BIOCHAR REDUCES THE RELEASE OF HEAVY METALS UNDER DYNAMIC REDOX CONDITIONS IN CONTAMINATED WETLAND SOILS

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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 (Frohne et al., 2014; Rinklebe and Shaheen, 2014). 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 (Shaheen and Rinklebe, 2015). Biochar (BC) as a carbon-rich material fulfils those requirements. 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), 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. Thus, we aimed i) to quantify the impact of pre-definite EH-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.

Methods

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. An automated biogeochemical microcosm system was exploited to simulate flooding of the contaminated soil (CS) and contaminated soil + biochar (CS+BC) in laboratory.

Results

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 PTEs even under dynamic redox conditions. Concentrations of Al, As, Cd, Cu, Ni, and Zn showed wide ranges during the experiment. 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. 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. 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). Our results demonstrate 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 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. (Rinklebe et al., 2016).

Conclusion

Our results demonstrate that the used biochar based material 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 seem 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.

References

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