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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.

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 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.

Table 1
Selected properties and element concentrations (microwave digestion[b]) of contaminated soil (CS) and biochar (BC).

	Unit	CS	BC
Basic properties			
pH [H_2O][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
Concentrations[b]			
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).

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).