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Amendment of biochar reduces the release of toxic elements under dynamic redox conditions in a contaminated floodplain soil

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HIGHLIGHTS

- Pre-set redox conditions affect release dynamics of metals via changes of pH.
- Amendment of biochar decreased release of metals under dynamic redox conditions.
- Contaminated floodplain soil (non-treated) and treated with biochar behave similarly.
- Addition of biochar to soil seems to have little effect on redox processes.

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ABSTRACT

Biochar (BC) can be used to remediate soils contaminated with potential toxic elements (PTEs). However, the efficiency of BC to immobilize PTEs in highly contaminated floodplain soils under dynamic redox conditions has not been studied up to date. Thus, we have (i) quantified the impact of pre-definite redox conditions on the release dynamics of dissolved aluminum (Al), arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn) in a highly contaminated soil (CS) (non-treated) and in the same soil treated with 10 g kg⁻¹ biochar based material (CS + BC), and (ii) assessed the efficacy of the material to reduce the concentrations of PTEs in soil solution under dynamic redox conditions using an automated biogeochemical microcosm apparatus. The impact of redox potential (E_H), pH, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), iron (Fe), manganese (Mn), and sulfate (SO_4^{2-}) on dynamics of PTEs was also determined. The E_H was lowered to +68 mV and afterwards increased stepwise to +535 mV. Significant negative correlation between E_H and pH in CS and CS + BC was detected. The systematic increase of E_H along with decrease of pH favors the mobilization of PTEs in CS and CS + BC. The material addition seems to have little effect on redox processes because pattern of E_H /pH and release dynamics of PTEs was basically similar in CS and CS + BC. However, concentrations of dissolved PTEs were considerably lower in CS + BC than in CS which demonstrates that BC is able to decrease concentrations of dissolved PTEs even under dynamic redox conditions.

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1. Introduction

Soil contamination with potentially toxic elements (PTEs) has become a global concern because of its adverse effects on ecosystem health and food security. Many floodplain soils are highly contaminated with PTEs (Rennert et al., 2010; Frohne et al., 2014; Rinklebe and Shaheen, 2014; Shaheen and Rinklebe, 2014). As the modern agenda seeks to engineer natural processes to meet remediation needs in cost-effective ways, application of amendments to contaminated soils to bind pollutants, whilst providing

material conditions that promote plant growth and stimulate ecological restoration, have become more popular (Adriano et al., 2004; Vangronsveld et al., 2009; Shaheen et al., 2015). Recently, there is an increasing demand for new, applicable, and economic amendments to use them as soil conditioners and immobilizing agents for PTEs in contaminated soils. These materials should be abundant, available, biodegradable, and originate from renewable sources (Ok et al., 2011; Shaheen and Rinklebe, 2015).

Biochar (BC) as a carbon-rich material fulfils those requirements; it is produced via pyrolysis of agricultural bio-waste such as wood chips or crop straw under oxygen limitation (Beesley et al., 2011; Ahmad et al., 2014a,b). Recent studies have highlighted the role of BC in immobilizing PTEs in soils (Beesley et al.,

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2010; Beesley and Marmiroli, 2011; Houben et al., 2013; Schweiker et al., 2014; Ahmad et al., 2014a). However, most of these studies investigated the impact of BC on the (im)mobilization of PTEs in soils under static soil moisture conditions. However, floodplain soils are frequently flooded and highly dynamic; thus, soil redox potential (E_H), pH, and element carriers such as iron (Fe), manganese (Mn), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), sulfate (SO_4^{2-}) and others differ considerably compared to field capacity conditions. These highly dynamic conditions have considerable impacts on the release dynamics of PTEs in soils (Du Laing et al., 2009; Frohne et al., 2011, 2014; Shaheen et al., 2014a,b,c). Although few studies have been conducted to evaluate the capabilities of biochar based material which is composed of bio-charcoal, humus, clay, alumina, shell limestone, perlite, microorganisms, and organic fertilizer to immobilize PTEs in floodplain soils (Shaheen and Rinklebe, 2015; Shaheen et al., 2015), no attempts have been made to study the efficiency of this material for the (im)mobilization of PTEs in a highly contaminated floodplain soil under dynamic redox conditions up to date.

Detailed knowledge about redox-induced behavior of PTEs in contaminated floodplain soils either treated or non-treated with biochar based material is required for a better understanding of the mobilization of PTEs and the controlling processes. This knowledge enables a more accurate prediction of metal(loid) release into ground- and surface waters in response to changing redox conditions which might contribute to apply an adequate risk assessment and management of contaminated floodplain soils. Thus, we aimed (i) to quantify the impact of pre-definite E_H -conditions on the release dynamics of dissolved aluminum (Al), arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn) in a contaminated floodplain soil treated with biochar based material and non-treated, and to elucidate the underlying redox-driven processes mechanistically, and (ii) to assess the efficacy of biochar based material as an immobilizing agent to reduce the concentrations of these elements in soil solution.

2. Materials and methods

2.1. Collection, characterization, and treatment of the soil and biochar

The soil sample was collected from a floodplain at the lower course of the Wupper River, Germany (E 2570359, N 5661521; 51°4'0.48"N, 6°4'0.48"E). The site is used as grassland and periodically flooded by the Wupper River, usually in spring time. The soil is classified as Eutric Fluvisol according to IUSS-FAO (2014). Major properties of the soil and BC are presented in Table 1. Soil texture was dominated by silt. The soil was weakly acidic and contained high organic carbon. Concentrations of Cd, Ni, and Zn exceeded the precautionary values and concentrations of As and Cu exceeded even the action values set by the German Federal Soil Protection and Contaminated Sites Ordinance (Bundes-Bodenschutz- und Altlastenverordnung, 1999). Moreover, the values of As, Cu, and Zn were higher than the upper limit of the trigger action values for PTEs in agricultural soils as reported by Kabata-Pendias (2011), implying harmful soil alterations which need remediation. The used biochar based material is commercially available via TERRA PRETA e.K., Company, Berlin, Germany. This product is well-known as "TERRA PRETA" and it is composed of bio-charcoal, humus, clay, alumina, shell limestone, perlite, microorganisms, and organic fertilizer. However, for brevity and consistency it is called "biochar" (BC) here. The BC was slightly alkaline and contained high concentrations of organic carbon and nitrogen and some inorganic carbon while concentrations of PTEs were low (Table 1).

The BC was applied to the soil at a rate of 10 g kg⁻¹. Soil and BC were mixed thoroughly and thereafter a pot experiment was

Table 1

Selected properties and element concentrations (microwave digestion^b) of contaminated soil (CS) and biochar (BC).

	Unit	CS	BC
<i>Basic properties</i>			
pH [H ₂ O] ^a		6.4	7.3
Silt	%	92	n.d.
Clay		2	n.d.
Total nitrogen		0.354	6.11
Total carbon		7.103	28.7
Total inorganic carbon		0.003	2.1
Total organic carbon		7.100	26.6
<i>Concentrations^b</i>			
As	mg kg ⁻¹	90.8	16.3
Cd		6.9	b.d.l.
Cu		2433.4	22.7
Ni		79.0	11.7
Zn		1050.1	71.7
Al	g kg ⁻¹	18.5	12.4
Fe		43.8	8.5
Mn		0.87	0.3
S		0.99	2.2

n.d. = not determined, b.d.l. = below detection limit.

^a pH determined according to DIN EN 15933 (2012).

^b According to US EPA 3051a (2007).

conducted (Shaheen and Rinklebe, 2015; Shaheen et al., 2015). Thereafter, the soil was dried, crushed, and incubated in the laboratory for ten months. Thus, the total incubation period was about one year before the soil was used for the experiment.

2.2. Experiment under pre-set redox conditions

An automated biogeochemical microcosm system was exploited to simulate flooding of the contaminated soil (CS) and contaminated soil + biochar (CS + BC) in laboratory. This system was successfully employed in previous studies (Antić-Mladenović et al., 2011; Rupp et al., 2010; Frohne et al., 2011, 2014, 2015; Shaheen et al., 2014a). Technical details are provided in Yu and Rinklebe (2011) and experimental specifics in Supplemental 1.

2.3. Calculations and statistical analysis

Mean values of E_H and pH levels for 3, 6, 12, and 24 h prior to sampling were calculated. The original values measured every 10 min served as the underlying dataset. Correlation analyses were conducted between E_H /pH and concentrations of DOC, DIC, SO_4^{2-} , Al, As, Cd, Cu, Fe, Mn, Ni, and Zn. The results 6 h before sampling generally resulted in best correlations and were therefore used for statistics. Origin Pro 7.5G (OriginLab Corporation, Northampton, USA) was used for creating Fig. 1. The program IBM SPSS Statistics, Version 22 was used for conducting correlations and factor analysis. The latter was carried out as Principal Component Analysis, used for factor extraction. The Varimax-rotation procedure was chosen to make components easier to interpret. The number of interaction calculations was limited to 25.

3. Results and discussion

3.1. Soil E_H , pH, DIC, DOC, Fe, Mn, and SO_4^{2-}

The minimum, maximum, and mean values of soil E_H and pH in CS and CS + BC are presented in Table 2. The E_H values (E_H all; data measured every 10 min during the experiment, $n = 10,261$) ranged between +68 and +521 mV in CS and between +72 and +535 mV in CS + BC (Table 2, Fig. 1).

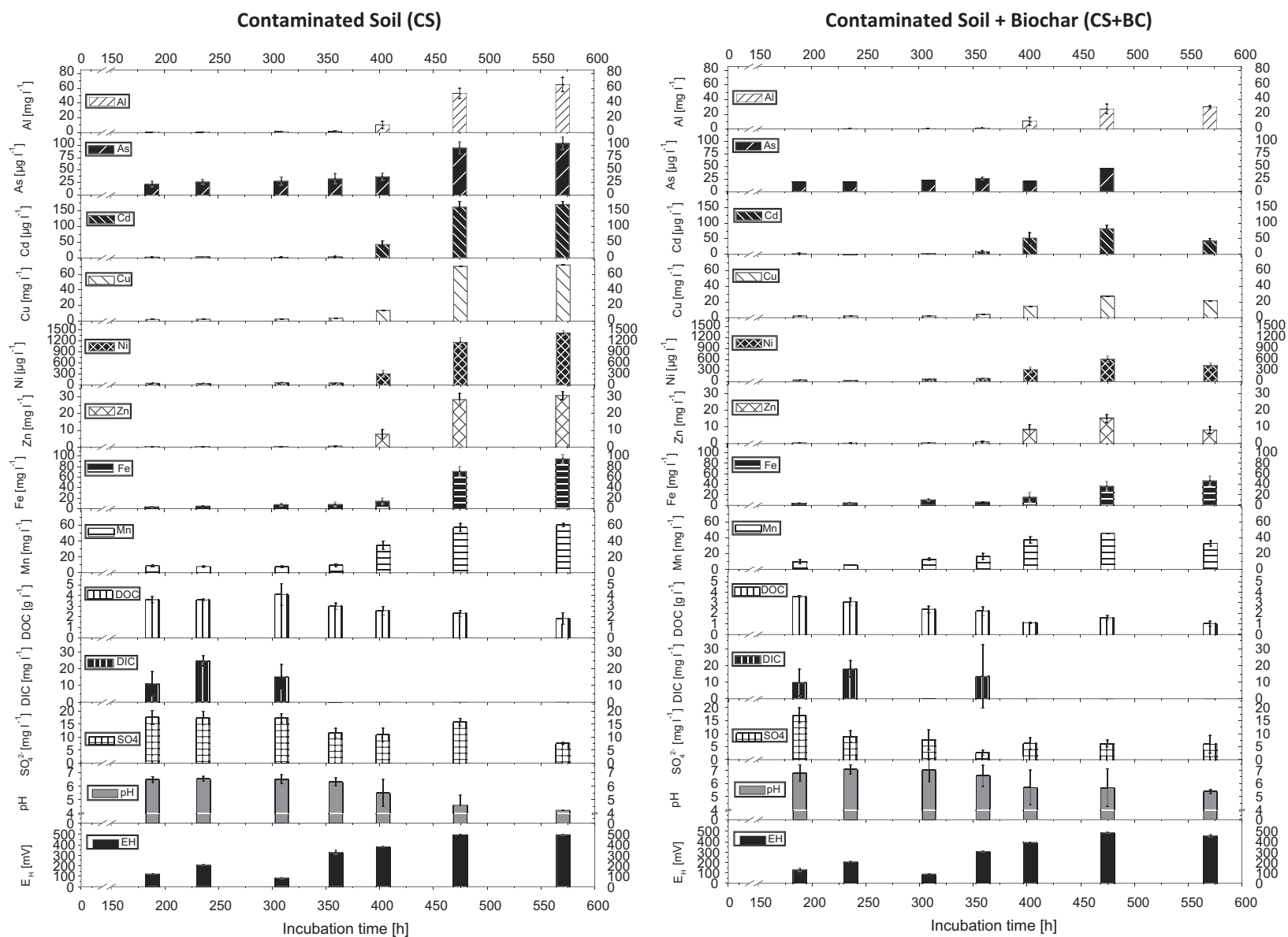


Fig. 1. Impact of pre-definite E_H -conditions on release dynamics of dissolved aluminum (Al), arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), iron (Fe), manganese (Mn), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), sulfate (SO_4^{2-}), and pH in a contaminated soil (CS) compared with a contaminated soil treated with biochar (CS + BC). Columns represent mean and whiskers represent standard deviation of three replicates using biogeochemical microcosm systems.

The pH values (pH all) ranged between 3.7 and 7.1 in CS and between 4.4 and 8.4 in CS + BC (Table 2). Soil pH shows an opposite behavior to E_H (Fig. 1). Therefore, the relation between soil E_H and pH was negative both for the dataset gained every 10 min ($r = -0.77$; $P < 0.01$; $n = 7,400$ in CS and $r = -0.56$; $P < 0.01$; $n = 10,261$ in CS + BC; data not shown) and for the dataset obtained at the sampling points ($r = -0.79$; in CS and $r = -0.54$; in CS + BC; Supplemental 2). An increase of pH with a decline in E_H might be due to the consumption of protons required for the reduction of NO_3^- , Mn^{4+} , and Fe^{3+} (Yu et al., 2007; Reddy and DeLaune, 2008). The results indicate that application of BC to the soil increased pH in soil slurry (pH mean) from 5.5 in CS to 6.3 in CS + BC (Table 2) which is considered to be a major reason for the decreased solubility and release of the PTEs in CS + BC compared to CS.

Concentrations of DOC and DIC decreased with rising E_H . Therefore, the relation between DOC and DIC with E_H was negative in CS ($r = -0.82$ and -0.60 for DOC and DIC, respectively) and in CS + BC ($r = -0.79$ and -0.30 for DOC and DIC, respectively; Supplemental 2). This opposite behavior of E_H and DOC was reported previously (Grybos et al., 2009; Shaheen et al., 2014a,b,c). This is probably because (i) complex organic matter is degraded to DOC by reductive fermentation and hydrolysis under reducing conditions and (ii) decreasing DOC with rising E_H can occur due to enhanced microbial carbon consumption under oxic conditions (Yu et al., 2007; Abel et al., 2012; Husson, 2013; Frohne et al., 2014), which might also have happened in our experiment.

The concentrations of soluble Fe and Mn were considerably higher under oxic and acidic than under reducing conditions with higher pH in CS and CS + BC (Fig. 1). Therefore, the relations between Fe and Mn on the one hand and soil E_H on the other hand were positive, while relations between both elements with soil pH were negative in CS and CS + BC (Supplemental 2). An increase of soluble Fe and Mn concentrations due to reductive dissolution under low E_H is commonly observed in soils (e.g., Antić-Mladenović et al., 2011; Frohne et al., 2015; Shaheen et al., 2014a,b,c). However, in our experiment, the concentrations of soluble Fe and Mn increased under high E_H very likely due to the associated decrease of pH (Fig. 1). Thus, Fe seems to be dominant in dissolved form as Fe^{2+} under our prevailing experimental E_H -pH-conditions (Takeno, 2005). A pH of 6 is dominant at the beginning of our experiment, this would require an E_H of approximately

200 mV for relevant Fe oxidation (and linked formation of Fe oxides/hydroxides) (Takeno, 2005). However, we measured an E_H of about 100 mV at the first sampling. Thus, it is likely that a certain amount of Fe occurs as Fe^{2+} here. Similar behavior can be observed for Mn; this phenomenon was already reported by Frohne et al. (2011) and Frohne et al. (2014). When rising the E_H the linked decrease of pH (3.7–4.4) favors the mobilization and release of Fe and Mn even under oxic conditions in both systems, CS and CS + BC.

Sulfate showed higher concentrations under reducing conditions than under oxidizing conditions (Fig. 1). In addition, the mean concentrations of SO_4^{2-} in CS were higher than in CS + BC (Table 2 and Fig. 1) what leads to the assumption that BC decreased the release of SO_4^{2-} to soil solution. The behavior of SO_4^{2-} might be affected by changes of soil pH and concentrations of DOC and DIC. One might assume that sulfur groups are attached to DOC and that the decrease in DOC might contribute to the decrease of SO_4^{2-} with rising E_H (Rinklebe and Du Laing, 2011).

3.2. Dynamics of PTEs as affected by E_H /pH, DOC, DIC, Fe, Mn, and SO_4^{2-}

Concentrations of Al, As, Cd, Cu, Ni, and Zn showed wide ranges during the experiment (Table 2 and Fig. 1). Concentrations of Al, As, Cd, Cu, Ni, and Zn were considerably higher under oxic and acidic than under reducing conditions with higher pH in CS and CS + BC (Fig. 1). Therefore, the relations between these elements (except As in the CS + BC) and E_H were positive, while relations between the same elements and pH were negative in CS and CS + BC (Table 3).

Lower solubility of Al, As, Cd, Cu, Ni, and Zn under reducing conditions as compared to oxidizing conditions might be explained by changes of controlling factors such as pH, DOC, DIC, Fe, Mn, and SO_4^{2-} . To determine the associations between the measured elements and controlling factors and to identify complex cause-and-effect interrelationships, we have conducted a factor analysis (Fig. 2). The total explained variance in CS is 89.4% (76.9% Component No. 1 and 12.5% Component No. 2) and in CS + BC is 84.8% (69.1% Component No. 1 and 15.7% Component No. 2).

Fig. 2A demonstrates that in CS, concentrations of Al, As, Cd, Cu, Ni, and Zn were associated in one group together with Fe, Mn, and E_H which indicates that the latter reveals a similar behavior like the studied PTEs. On the other hand, pH, DOC, DIC, and SO_4^{2-} were together in another cluster clearly differentiated from the first

Table 2
Variations of concentrations of elements and compounds in soil solution as well as redox potential (E_H) and pH in the slurry of the contaminated soil and of the contaminated soil plus biochar during the experiment.

Parameter	Unit	Contaminated soil				Contaminated soil + biochar			
		N	Minimum	Maximum	Mean	N	Minimum	Maximum	Mean
Al	$\mu\text{g L}^{-1}$	19	188.4	78428.3	20953.3	16	316.7	32914.1	13035.0
As		21	17.1	118.4	49.3	7	18.7	46.5	25.7
Cd		18	0.3	185.8	64.2	17	0.3	95.9	33.2
Cu		21	2040.1	85313.5	23809.4	21	1784.4	32054.9	10595.7
Ni		21	38.6	1502.8	444.5	19	33.5	683.5	248.9
Zn		21	213.1	34135.9	9783.6	21	135.0	16804.7	4800.1
Fe		21	2143.3	104657.1	29329.4	21	2843.0	58812.8	17712.2
Mn		21	6786.4	64017.3	26566.8	21	5065.0	46078.7	22771.4
DOC	mg L^{-1}	21	1197.5	5509.2	2994.3	21	725.4	3715.3	2134.4
DIC		21	0.0	29.1	6.6	21	0.0	40.3	5.9
SO_4^{2-}		19	7.2	20.3	14.1	21	1.4	20.5	7.8
E_H 6h ^a	mV	21	74	503	303	21	86	493	295
E_H all ^b		10261	68	521	329	10261	72	535	320
pH 6h ^a		21	4.0	6.9	5.7	21	4.6	8.2	6.3
pH all ^b		7400	3.7	7.1	5.5	10261	4.4	8.4	6.3

DOC: dissolved organic carbon; DIC: dissolved inorganic carbon.

^a Means of data 6 h before sampling.

^b Data measured every 10 min during the experiment.

Table 3

Correlation coefficients (Pearson) between elements (Al, As, Cd, Cu, Ni, Zn) and factors involved in their release dynamics (E_H , pH, DOC, DIC, Fe, Mn) ($n = 21$) of the contaminated soil (CS) and the contaminated soil + biochar (CS + BC).

Element	Soil	E_H	pH	DOC	DIC	Fe	Mn	SO_4^{2-}
Al	CS	0.812 ^a	-0.778 ^a	-0.668 ^a	-0.521 ^b	0.994 ^a	0.946 ^a	ns
	CS + BC	0.818 ^a	-0.686 ^a	-0.651 ^a	ns	0.929 ^a	0.788 ^a	ns
As	CS	0.812 ^a	-0.734 ^a	-0.624 ^a	ns	0.982 ^a	0.922 ^a	ns
	CS + BC	ns	ns	ns	ns	0.891 ^a	0.765 ^b	ns
Cd	CS	0.833 ^a	-0.786 ^a	-0.696 ^a	ns	0.974 ^a	0.971 ^a	ns
	CS + BC	0.826 ^a	-0.608 ^a	-0.673 ^a	ns	0.712 ^a	0.963 ^a	ns
Cu	CS	0.824 ^a	-0.783 ^a	-0.679 ^a	-0.463 ^b	0.981 ^a	0.952 ^a	ns
	CS + BC	0.870 ^a	-0.656 ^a	-0.717 ^a	ns	0.915 ^a	0.916 ^a	ns
Ni	CS	0.829 ^a	-0.803 ^a	-0.706 ^a	-0.474 ^b	0.991 ^a	0.963 ^a	ns
	CS + BC	0.866 ^a	-0.640 ^a	-0.717 ^a	ns	0.854 ^a	0.941 ^a	ns
Zn	CS	0.843 ^a	-0.793 ^a	-0.709 ^a	-0.483 ^b	0.979 ^a	0.974 ^a	ns
	CS + BC	0.842 ^a	-0.658 ^a	-0.691 ^a	ns	0.779 ^a	0.946 ^a	ns

ns = not significant.

DOC: dissolved organic carbon; DIC: dissolved inorganic carbon.

^a Correlation significant at 0.01 level.

^b Correlation significant at 0.05 level.

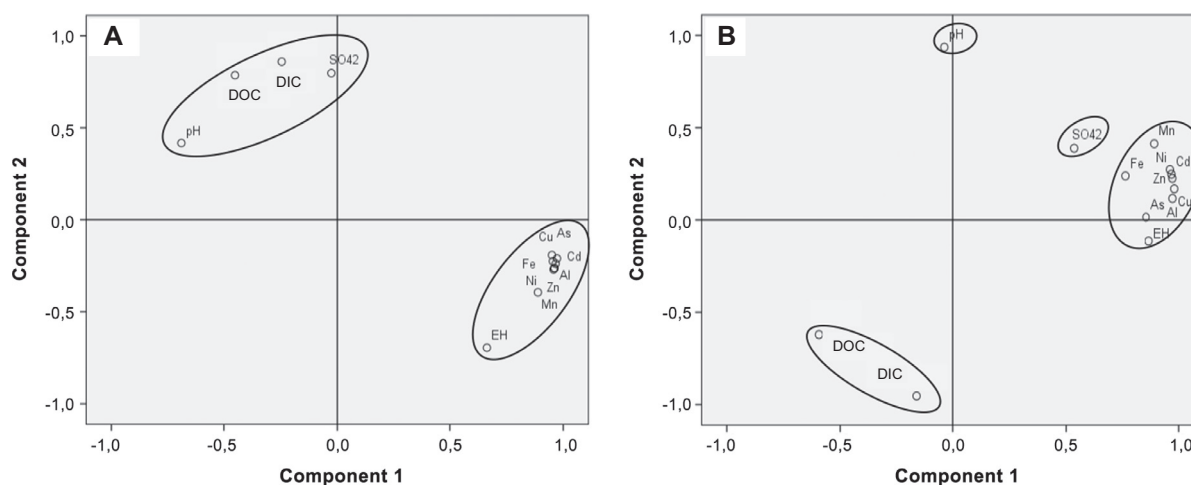


Fig. 2. Factor analysis of the contaminated soil (A) and of the contaminated soil + biochar (B).

mentioned cluster demonstrating that the behavior of these parameters differ substantially from the first group. Moreover, this shows that pH, DOC, DIC, and SO_4^{2-} have a relative similar geochemical behavior in our experiment. This is plausible because the concentrations of Al, As, Cd, Cu, Ni, Zn as well as Fe and Mn in soil solution increase with rising E_H due to the E_H -induced decrease of pH, DIC, and DOC.

In CS + BC, the studied metals behave very similar while their controlling factors differ slightly in comparison to CS (Fig. 2B). Aluminum, As, Cd, Cu, Ni, Zn as well as Fe, Mn, and E_H were clustered in one group too, while SO_4^{2-} was relatively close to this group. The DOC, DIC and pH are separated from the first group which seems logic because they decreased with rising E_H while Al, As, Cd, Cu, Ni, Zn and Fe, Mn increased (Fig. 1). The association of E_H together with Al, As, Cd, Cu, Fe, Mn, Ni, and Zn in one group in both systems, CS and CS + BC shows that release of PTEs under dynamic redox conditions is relatively similar for both, CS and CS + BC. This might mean that the addition of BC seems to have little effect on natural redox processes in the studied soil and thus, dynamics of soluble elements in CS and CS + BC show basically a similar pattern.

The separation of pH, DOC, DIC, and SO_4^{2-} in a group different from the group of PTEs indicate that these factors followed an

opposite behavior compared to PTEs and might affect the solubility and release of these elements to soil solution (Fig. 2A).

The decrease of pH under oxidizing conditions seems to lead to the increased mobilization and release of Al, As, Cd, Cu, Ni, and Zn under oxic conditions in CS and CS + BC (Fig. 1). This is because a low pH in soil–water systems tends to favor the formation of soluble species of many elements; whereas in nonacidic systems, slightly soluble or insoluble forms tend to be predominant (DeLaune and Seo, 2011). In addition, pH affects surface charge characteristics and speciation of element ions; thus, influencing adsorption–desorption behavior of the involved ions (Houben et al., 2013). Also, at low pH the PTEs can be desorbed of organic matter or the surface of clay minerals and other sorbents (Hooda, 2010). Vice versa: an increase in pH likely increased negative charges on soil surface, resulting in higher affinity of PTEs to biochar-amended soil surface (Bakshi et al., 2014; Ahmad et al., 2014b).

Concentrations of water soluble Al, As, Cd, Cu, Fe, Mn, Ni, and Zn in CS + BC were lower than in CS (Table 2 and Fig. 1); mean values of PTEs in soil solution of CS + BC were considerably decreased compared to CS (Al: 37.8%, As: 47.9%, Cd:48.3%, Cu: 55.5%, Fe: 39.6, Mn: 14.2%, Ni: 44.0%, Zn: 50.9%). These results highlight that the used biochar based material is able to act as an immobilizing

agent to reduce the concentrations of dissolved Al, As, Cd, Cu, Ni, and Zn as well as Fe and Mn in CS under dynamic redox conditions. The material contains shell limestone (carbonate) and hence causes a higher pH in CS + BC than in CS (and less decrease of pH under oxic conditions in CS). This higher pH in CS + BC compared to CS induces element immobilization because it favors precipitation of several PTEs, decreases its solubility, and promotes sorption of PTEs by increasing the net negative charge of variably charged soil constituents (McBride et al., 1997; Bradl, 2004; Uchimiya et al., 2010; Karami et al., 2011). It is also likely that the higher pH induced by the application of the biochar based material promoted element sorption on the particles of the material since the density of cation exchange sites increases on the biochar surface with pH (Harvey et al., 2011). Nevertheless, the response of Al, As, Cd, Cu, Ni, and Zn as well as of Fe and Mn to change of pH during the experiment and the release of PTEs under acidic conditions was basically similar in CS + BC and in CS. Moreover, CS + BC has received considerable input of organic matter via the biochar based material and have thus more binding sites compared to CS; in consequence sorption of PTEs increases. Biochar has a large surface area and can thus reduce the solubility of elements (Zhang et al., 2013), particularly in combination with bio-charcoal, humus, and clay of the used material. It is thought that oxidation of BC occurs most rapidly on its outer surface, followed by interior pores, which might result in different element retention between surface and interior sites as a result of shifting cation exchange capacity (CEC) for example (Beesley et al., 2011). The clay component of the added material also contributes to the increase of specific surface area and is thus able to increase the sorption of PTEs. The used biochar based material has been proven to be effective to reduce concentrations of soluble elements originating from a contaminated soil (Shaheen and Rinklebe, 2015; Shaheen et al., 2015).

Copper, which was highly enriched in our soil (total: 2,433 mg kg⁻¹, water soluble: 23.8 mg L⁻¹) showed the highest decreasing rate in CS + BC (55.5%) compared to CS. These results indicate the high efficiency of the used biochar based material to immobilize and reduce the solubility of Cu in this highly Cu contaminated soil. The high efficiency of this material to reduce Cu solubility might be explained by the retain of Cu both to outer surfaces and, when those retention sites were effectively saturated, further adsorbed to the network of pores and fissures that form BC's complex inner micro-structure. Copper was likely retained on BC surfaces through complexation, as reported by Bakshi et al. (2014). They also found that amendment of BC converts a portion of Cu from available pool to more stable forms; thus, resulting in decreased activities of free Cu²⁺ and increased activity of organic Cu complexes in leachate. In addition, the higher pH in CS + BC compared to CS might have enhanced the hydrolysis of Cu²⁺ to form Cu(OH)⁺, Cu(OH)₂, or even precipitation of Cu as hydroxides (Cu²⁺ + 2OH⁻ = Cu(OH)₂) (Stumm and Morgan, 1996). With an increase in pH, more Cu²⁺ was likely sorbed by variable-charge soil components, which have a higher sorption affinity for Cu–OH than Cu²⁺ (Ma et al., 2010).

4. Conclusions

Our results demonstrate that the used biochar based material "TERRA PRETA" is an effective immobilizing agent and able to decrease dissolved concentrations of Al, As, Cd, Cu, Ni, and Zn in comparison to non-treated CS even under dynamic redox conditions. We also found that under prevailing acid conditions the systematic increase of E_H along with reverse decrease of pH favors the mobilization of Al, As, Cd, Cu, Ni, and Zn in both systems, CS and CS + BC. We were able to mechanistically quantify the impact of

pre-definite E_H -conditions on the release dynamics of dissolved metals studied in CS and CS + BC, and to elucidate underlying redox-driven processes. Our results show that the pattern of E_H /pH and the release mechanisms of the studied metals in CS and in CS + BC are basically similar. Thus, the addition of biochar based material seems to have little effect on natural redox processes and linked environmental conditions in acid contaminated floodplain soils, which is important with view to a sustainable management of these ecosystems when consider to use BC as an amendment to decrease mobilization of metals. For a better understanding of mobilization processes of metals, similar studies should be conducted with a variety of wetland soils around the world. In future, it will be challenging to determine different metal species in floodplain soils under dynamic redox conditions which is important for an appropriate risk assessment. In conclusion, the amendment of biochar based material to floodplain soils might lead to a decreased release of metals under changing redox conditions in highly dynamic floodplain ecosystems. This might be worth proving under field conditions with view to an adequate remediation option aiming to minimize the potential risk to humans and environment.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.03.067>.

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