al. 2013). Parts of the BC-derived TEs may be water-extractable and thus bioavailable (Zhao et al. 2013), which may increase TE concentrations in both plants and leachates. The potential accumulation of TEs in BCs has been addressed in voluntary quality control efforts such as the European Biochar Certificate (EBC; Schmidt et al. 2012) and International Biochar Initiative (IBI 2013) guidelines introducing TE limit values in order to promote the production and application of “low-hazard” BCs.

Prior to the present study, we found that especially anionic TEs were mobilized upon application of wood-derived BC to three different soils, which was not only due to liming, but also due to direct release of TEs and salt input from the BC (Kloss et al. 2014b). Straw-derived BC may stand out from other BC types due to its high ash and salt content as well as high level of P, K, and other cations (Kloss et al. 2012; O’Toole et al. 2013; Ronsse et al. 2013; Wu et al. 2012). Based on this knowledge, the addition of different BC types may thus affect TE behavior in soils not only by changing soil pH, but also by changing other soil properties, for example, the ionic strength of the soil solution (Young 2013). BC-driven increase in soil electrical conductivity (Méndez et al. 2012; Singh et al. 2010) may enhance ion competition for binding sites (Acosta et al. 2011; Khanmirzaei 2012) between BC-derived salts and TEs and result in increased TE solubility irrespective of their charge.

Based on the above discussion, assets and drawbacks must be carefully considered before applying BC to the soil. The present study aims at improving our knowledge on environmental impacts of BC application to soils. To this end, we focused on the effects of different BC types (with regard to feedstock type and pyrolysis temperature) on the biogeochemistry of cationic and anionic TEs in the soil-water-plant system of a temperate agricultural soil using a greenhouse pot experiment under controlled conditions. We hypothesized that

– TEs introduced by BCs lead to increased TE leaching and plant uptake (H_1),
– Beyond a BC-induced liming effect (known to decrease the mobility of cationic TEs and increase the mobility of anionic TEs), BCs with high salt concentrations further promote the leaching of both anionic and cationic TEs (H_2).

Materials and methods

Soil and biochar characterization

The top 0.3 m of an agricultural soil was sampled in Lower Austria (48° 46′ 32.9″ N, 15° 14′ 28.6 E) in summer 2010, air-dried, and homogenized. The soil developed over granite and was classified as Planosol, exhibiting a sand content of approximately 70 % (sandy loam), a pH (in 0.01 M $CaCl_2$) of 5.4, an electrical conductivity (EC) of 41.2 $\mu S\ cm^{-1}$, and a CEC amounting to 75.1 $mmol_c kg^{-1}$.

Three different plant-derived feedstocks were chosen for BC production: wheat straw (*Triticum aestivum*), vineyard pruning (*Vitis vinifera*), and mixed woodchips. The BCs from wheat straw (WS) and mixed woodchips (WC) were produced by slow pyrolysis in a rotary furnace with an HTT of 525 °C (residence time 60 min). Slow pyrolysis of pruning-derived BC was conducted in a stainless tube furnace at two HTTs: 400 °C (VP400; residence time 8 h) and 525 °C (VP525; residence time 6 h). Pyrolysis was carried out at bench scale under argon atmosphere.

The determination of pH, EC, ash content, CEC, SSA, and organic carbon (OC) of the BCs was performed according to standard methods as described in Kloss et al. (2012). The volatile matter (VM) content was determined in duplicate according to Enders et al. (2012), based on ASTM D-1762-84 Chemical Analysis of Wood Charcoal. To this end, 1.00 g of BC was weighed into crucibles and dried overnight at 105 °C. Samples were reweighed, then placed into a preheated furnace at 950 °C for 10 min. Crucibles were then cooled, each in its own dessicator, prior to reweighing. The VM (wt%) was calculated as follows:

$$Volatile\ matter\ \% = \frac{weight_{105^\circ C\ dried} - weight_{950^\circ C\ devolatilized}}{weight_{105^\circ C\ dried}} \times 100$$

The basic BC characterization is compiled in Table 1 and discussed in detail in Kloss et al. (2014a).

TEs in the BCs were determined by aqua regia (AR) digestion and water extraction, respectively. AR digestion was carried out with 30 % HCl/65 % HNO_3=3:1 (*v*/*v*) including backflow capture (according to ÖNorm L 1085 2009). For the water extraction, 2 g of ground BC was weighed into plastic flasks; 40 mL of distilled water was added, shaken for 24 h, filtered, and then stabilized using 1 vol.% HNO_3 (65 %). The TE concentrations in all extractions were measured by inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer, Elan DRCe 9000).

Experimental setup and crops

The pot experiment was set up in a greenhouse starting in October 2010. BC application rate to the soil was 3 wt%, which corresponds to 90 t ha^{-1} at an incorporation depth of 0.2 m. The air-dried soil-BC mixtures were generated and homogenized in a closed cement mixer and then filled into pots with a height of 0.4 m and a diameter of 0.235 m. For the collection of leachate water, the bottom of each pot was equipped with a siphoned outlet, covered with a mesh followed by two layers of quartz sand (15 mm coarse sand and 15 mm fine sand). In total, the study comprised five treatments: control (Planosol without BC), Planosol +3 % WC, Planosol +3 % WS, Planosol +3 % VP400, and Planosol +3 % VP525. Each treatment consisted of five replicates. TDR (Trase multiplex system 1 6050X1, Soil Moisture Equipment Corp., Santa Barbara, USA) or Echo (10 HS, Decagon Devices Inc., WA, USA) probes were installed in one replicate of each treatment to control the water content and carry out the irrigation according to the requirements of each treatment. Irrigation was performed using artificial rainwater (3 mg Ca L^{-1}; 50 % $CaCl_2 \times 2H_2O$, 50 % $CaSO_4 \times 2H_2O$). The pots were planted with mustard (*Sinapis alba* L. cv. Serval; November 26, 2010 to February 17, 2011; 50 seedlings per pot, sowing density of 3 g m^{-2}), followed by barley (*Hordeum vulgare* cv. Xanadu; February 18 to June 20, 2011; 10 seedlings per pot, thinned to 7 per pot in the 2-leaf stage in order to achieve a homogenous canopy). Each pot additionally received mineral fertilizer ($N/P_2O_5/K_2O/S = 15:15:15+3$; *Linzer Star*) amounting to 40 kg N ha^{-1} for mustard and 100 kg N ha^{-1} for barley. Temperature was controlled as follows: night minima, 14±2 °C in winter, 18±2 °C in summer; day maxima, 20

Table 1 Basic characterization of the four different biochars (*n*=3)

	Woodchips (525 °C)	Wheat straw (525 °C)	Vineyard pruning (400 °C)	Vineyard pruning (525 °C)
Ash content (wt%)[a]	15.2	28.1	4.3	7.7
pH (0.01 M $CaCl_2$)	8.9±0.1 b	9.7±0.0 c	8.3±0.0 a	8.8±0.1 b
EC (mS cm^{-1})	1.58±0.02 c	5.18±0.06 d	1.48±0.03 b	1.08±0.03 a
CEC ($mmol_c kg^{-1}$)	93.0±1.9 b	148.5±0.8 d	123.5±1.3 c	78.8±1.4 a
OC (%)	67.1±1.3 b	56.3±2.4 a	69.3±0.2 b	73.1±0.9 c
BET-N_2 SSA (m^2 g^{-1})	26.4±0.8 d	12.3±1.3 c	1.7±0.1 a	4.8±0.3 b
VM (wt% $_{\text{ash free mass}}$)	16.9±1.1 b	11.0±1.0 a	35.2±0.4 d	21.0±0.1 c

Values are reported as means±standard deviation

EC electrical conductivity, *CEC* cation exchange capacity, *OC* organic carbon, *SSA* specific surface area, *VM* volatile matter

Different letters indicate significant differences within one line ($p<0.05$; one-way ANOVA; Tukey's post hoc test). Parenthesized temperature stands for pyrolysis temperature

[a] Single determination

±2 °C in winter, 25±2 °C in summer. Mustard was cultivated under natural light conditions characteristic for late autumn (9/15 h day/night) and also spring barley experienced a natural photoperiod (shift from 12/12 to 15/9 h day/night during the growth period).

Soil, plant, and leachate sampling and analyses

Before filling the pots, a subsample of each newly generated soil-BC mixture was taken (*n*=3; sampling date November 23, 2010) to investigate the immediate effects of BC addition to the soil. Another soil sampling was carried out after 7 months (July 8, 2011; *n*=4; pots containing moisture probes were not sampled to avoid probe damages). For sorption experiments, a third soil sampling was additionally carried out 15 months after the start of the pot experiment (March 19, 2012; *n*=3). Prior to analyses, all soil samples were air-dried, sieved to 2 mm, and stored under ambient air. All analyses were performed shortly after soil sampling.

Leachate water was collected five times between November 2010 and May 2011 (November 25, December 14, January 18, April 16, May 10). For the present study, two leachate batches (first sampling on November 25, 2010; second sampling 54 days later on January 18, 2011) were chosen for TE analysis. For the first leachate water collection, artificial rainwater was added, which corresponded to 115–130 mm (0.63–0.71 pore volumes; depending on the respective treatment). For the second sampling, the addition of artificial rainwater corresponding to 67–99 mm (0.37–0.54 pore volumes) was sufficient to induce leaching. At each leachate sampling, two polypropylene bottles with 100-mL capacity each were placed under each pot and connected to the pipe. The collected leachate water was sterilized with ^{60}Co and stored at 4 °C.

Basic soil parameters (pH in 0.01 M $CaCl_2$, EC, CEC, calcium-acetate-lactate extractable P and K) were determined according to standard methods as described in Kloss et al. (2014a). The pH of the leachates was measured with a pH meter (SCHOTT, A7780 NTC30 DIN-N), EC was determined using an InoLab Cond Level 2 conductometer and dissolved OC (DOC) with a total OC (TOC)/DOC total analyzer (Shimadzu, Kyoto, Japan). In addition, P and K in the leachates were measured by ICP-MS (Perkin-Elmer, Elan DRCe).

Effects of BC application on basic soil and leachate characteristics are compiled in Table 2 and were partly already discussed in Kloss et al. (2014a).

The sampled soil and soil-BC mixtures were extracted with 1 M NH_4NO_3 according to ÖNorm L 1094 (1999). Briefly, 20 g of air-dried soil was weighed into flasks and filled with 50 mL of 1 M NH_4NO_3 solution. The flasks were shaken for 2 h, let stand, and filtered. The filtrate was stabilized with 1 vol.% of HNO_3 (65 %). Mustard was harvested on February 17, 2011, by manually cutting the aboveground biomass. The barley plants were harvested on June 20, 2011 but not analyzed for TEs and therefore not discussed in this paper. Mustard plant tissue was dried at 80 °C until constant weight was reached and then ball-milled for further analyses. Elemental composition of the mustard tissue was determined after full acid digestion ($HNO_3/HClO_4$=20+4 mL; on the basis of ÖNorm L 1085 2009).

TE analysis (Al, Mn, Cu, Cd, Pb, B, As, Se, Mo) for all sample types (leachates, NH_4NO_3 soil extracts, and plant digests) was performed by ICP-MS (Perkin Elmer, Elan DRCe 9000).

Sorption experiments with Cd and Cu were additionally performed using eight concentrations ranging from 0 to 200 mg L^{-1} for Cd and from 0 to 400 mg L^{-1} for Cu. All solutions were prepared from chloride salts and with 0.01 M $CaCl_2$ as background electrolyte. Four grams of soil-BC mixture was weighed into centrifuge tubes, treated with 40-mL metal solution, shaken for 24 h, filtered, and stabilized with 65 % HNO_3. The remaining Cd and Cu in solution were measured by AAS (Buck Scientific Atomic Absorption Spectrometer Model 210 VGP; air-acetylene method). The amount of sorbed Cd or Cu was calculated by subtracting the concentration of Cd or Cu in the final solution from the concentration of Cd or Cu in the original solution. Sorption isotherms were obtained by plotting the amount sorbed to the soil-BC mixtures against the equilibrium concentration in solution.

Statistical analyses

Reported results are the means of the replicates±standard deviation. Statistical analyses were made with Statistica 7 for Windows (Statsoft Inc., Tulsa, USA). Homogeneity of variance was tested using the Levene test. One- and two-way analyses of variance (ANOVA) with Tukey's post hoc HSD test ($p<0.05$) were performed to identify statistical differences between individual treatments. In addition, correlations were calculated to reveal relationships between selected leachate parameters (pH, DOC, EC, P, and K) and TE concentrations in the leachates and plants for the BC treatments. As P and K largely contribute to EC, partial correlation coefficients were computed for P and K after adjusting for EC.

Results

Aqua regia and water-extractable trace elements in biochars

In contrast to the other investigated BCs, WS showed a significantly higher AR-digestable Cd concentration (0.20±0.00 mg kg^{-1}); however, this distinction was not found in the water extract. Moreover, WS exhibited a significantly higher AR-digestable Mo concentration than the other BCs. With their significantly higher AR-digestable Cu concentrations

Table 2 Effects of different biochar (BC) types and sampling time on soil (n=3 to 4) and leachate (n=5) parameters (3 wt% BC application rate)

		Leachate properties after 3 wt% BC application							
		Control	Woodchips	Straw	Vineyard pruning	Vineyard pruning	p Value		
			525 °C	525 °C	400 °C	525 °C	time	BC type	time×BC type
pH	Day 1	7.4±0.0 c	7.8±0.0 f	7.6±0.0 d	7.6±0.0 de	7.7±0.1 ef	< 0.001	< 0.001	< 0.001
	Day 54	6.6±0.1 a	7.3±0.0 c	7.0±0.1 b	7.3±0.1 c	7.3±0.1 c			
DOC (mg L^{-1})	Day 1	37.5±7.2 ab	29.2±1.8 ab	20.2±1.2 a	161.0±28.2 c	50.4±1.7 b	< 0.001	< 0.001	< 0.001
	Day 54	29.7±2.7 bc	23.6±5.3 ab	19.8±0.5 a	33.4±5.7 cd	39.8±5.4 d			
EC (μS cm^{-1})	Day 1	1520±323 a	2095±133 ab	7482±683 c	2316±164 b	2568±29 b	< 0.001	< 0.001	< 0.001
	Day 54	366±197 a	691±41 a	4028±414 b	556±67 a	587±62 a			
P (mg L^{-1})	Day 1	0.20±0.02 b	0.06±0.04 ab	0.51±0.15 c	0.09±0.03 ab	0.05±0.03 a	< 0.001	< 0.001	< 0.001
	Day 54	0.10±0.09 a	0.27±0.04 b	0.45±0.07 c	0.17±0.02 ab	0.26±0.03 b			
K (mg L^{-1})	Day 1	37.9±7.1 a	150.2±11.1 b	534.5±74.7 c	134.2±2.1 b	136.2±19.5 b	< 0.001	< 0.001	< 0.001
	Day 54	12.7±2.4 a	73.5±8.5 b	275.1±29.7 c	54.4±5.2 b	65.4±8.4 b			
		Soil properties after 3 wt% BC application							
		Control	Woodchips	Straw	Vineyard pruning	Vineyard pruning	p Value		
			525 °C	525 °C	400 °C	525 °C	time	BC type	time×BC type
pH	0 months	5.4±0.0 a	6.8±0.0 de	6.7±0.0 cd	6.5±0.0 b	6.5±0.0 b	n.s.	< 0.001	< 0.001
	7 months	5.3±0.1 a	6.9±0.1 e	6.5±0.1 b	6.6±0.0 b	6.6±0.1 bc			
CEC ($mmol_c kg^{-1}$)	0 months	75.1±0.4 a	92.2±0.8 c	84.1±1.1 b	91.5±1.2 c	85.9±0.4 b	< 0.001	< 0.001	< 0.001
	7 months	75.1±2.4 a	101.1±1.5 e	94.0±1.1 cd	97.2±1.3 d	96.5±1.8 d			
EC (μS cm^{-1})	0 months	43.1±0.4 a	121.1±7.6 d	188.9±2.8 e	90.8±0.2 c	95.2±2.2 c	< 0.001	< 0.001	< 0.001
	7 months	34.5±3.6 a	74.7±2.7 b	71.8±5.5 b	66.0±4.0 b	68.7±6.2 b			
P_{CAL} (mg kg^{-1})	0 months	61.3±0.8 a	83.8±2.4 bc	103.7±1.4 e	82.8±0.4 b	81.4±1.6 b	n.s.	< 0.001	< 0.001
	7 months	54.5±2.2 a	92.5±1.8 d	95.5±1.8 de	92.2±8.1 cd	88.0±2.1 bcd			
K_{CAL} (mg kg^{-1})	0 months	107.2±1.7 a	339.6±3.1 c	562.3±5.8 e	266.4±1.2 b	260.7±4.8 b	< 0.001	< 0.001	< 0.001
	7 months	73.2±1.8 a	289.9±20.3 bc	462.5±47.8 d	260.8±13.0 b	285.8±21.4 b			

Values are reported as means±standard deviation. Statistical evaluation included two-way ANOVA with the factors BC type and sampling time. Different letters indicate significant differences within one parameter (p<0.05; Tukey's post hoc test). Parenthesized temperature stands for pyrolysis temperature

DOC dissolved organic carbon, *EC* electrical conductivity, *CEC* cation exchange capacity, P_{CAL} *and* K_{CAL} calcium-acetate-lactate extractable P and K, *n.s.* not significant

amounting to 61.0±5.2 and 144±14 mg kg^{-1}, VP400 and VP525 stood out against the other BCs. WC, on the other hand, showed a significantly higher AR-digestable B concentration (83.7±5.2 mg kg^{-1}) than the other BCs.

The water-extractable portion of most TEs was well below 20 % of the AR-digestable contents. Only B showed higher water-extractable portions ranging from 20 % for WC to 42 % for WS. Correlation analyses between the AR-digestable and water-extractable TE fraction for the four investigated BCs showed almost no significant correlations (Table 3). Significant correlations were only found for B and Mo (r=0.978 and r=0.989, p<0.05; Table 3).

Effects of different biochar types on trace element biogeochemistry in soil and leachate water

The sorption isotherms show that BC application significantly increased sorption of Cd and Cu (Fig. 1).

The Cd sorption isotherm of the WC treatment was significantly higher than the other BC treatments. The smallest increase of the Cd sorption potential was caused by WS, which, however, was still significantly higher than the control without BC. Comparing VP400 and VP525, no significant influence of pyrolysis temperature was observed. For Cu, a similar pattern in sorption behavior in response to BC application was found.

Our results showed a significant reduction of NH_4NO_3-extractable Al, Pb, and Cd for all BC types (Table 4). In relation to the control, the NH_4NO_3-extractable fraction was most distinctly reduced in the WC treatment by up to 88 % for Al, 86 % for Pb, and 78 % for Cd (first sampling). In addition, there was a clear initial effect of pyrolysis temperature with VP400 showing significantly higher NH_4NO_3-extractable Al, Pb, and Cd compared to VP525.

Two-way ANOVA revealed the importance of both BC type and sampling date in the leachates (except Pb; Fig. 2).

Table 3 Aqua regia (AR) and water-extractable trace elements of four different biochars ($n=3$) and Pearson correlation coefficients between AR and water-extractable trace elements ($n=4$)

	Aqua regia-digestable trace elements																
mg kg^{-1}	Woodchips (525 °C)				Wheat straw (525 °C)				Vineyard pruning (400 °C)				Vineyard pruning (525 °C)				*r*
Al	2000	±	450	b	355	±	75	a	67.2	±	11.9	a	505	±	71	a	0.320
Cd	0.00	±	0.00	a	0.20	±	0.00	b	0.10	±	0.00	a	0.10	±	0.00	a	0.500
Cu	17.6	±	3.8	a	7.7	±	0.8	a	61.0	±	5.2	b	144	±	14	c	0.115
Mn	168	±	38	b	93.3	±	3.7	a	193	±	16	b	256	±	20	c	0.096
Pb	6.0	±	1.8	b	5.8	±	2.6	b	0.40	±	0.10	a	2.00	±	0.20	ab	−0.213
As	1.5	±	0.1	b	< LOQ			a	1.4	±	0.1	b	3.3	±	0.4	c	−0.390
B	83.7	±	5.2	d	19.7	±	6.4	a	41.7	±	2.1	b	55.8	±	3.6	c	**0.978**
Mo	1.1	±	0.4	b	3.6	±	0.1	c	0.10	±	0.00	a	0.20	±	0.00	a	**0.989**
Se	<LOQ			a	< LOQ			a	< LOQ			a	< LOQ			a	n.d.
	Water-extractable trace elements																
mg kg^{-1}	Woodchips (525 °C)				Wheat straw (525 °C)				Vineyard pruning (400 °C)				Vineyard pruning (525 °C)				
Al	5.01	±	1.20	ab	3.59	±	1.34	a	2.74	±	0.35	a	7.05	±	0.36	b	
Cd	0.00	±	0.00	a	0.01	±	0.00	a	0.02	±	0.03	a	0.01	±	0.02	a	
Cu	0.32	±	0.11	b	0.06	±	0.02	a	0.26	±	0.12	ab	0.20	±	0.04	ab	
Mn	0.31	±	0.09	a	0.39	±	0.02	a	1.88	±	0.05	b	0.28	±	0.02	a	
Pb	0.04	±	0.01	a	0.03	±	0.01	a	0.05	±	0.04	a	0.02	±	0.00	a	
As	0.06	±	0.00	a	0.02	±	0.00	a	0.04	±	0.04	a	0.01	±	0.00	a	
B	17.01	±	3.34	b	8.31	±	3.24	a	11.69	±	0.65	ab	11.87	±	0.27	ab	
Mo	0.08	±	0.01	b	0.56	±	0.03	c	0.00	±	0.00	a	0.01	±	0.00	a	
Se	0.01	±	0.00	a	0.06	±	0.00	c	0.02	±	0.00	b	0.01	±	0.00	a	

Values are reported as means±standard deviation. Different letters indicate significant differences within one line ($p<0.05$; one-way ANOVA; Tukey's post hoc test). Parenthesized temperature stands for pyrolysis temperature

LOQ limit of quantification, *n.d.* not determined

Initially, Cd concentration in the leachates significantly increased by 250 % for the WS treatment compared to the control, whereas the other BCs had no significant effect on the Cd leachate concentration (Fig. 2).

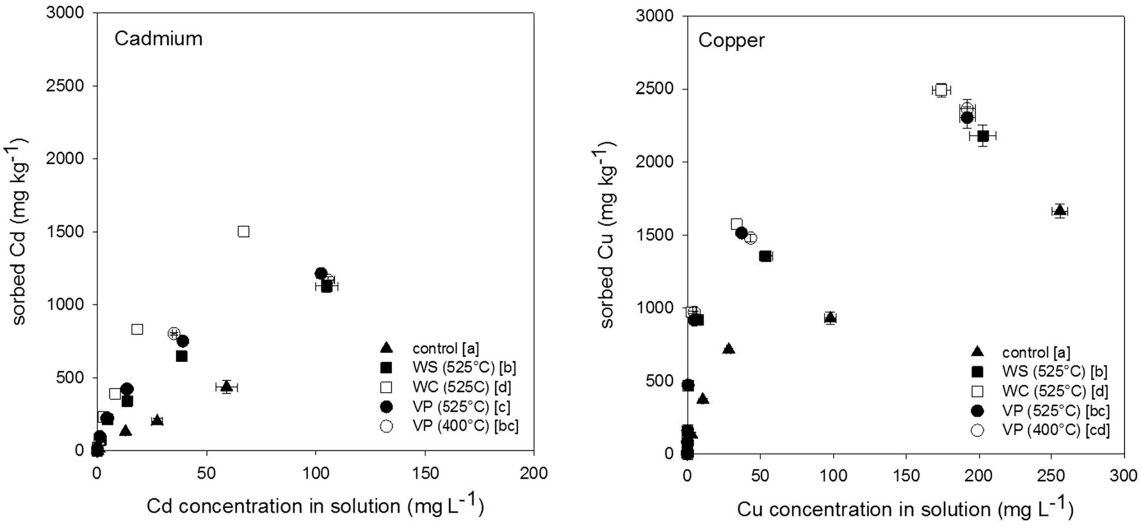

Fig. 1 Cadmium and copper sorption isotherms and soil pH (measured in 0.01 M $CaCl_2$) 15 months after soil application of different biochar (BC) types ($n=3$; 3 wt% BC application rate). *WS* wheat straw BC; *WC* woodchips BC; *VP* vineyard pruning BC. *Parenthesized temperatures* represent pyrolysis temperature; *different letters in brackets* indicate significant differences of metal sorption at the highest applied concentration ($p<0.05$; Tukey's post hoc test)

NH_4NO_3-extractable Cu significantly increased in all BC treatments with VP525 showing the highest increase (Table 4). Correspondingly, the leachate analyses showed a more than 1,000 % higher Cu concentration in the leachate water of both

Table 4 Effects of different biochar (BC) types on NH_4NO_3-extractable trace elements after 0 (n=3) and 7 (n=4) months (3 wt% BC application rate)

		µg kg^{-1}																				*p* Value		
		control				Woodchips (525 °C)				Wheat straw (525 °C)				Vineyard pruning (400 °C)				Vineyard pruning (525 °C)				time	BC type	time×BC type
Al	0 months	1930	±	40	c	239	±	18	a	311	±	25	a	1220	±	103	b	259	±	27.9	a	<0.001	<0.001	<0.001
	7 months	1921	±	340	c	98	±	10	a	108	±	19	a	137	±	12	a	105	±	3	a			
Cd	0 months	9.6	±	0.4	f	2.1	±	0.1	abc	3.2	±	0.3	d	7.3	±	0.3	e	2.5	±	0	cd	<0.001	<0.001	<0.001
	7 months	13.8	±	0.7	g	1	±	0.1	a	1.7	±	0.3	abc	2.2	±	0.2	bc	1.5	±	0.3	ab			
Cu	0 months	42.7	±	1	c	63.6	±	0.3	e	58.5	±	1	e	51.2	±	1.5	d	72.4	±	1.6	f	<0.001	<0.001	<0.001
	7 months	19	±	0.8	a	41.5	±	4.3	c	29.1	±	3.2	b	34	±	3.1	bc	34.1	±	1.8	b			
Mn	0 months	1061	±	43	ab	253	±	7	a	527	±	21	ab	817	±	29	ab	641	±	16	a	<0.001	<0.001	<0.001
	7 months	18110	±	1260	e	831	±	197	ab	2803	±	702	c	5866	±	495	d	2094	±	142	bc			
Pb	0 months	4.2	±	0.4	d	0.6	±	0.08	ab	1.5	±	0.8	b	3.3	±	0.4	cd	0.63	±	0.06	ab	<0.001	<0.001	<0.001
	7 months	3.1	±	0.4	c	0.29	±	0.06	a	0.5	±	0.24	a	0.6	±	0.29	ab	0.45	±	0.19	a			
As	0 months	5.7	±	0.1	b	8	±	0.3	d	7.3	±	0.2	cd	6.5	±	0.4	bc	8.2	±	0.3	de	0.013	<0.001	<0.001
	7 months	4.1	±	0.1	a	10.1	±	0.6	f	9.2	±	0.7	ef	6.8	±	0.5	bc	7.3	±	0.2	cd			
B	0 months	52.2	±	8	ab	128.4	±	2.1	c	26.9	±	0.2	a	31.4	±	1.1	a	55.3	±	9.8	ab	<0.001	<0.001	<0.001
	7 months	65.3	±	3.6	ab	282.4	±	37.6	e	77.5	±	4.1	b	164	±	15.9	cd	177.5	±	22.9	d			
Mo	0 months	0.16	±	0.14	ab	5.9	±	0.2	ef	5.2	±	0.4	def	0.4	±	0	ab	3.8	±	0.2	bcd	n.s.	<0.001	n.s.
	7 months	0.08	±	0.02	a	8	±	3.4	f	4.6	±	1.1	cde	1.8	±	0.2	abc	2.8	±	0.7	abcd			
Se	0 months	3	±	0.7	abc	3.8	±	0.4	d	4.4	±	0.6	bcd	3.5	±	0.6	abc	4.8	±	0.6	d	< 0.001	< 0.001	0.04
	7 months	2.6	±	1	a	3.3	±	0.7	abc	3.2	±	0.2	abc	3.1	±	0.7	abc	3	±	0.6	ab			

Values are reported as means±standard deviation. Statistical evaluation included two-way ANOVA with the factors BC type and sampling time. Different letters indicate significant differences within one trace element ($p<0.05$; Tukey's post hoc test). Parenthesized temperature stands for pyrolysis temperature

n.s. not significant

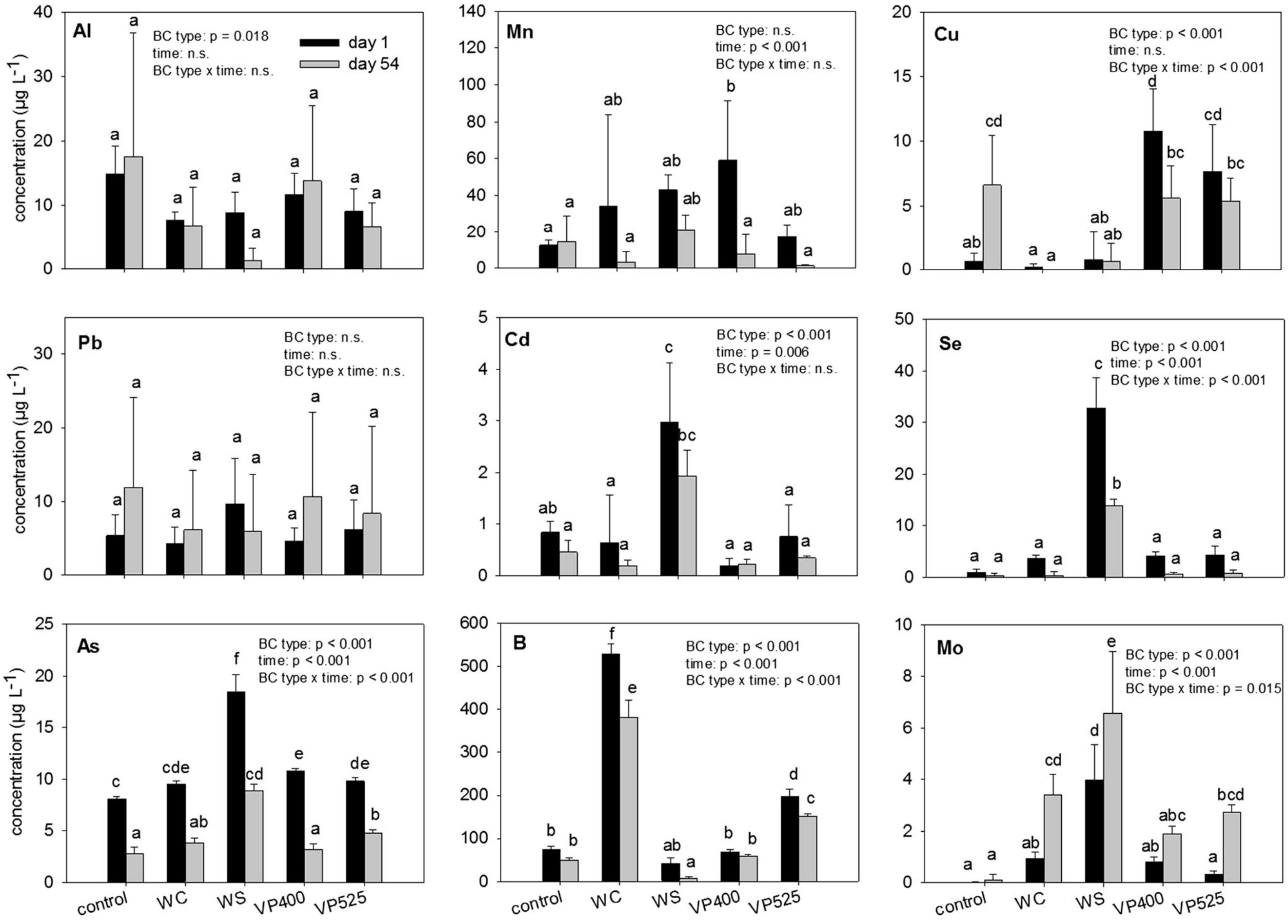

Fig. 2 Effects of different biochar (BC) types on trace element concentrations in the leachates 1 and 54 days after start of the pot experiment (3 wt% BC application rate). Statistical evaluation included two-way ANOVA with the factors BC type and sampling time; *different letters* indicate significant differences within *one panel* ($p<0.05$; Tukey's post hoc test; *n.s.* not significant ($p>0.05$)). *WC* woodchips BC (pyrolysis temperature 525 °C); *WS* wheat straw BC (pyrolysis temperature 525 °C); *VP400* vineyard pruning BC (pyrolysis temperature 400 °C); *VP525* vineyard pruning BC (pyrolysis temperature 525 °C)

VP treatments compared to the control (Fig. 2). NH_4NO_3-extractable Se generally increased after BC application (Table 4); a clear effect of BC type was seen in the leachates where WS caused a 3,200 % higher Se concentration compared with the control (Fig. 2). A similar pattern was observed for As and Mo, where WS caused the highest leachate concentrations compared to the other BC treatments. In contrast, WC caused the most pronounced increase of B in the NH_4NO_3-extracts, which was reflected in a 600 % increase of the B concentration in the leachates.

Effects of different biochar types on trace elements in mustard plants

BC application showed no significant effects on Al, As, and Se concentrations in the mustard plants (Fig. 3). However, Cu and Mn concentrations were significantly reduced by up to 29 % (VP400) and 56 % (WS treatment), respectively. Likewise, Pb concentrations significantly decreased in the mustard plants by approximately 36 % in the WC and VP525 treatments, and Cd concentrations were significantly reduced by 38 % in WS, 48 % in VP400, and 20 % in VP525 treated pots compared to the control. B concentration in the plants, on the other hand, significantly increased by up to 42 % for WC, followed by VP525 with a B increase of 34 %. Mo concentrations significantly increased in all BC treatments showing the highest increase for WC and WS with approximately 640 and 700 %, respectively.

Correlations between leachate characteristics and trace elements in leachates and plants

Leachate pH, DOC, and EC were strongly related to the majority of TEs (Table 5). Relationships between P, K (after adjusting for EC), and TE concentrations in the leachates were only found for Mn, As, and Mo. Significant correlations between leachate characteristics and TE concentrations in the plants were found for Cd, As, B, and Mo.

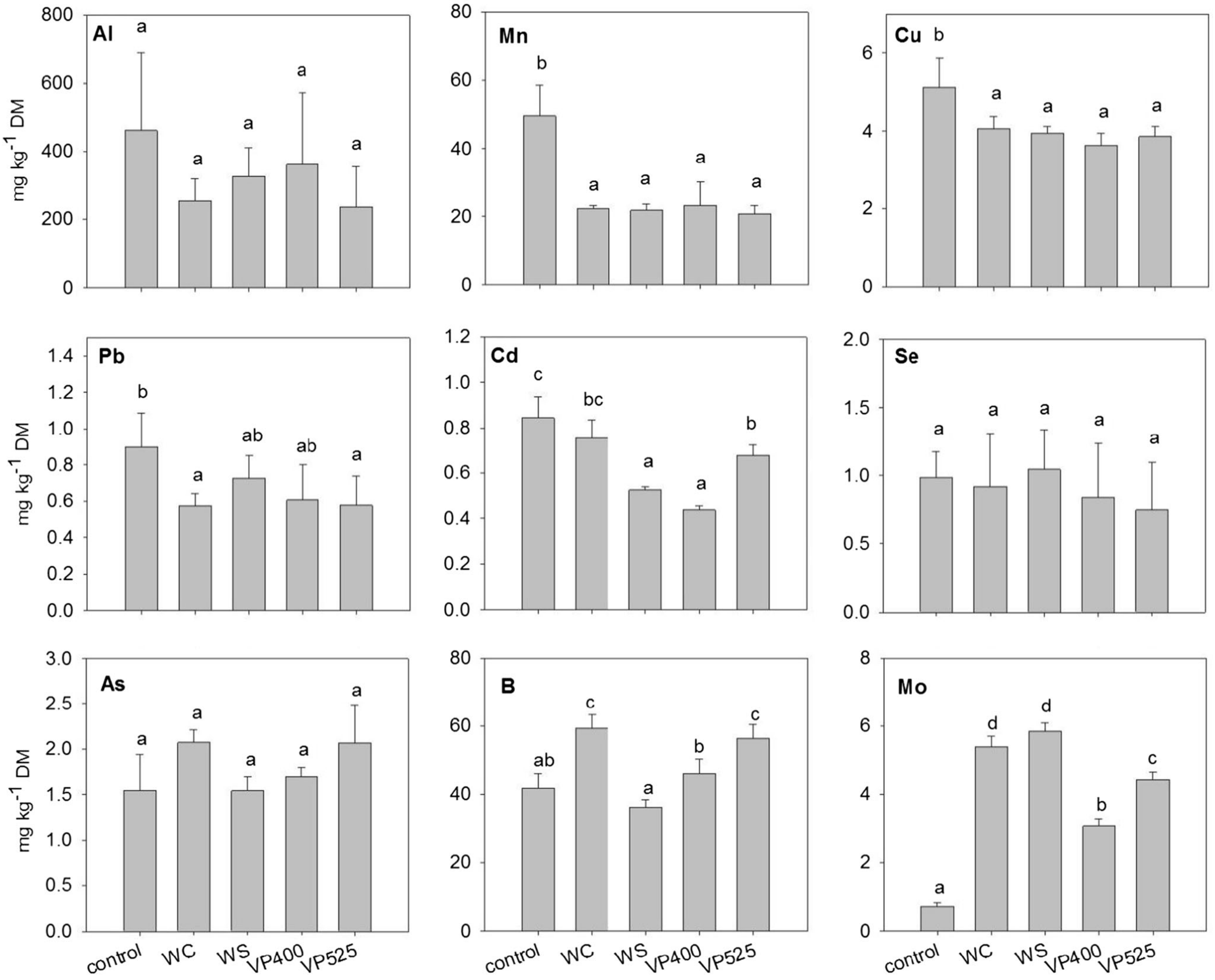

Fig. 3 Trace element concentrations of mustard aboveground dry matter (DM) after soil application of different biochar (BC) types (3 wt% BC application rate). *Different letters* indicate significant differences within *one panel* ($p<0.05$; one-way ANOVA; Tukey's post hoc test). *WC* woodchips BC (pyrolysis temperature 525 °C); *WS* wheat straw BC (pyrolysis temperature 525 °C); *VP400* vineyard pruning BC (pyrolysis temperature 400 °C); *VP525* vineyard pruning BC (pyrolysis temperature 525 °C)

Discussion

Trace element extractability from biochars and compliance with selected biochar certificates

AR- and water-extractable TE concentrations differed strongly among the investigated BC types (Table 3), which depicts the specific nature of the feedstocks used in our study. Feedstock-related differences in TE contents of BCs were also found by Oleszczuk et al. (2013) and Zhao et al. (2013). Most regulations for soil additives do not include BCs and refer to total metal concentrations, which, however, are not indicative of the plant-available fraction (Farrell et al. 2013). Previous studies found that a large portion of TEs in BCs was not plant-available, which was partly attributed to the BC recalcitrance and may justify their accreditation for safe soil application (Hossain et al. 2010; Oleszczuk et al. 2013; Santos et al. 2012).

In our study, VP400 and VP525 showed significantly higher AR-digestable Cu contents than WS and WC (Table 3). This likely originates from the application of Cu compounds as fungicide during viticultural use (Chaignon et al. 2003). Moreover, significantly higher Cu contents in VP525 compared to VP400 demonstrate the accumulation of Cu at higher pyrolysis temperature (Lu et al. 2013). An elevated accumulation of TEs with increasing pyrolysis temperature was also found for Mn, As, and B (Table 3). According to EBC (Schmidt et al. 2012) guidelines, VP525 may not be considered for soil application as its Cu concentration (143.9 mg kg^{-1}; Table 3) exceeded the Cu limit value by almost 50 %. The maximum allowed thresholds for Cu cited by IBI (2013)

Table 5 Correlation coefficients between leachate parameters (pH, DOC, EC, P, and K; leachates sampled after 54 days) and trace element concentrations in leachates and mustard plants for the different biochar treatments (without controls; n=20)

		pH	DOC	EC	P	K
Leachates	Al	**0.571**	0.333	**−0.463**	−0.140	−0.170
	Cd	**−0.806**	**−0.518**	**0.956**	−0.201	−0.170
	Cu	**0.470**	**0.686**	**−0.462**	−0.352	−0.290
	Mn	**−0.559**	**−0.536**	**0.727**	**−0.471**	−0.217
	Pb	0.229	0.265	−0.107	−0.020	0.078
	As	**−0.853**	**−0.445**	**0.937**	**0.767**	**0.503**
	B	0.389	−0.040	**−0.537**	0.384	0.213
	Mo	**−0.814**	**−0.559**	**0.761**	**0.865**	**0.789**
	Se	**−0.863**	**−0.563**	**0.994**	0.046	0.146
Plants	Al	−0.062	−0.334	0.221	−0.330	−0.318
	Cd	0.099	−0.052	−0.249	**0.513**	0.170
	Cu	−0.215	−0.430	0.195	0.085	−0.199
	Mn	0.097	−0.272	−0.017	−0.277	−0.308
	Pb	−0.302	−0.315	0.388	−0.048	−0.265
	As	**0.553**	0.353	−0.464	0.139	0.107
	B	**0.599**	0.302	**−0.765**	0.339	0.150
	Mo	**−0.685**	**−0.616**	**0.625**	**0.636**	0.332
	Se	−0.231	−0.318	0.329	−0.329	−0.416

DOC dissolved organic carbon, *EC* electrical conductivity

Values for P and K represent partial correlation coefficients controlled for EC. Significant correlation coefficients (p<0.05) are given in bold

guidelines were partly also exceeded. The remaining TE concentrations of the investigated BCs were in compliance with both guidelines. However, some TEs are not included in these guidelines, e.g., Al, Mn, and B. The EBC guidelines do presently not include any other here investigated TEs but Cd, Cu, and Pb.

The water-extractable portion of TEs was generally well below 20 %, which may partly be due to the BCs' high pH ranging from 8.3 to 9.7 (Table 1). Correlations between AR-digestable and water-extractable TEs (Table 3) revealed no significant correlations except for B and Mo (r=0.978 and 0.989, respectively). Hence, it seems as though the determination of AR-digestable TEs hardly reflects their water extractability. It should therefore be advisable that besides total TE contents of BCs, also more mobile fractions such as the water-extractable be included in BC certificate regulations.

Temporal changes of the soil-water-plant system after biochar application

The effects of BC application on TE mobility and availability have often been attributed to a BC-induced liming effect (e.g., Beesley et al. 2013; Tang et al. 2013; Uchimiya et al. 2010). Correspondingly, decreased plant concentrations of Cd, Cu, As, and Pb upon BC application have been found (Cui et al. 2011; Houben et al. 2013b; Namgay et al. 2010; Park et al. 2011), which illustrates the potential of BC in soil remediation while pointing out the risks of insufficient micronutrient uptake.

In a previous study using the same experimental setup, we found that the alteration of the Planosol's characteristics after BC application largely depended on the BC type (Kloss et al. 2014a). Briefly, the highest increase of EC and calcium-acetate-lactate (CAL) extractable P and K was caused by WS with its comparatively high ash content (cf. Tables 1 and 2). The highest rise in pH and CEC, on the other hand, was induced by WC application. Some of these BC-type specific changes including EC and CAL-extractable P were only short-lived and disappeared within 7 months (Kloss et al. 2014a), which was also reflected in significant reductions of EC in the second leachate sampling for WS, VP400, and VP525 (Table 2). The rapid decrease of EC in the leachates of WS-treated pots (by almost 50 % within 54 days) may be due to leaching of salts at the beginning of the pot experiment and/or a subsequent plant uptake of salts that remained in the soil (Kloss et al. 2014a; Revell et al. 2012).

Changes of the Planosol's characteristics after BC application, especially due to a BC-induced liming effect (Table 2), were reflected in a modified extractability and solubility of cationic and anionic TEs (Table 4; Fig. 2). Decreased NH_4NO_3 extractability was detected for the cations Al, Cd, and partly Mn, whereas the extractability of all investigated anions (Se, As, B, and Mo) increased (Table 4). These changes were not necessarily reflected in the respective TE concentrations of the mustard plant tissue (Fig. 3), because the solubility of TEs seemed to be time-limited. Leachate pH of all BC treatments significantly decreased within 54 days (Table 2); likewise, TE concentrations declined for Se, As, and B within the same time period (Fig. 2), which may be related to the decline of leachate pH (Castaldi et al. 2011; Jones et al. 2012). Significant correlation coefficients proved a close linkage between leachate pH and the majority of TEs in the leachates (Table 5).

Based on our results, a remediation potential of BC in terms of plant uptake could only be inferred for Pb and Cd, for which the application of certain BC types resulted in decreased plant concentrations (Fig. 3). Simultaneously, the application of the four investigated BC types and the concurrent increase of soil pH could become a matter of concern in terms of adequate micronutrient supply (Bolan et al. 2003), because decreased Cu and Mn concentrations in the mustard plants were found in all BC treatments (Fig. 3).

Biochar-specific release of trace elements modifying trace element biogeochemistry

Wheat straw versus woodchip-derived biochar

Despite proven TE concentrations in BCs, the transfer of BC-derived TEs and their environmental impact have been assumed to be ineffectual or of low risk; only certain BCs derived from contaminated feedstocks such as sewage sludge or Cu-impregnated wood have been found to potentially pose a risk (Hossain et al. 2010; Jones and Quilliam 2014; Lucchini et al. 2014; Oleszczuk et al. 2013; Waqas et al. 2014).

Although only a minor fraction of the BC-derived TEs was water-extractable in our study (Table 3), significant increases of some TEs in the leachates were observed. The WS treatment showed the strongest increases of anionic TEs (notably As, Se, and Mo) in the leachate water. Conversely, WC hardly changed the leachate concentration of these anionic TEs, even though soil pH in WC-treated pots was initially in the same range as in WS-treated pots (Table 2). On the other hand, WC application and to a lesser extent VP525 strongly increased B concentration in the leachates and mustard plants (Figs. 2 and 3). The latter was unexpected as an increase in pH generally decreases the plant availability of B (Goldberg 1997). These discrepancies cannot be fully explained by changes of soil pH, but rather by a direct release of TEs from specific BCs, despite a rather low water extractability (approximately 20 % for B, 16 % for Mo; cf. Table 3). The accumulation of B in mustard plants even reached the upper thresholds for sensitive crops (10–50 mg kg^{-1}; Gupta and Gupta 1998). For soils with high B levels, the application of wood-derived BCs introducing additional B could be combined with straw-derived BCs introducing higher amounts of soluble salts, as the combination of B and salts in the soil system was found to reduce the toxic effects at high B concentrations (Yermiyahu et al. 2008). In our case, the high EC of the leachate water could indeed have decreased B uptake as indicated by the correlation analysis ($r=-0.765$; Table 5). On the other hand, in soils with low B supply, the B nutrition of crops with high B demand like sugar beet (Dordas et al. 2007) could be supported.

Short-term discrepancy in copper biogeochemistry in response to various biochar types

We found decreased Cu concentrations in the leachates for the WC and WS treatments (Fig. 2), which is in agreement with Karami et al. (2011), who noted decreased Cu mobility upon BC application along with an increase in pore water pH. In our study, Cu concentration in the leachates was hardly affected by WC and WS application (Fig. 2). However, both VP treatments had significantly elevated Cu concentrations in the leachates despite increased soil and leachate pH (Table 2). This may be attributed to the high Cu contents of both VPs compared to the other BCs (Table 3) and a subsequent release of Cu despite an extremely low water extractability (<1 %). DOC (highest in the VP treatments; Table 2) could also play a role through the mobilization of Cu in the form of soluble organic complexes (Beesley et al. 2010; Uchimiya and Bannon 2013). This is also indicated by a significant positive correlation between DOC and Cu concentrations in the leachates (Table 5). However, the noticeable release of Cu from the BCs into the leachate water may be only a short-term effect and replaced by an increased sorption potential (Uchimiya and Bannon 2013) as revealed by the sorption isotherms after VP application (Fig. 1). In addition, Cu concentrations in mustard plants grown on VP-amended soil were up to 29 % lower than those in the control soil (Fig. 3). Indeed, this could indicate a potentially insufficient supply of micronutrients, as Cu (and Mn) concentrations were already in a critical range (1–5 mg Cu kg^{-1} dry matter; 10–20 mg Mn kg^{-1} dry matter) reported for many plant species (Broadley et al. 2012; Robson and Reuter 1981; Thiel and Finck 1973). This may be partly responsible for the suppressed mustard yield that we reported in a previous study using the same experimental design including the Cu-rich VPs (Kloss et al. 2014a).

Provided that the contamination is not too high, the usage of Cu-contaminated BC as a soil amendment specifically for Cu-deficient soils was proposed by Jones and Quilliam (2014). However, our results show that the addition of Cu-rich BCs such as VP may not be suitable for overcoming the risk of BC-induced Cu deficiency. At high percolation rates, leaching of Cu from VPs may occur more rapidly than the development of plants and a concomitant uptake of Cu.

When applied at high rates as done here, the application of BC derived from VP may instead (at least in the short term) pose a risk to groundwater by elevating the Cu concentration in leachate water, which justifies the rejection of VP for soil application according to EBC guidelines (Schmidt et al. 2012).

Biochar-induced salinity triggering trace element solubility

In the leachates of WS-treated pots, we found not only increased concentrations of various anionic TEs including As, Se, and Mo, but also of Cd (Fig. 2). This contradicts the general cationic TE behavior upon pH increase and also the sorption isotherm (Fig. 1). Straw-derived BC stands out from other BCs due to its higher nutrient, ash, and salt content (Alburquerque et al. 2014; Kloss et al. 2012; Table 1). In our study, WS application caused a 338 % higher EC in the WS-treated soil than that in the control (Table 2). The higher salinity in soils treated with straw-based BCs may be responsible for a short-term increase of TE solubility that included both anionic and cationic TEs such as Cd (Acosta et al. 2011; Khanmirzaei 2012; Fig. 2).

The results of the correlation analyses (Table 5) confirm that Cd leaching positively correlated with leachate EC. However, the increased mobility of Cd did not affect the plants. In fact, Cd concentration in the plants was significantly reduced by up to 48 % (Fig. 3). Besides Cd, EC correlated with most other TEs in the leachates (except Pb; Table 5), and after adjusting for EC, P, and K were found to correlate with Mn, As, and Mo in the leachates (Table 5). As the highest EC as well as P and K contents in both soil and leachates were found for WS (Table 2), potential ion competition for binding sites, such as between As and P (Qian et al. 2013; Sadiq 1997), could trigger TE solubility, which is underlined by a significant positive correlation between leachate As and P (Table 5).

Summary and conclusions

Amending soils with different BC types at high application rates as performed in this pot experiment showed that changes in TE biogeochemistry may not be limited to a pH effect. Depending on the original feedstock, further factors including the input of BC-derived TEs, DOC, and salts may trigger the leaching of both anionic and cationic TEs in the short term (Fig. 4).

The application of WC increased B solubility; similarly, Cu was mobilized in both VP treatments, which was reflected in initially high leachate concentrations. Hence, a direct release of TEs into the soil system may occur despite the fact that the water extractability of most TEs was below 20 % (H_1 could not be rejected).

Regarding BC application as a soil remediation measure, the desired liming effect may in the short term be overridden when applying alkaline, but salt-rich BCs such as WS. BCs with a higher salt content may exert a mobilizing effect even on cationic TEs like Cd (H_2 could not be rejected).

In analogy to other soil amendments, quality standards have to be maintained when applying BC to agricultural soils. Establishing BC quality guidelines such as the EBC is a useful concept to ensure safe BC application without putting the food chain and water resources at risk. BCs with TE concentrations exceeding the limit values of the EBC guidelines, as was found for Cu in one of the VP treatments, may indeed increase the risk of an elevated short-term TE mobility. However, increased TE mobility may still occur upon BC application even when BCs comply with guidelines, as observed for Cd in our study. Nevertheless, our findings still require confirmation under field conditions over a longer period of time and at lower BC application rates.

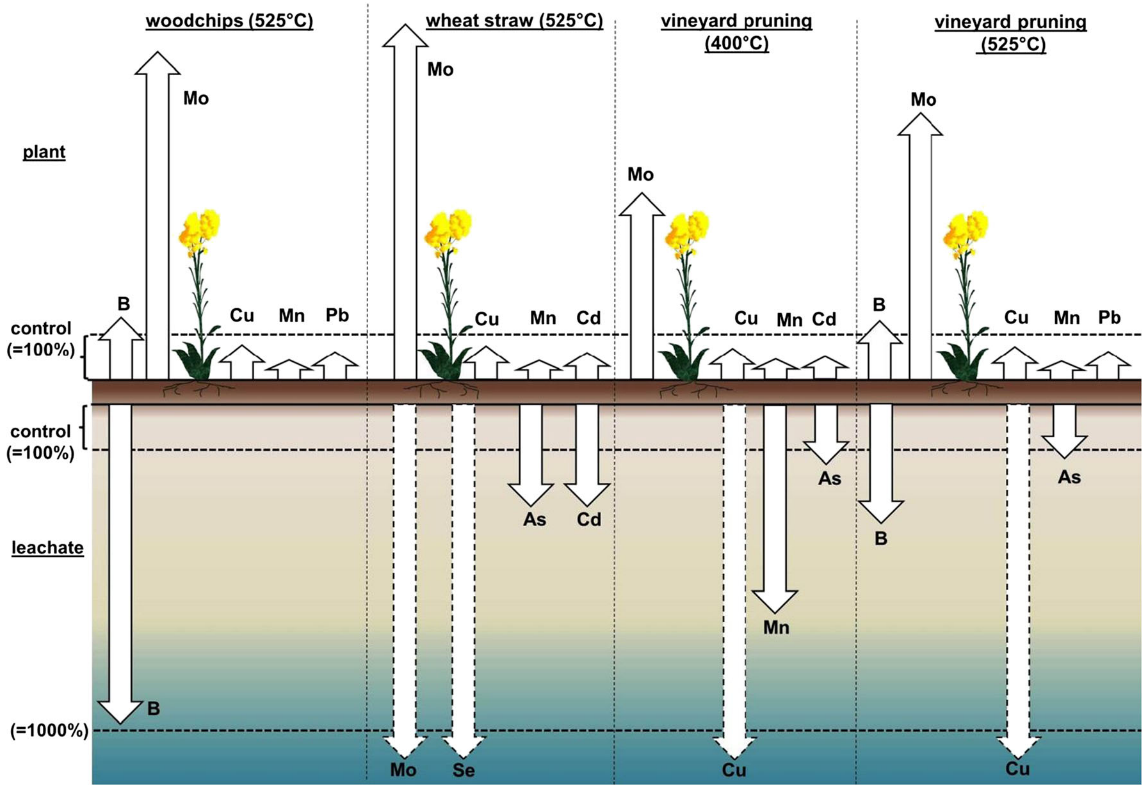

Fig. 4 Graphical summary of the most significant effects of different biochar (BC) types on trace element concentrations in mustard plants and leachates (first sampling) on an acidic, sandy agricultural soil. The *lengths of the arrows* are based on mean quantitative changes relative to the control concentration without BC (reference line=100 %). *Dashed arrows* exceeding the 1,000 % reference line are not to scale. Pyrolysis temperature of each BC type is *parenthesized*

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