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Research article

Sugar beet factory lime affects the mobilization of Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn under dynamic redox conditions in a contaminated floodplain soil

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ABSTRACT

The impact of sugar beet factory lime (SBFL) on the release dynamics and mobilization of toxic metals (TMs) under dynamic redox conditions in floodplain soils has not been studied up to date. Therefore, the aim of this study was to verify the scientific hypothesis that SBFL is able to immobilize Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn under different redox potentials (E_H) in a contaminated floodplain soil. For this purpose, the non-treated contaminated soil (CS) and the same soil treated with SBFL (CS+SBFL) were flooded in the laboratory using a highly sophisticated automated biogeochemical microcosm apparatus. The experiment was conducted stepwise from reducing (−13 mV) to oxidizing (+519 mV) soil conditions. Soil pH decreased under oxic conditions in CS (from 6.9 to 4.0) and in CS+SBFL (from 7.5 to 4.4). The mobilization of Cu, Cr, Pb, and Fe were lower in CS+SBFL than in CS under both reducing/neutral and oxic/acidic conditions. Those results demonstrate that SBFL is able to decrease concentrations of these elements under a wide range of redox and pH conditions. The mobilization of Cd, Co, Mn, Mo, Ni, and Zn were higher in CS+SBFL than in CS under reducing/neutral conditions; however, these concentrations showed an opposite behavior under oxic/acidic conditions and were lower in CS+SBFL than in CS. We conclude that SBFL immobilized Cu, Cr, Pb, and Fe under dynamic redox conditions and immobilized Cd, Co, Mn, Mo, Ni, and Zn under oxic acidic conditions; however, the latter elements were mobilized under reducing neutral conditions in the studied soil. Therefore, the addition of SBFL to acid floodplain soils contaminated with TMs might be an important alternative for ameliorating these soils with view to a sustainable management of these soils.

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1. Introduction

Soil contamination with toxic metals (TMs) has become a global concern because of its adverse effects on ecosystem health and food security (Antoniadis et al., 2016). The increasing demand for new and costly processes for the immobilization of TMs in contaminated soils has led many researchers to investigate the possibility of using waste materials for metal immobilization (Bolan et al., 2014). Recently, many studies have focused on the development of non-conventional alternative immobilizing agents and amendments produced from low-cost resources which can be used for the

remediation of TMs contaminated soils (Ok et al., 2011; Shaheen and Rinklebe, 2015; Soares et al., 2015) and waters (Akunwa et al., 2014; Shaheen et al., 2013).

One of the low-cost sorbents is sugar beet factory lime (SBFL). Sugar beet factories have traditionally stockpiled factory lime near them which is produced during the sugar beet juice purification process. This factory lime meets the definition of a liming product and can be used for remediation of metal contaminated soils and waters (Dutton and Huijbregts, 2006). The SBFL is expected to be more efficient in immobilization of TMs compared to other liming materials such as limestone due to its alkalinity and finer texture (Shaheen et al., 2015). Additionally, no attempt has been made to assess the effects of SBFL to immobilize TMs under controlled redox conditions.

Recent studies have highlighted the role of SBFL in immobilization of TMs in soils (Shaheen and Rinklebe, 2015; Shaheen et al.,

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2015). However, these studies investigated the impact of SBFL on the (im)mobilization of TMs in soils under static soil moisture conditions. Floodplain soils are frequently flooded and highly dynamic; thus, soil redox potential (E_H), pH, and governing factors such as iron (Fe), manganese (Mn), dissolved organic carbon (DOC), sulphate (SO_4^{2-}) and others differ significantly compared to field capacity conditions. These highly dynamic conditions have considerable impacts on the release dynamics of TMs in soils (Frohne et al., 2011; Shaheen et al., 2014, 2016a,b).

Detailed knowledge about the redox-induced behavior of TMs in contaminated floodplain soils treated with SBFL and compared with non-treated soil is required for a better understanding of the mobilization of TMs and their controlling processes. This knowledge enables a more accurate prediction of metal release into ground- and surface waters in response to changing redox conditions which might contribute to develop an adequate risk assessment and management of contaminated floodplain soils. Thus, we aimed to assess the impact of SBFL on the mobilization and release dynamics of cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), and zinc (Zn) under dynamic redox conditions in a highly contaminated floodplain soil treated with SBFL and non-treated. The obtained results will be an aid to verify the scientific hypotheses that the liming material SBFL is able to immobilize toxic metals in floodplain soils under different redox conditions. In addition the obtained results will help to quantify the impact of pre-definite E_H -conditions on the release dynamics and mobilization of TMs in the SBFL treated soils. Moreover, these results could serve as a precondition for the development of innovative technologies for management of wetland soils aimed at avoiding pollutant exposure to plants, water, soil, and riverine ecosystems.

2. Materials and methods

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

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 SBFL are presented in Table 1.

Soil texture was dominated by silt. The soil was weakly acidic and contained high organic carbon. The soil has elevated total content of the elements. Total concentration of the studied elements in the soil was 6.0, 20.4, 490.3, 2433.4, 6.8, 80.9, 412.0, and 1050.1 mg kg⁻¹ for Cd, Co, Cr, Cu, Mo, Ni, Pb, and Zn, respectively. The total metal concentrations exceeded the precautionary values of the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999). Moreover, the values of Cd, Cr, Cu, Pb, and Zn were higher than the upper limit of the trigger action values for TMs in agricultural soils as reported by Kabata-Pendias (2011), implying harmful soil alterations which need remediation. High total content of TMs in the studied soil may be due to the contamination of the water and sediments of Wupper River originate from anthropogenic activities (Frohne et al., 2011).

The SBFL was obtained from the Delta sugar beet factory in El-Hamoul, Kafr El-Sheikh governorate, Egypt. The SBFL was alkaline (pH = 8.7), contained high amounts of total carbonates (82.5%), total sulfur (S), aluminium (Al), Fe, and contained low concentrations of TMs (Table 1). The SBFL was applied to the soil at a rate of 10 g kg⁻¹ soil. Soil and SBFL 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

Table 1

Properties and element concentrations (microwave digestion²) of contaminated soil (CS) and sugar beet factory lime (SBFL).

	Unit	CS ^a	SBFL ^b
Basic properties			
pH [H ₂ O] ^c		6.4	8.70
Silt	[%]	92.0	n.d. ^d
Clay		2.00	n.d.
Total nitrogen		0.35	n.d.
Total carbon		7.10	n.d.
Total carbonates		b.d.l.	82.5
Concentrations ^e			
Cd	[mg kg ⁻¹]	6.9	b.d.l. ^f
Co		20.4	b.d.l.
Cr		490.3	9.96
Cu		2433.4	7.43
Mo		6.83	b.d.l.
Ni		80.9	3.60
Pb		412.0	b.d.l.
Zn		1050.1	14.03
[g kg ⁻¹]			
Al		18.5	1.71
Fe		43.8	0.85
Mn		0.87	0.08
S		0.99	2.03

^a CS: contaminated soil.

^b SBFL: sugar beet factory lime.

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

^d n.d. = not determined.

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

^f b.d.l. = below detection limit.

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 + sugar beet factory lime (CS+SBFL) in laboratory. This system was successfully employed in previous studies (Frohne et al., 2011; Rinklebe et al., 2016a,b; Shaheen et al., 2014, 2016a,b). Technical details are provided in (Yu and Rinklebe, 2011) and 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, SO_4^{2-} , Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn. The results 6 h before sampling generally resulted in closest correlations and were therefore used for statistics. The program IBM SPSS Statistics, Version 22 was used for conducting correlations and descriptive analysis.

3. Results and discussion

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

The minimum, maximum, and mean values of soil E_H and pH in CS and in CS+SBFL are presented in Table 2. The relationships between E_H and pH with DOC, Fe, Mn, and SO_4^{2-} are presented in Figs. 1 and 2, respectively. The E_H values ranged between +74 and +503 mV in CS and between -13 and +519 mV in CS+SBFL. The pH values ranged between 4.0 and 6.9 in CS and between 4.4 and 7.5 in CS+SBFL. Soil pH shows an opposite behavior to E_H (Fig. 1). Therefore, the relation between soil E_H and pH was negative

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