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EFFECT OF SUBSTRATE PROPERTIES ON THE MOBILITY OF SELECTED TRACE ELEMENTS IN SOIL AND CONCENTRATIONS IN SHOOTS OF *PHALARIS ARUNDINACEA*

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Abstract: Phytomining is a phytoassisted technique for the extraction of economically valuable elements from soils and offers a promising chance to improve the supply of critical raw materials such as germanium (Ge) and rare earth elements (REEs). The efficiency of phytoextraction depends on numerous soil-associated and plant-associated factors (e.g. concentrations of target elements in potentially plant available soil fractions, rhizosphere processes and uptake mechanisms of plants). The aim of this study was to evaluate the effect of different soil properties (pH, compost amendment) on the mobility of selected target elements for phytoremediation (As, Pb, Cd, Zn) and phytomining (Ge, REEs) in soil and shoot concentrations in *Phalaris arundinacea*. Until today, only little is known about the influence of soil-associated factors on the availability of trace elements for *Phalaris arundinacea*, especially for the target elements Ge and REEs. In a field experiment we cultivated 10 different genotypes of *Phalaris arundinacea* on four different substrates with similar element concentrations but different pH-values (pH 6.6 – 7.8) and levels of compost amendment (5 l/m^2 compost or without compost). On each of the substrates we cultivated *Phalaris arundinacea* (genotypes) with two replicates on plots 4 m^2 each and installed suction cups to collect soil solution. After harvest concentrations of Ge, REEs, P, Fe, Mn, Zn, Pb, As and Cd in shoots and soil solution were determined with ICP-MS. Compared to the slight alkaline soil, acidic soil conditions significantly increased shoot concentrations of Fe, Mn, As, Cd, Pb and REEs. Under acidic soil conditions addition of compost further increased the concentrations of all investigated target elements in shoots of *P. arundinacea* except of As. In soil solution only concentrations of Fe and Mn significantly increased due to the compost amendment, while concentrations of P, Ge, REEs, Cd and Pb decreased. Lower concentrations of elements in soil solution may result from increased adsorption of the elements onto soil particles (in case of P and Ge) or the uptake of the elements by plants (in case of Cd and Pb). We conclude that amendment of soil with compost seems to be a sustainable approach to enhance the uptake of plant nutrients such as Fe and Mn as well as REEs into shoots of *Phalaris arundinacea* and to reduce the mobility of potential toxic trace elements (Cd, Pb) in soil solution.

Keywords: Germanium, rare earth elements, heavy metals, phytomining, phytoremediation, *Phalaris arundinacea*, soil solution

1. INTRODUCTION

The mineralization of soils in post-mining landscapes is typically affected by anthropogenic element inputs from mining and ore processing activities which led to elevated element concentrations in soils compared to the naturally occurring background levels. Pollution of soils with elements from anthropogenic sources are of particular concern since these elements enter the environment mostly in ionic forms, accumulate in soils, bioaccumulate in crops and may enter the food chain (Antoniadis et al., 2017) posing a risk to the environment and human health. (Chour et al., 2018). Therefore, contaminated sites in post-mining landscapes often are restricted in land use and crop production is prohibited (Kumar 2013). However, soil is one of the most important and essential natural resources providing essential ecosystem services and consequently the sustainable treatment and remediation of polluted soils is of increasing research interest. Besides potentially toxic elements, these soils may also contain considerable concentrations of economically valuable elements such as germanium and rare earth elements (Wiche et al., 2017). Therefore, phytoextraction technologies have become high public and scientific interest since they potentially offer an economically and environmentally friendly alternative to clean up polluted soils (Kumar, 2013) and not at least the recovery of raw materials. Compared to phytoremediation, phytomining describes the use of plants to extract valuable trace elements from ore bodies or metal-contaminated environments, where the target metal concentration is too low for conventional mining (Brooks et al., 1998; Robinson 1999). The typical steps of phytomining involve the accumulation of the target elements in plants, harvesting the biomass for bio-energy purposes and the extraction of the elements out of the bio-energy residues (Sheoran et al., 2009). A successful phytomining process depends on adequate biomass yield and high metal concentrations in the harvestable parts of the plants in order to maximize the element amounts in above ground plant parts which can be harvested (Sheoran et al., 2009). Availability of elements to plants generally depends on a number of soil-associated and plant-associated factors controlling the distribution of elements in stable and labile elements pools as well as the mobility and chemical speciation in the rhizosphere of the plants (Sheoran et al., 2016). It is generally assumed that total concentrations in soils are not an adequate proxy to describe the availability of target elements to plants since elements present in different element pools/soil fractions vary considerably in their chemical reactivity. Generally, plants can only take up elements from soils, if the elements are present in dissolved, ionic form or in labile (exchangeable, easily soluble chemical forms) which can dissolve to replenish the elements in soil solution taken up by roots. Moreover, in the rhizosphere myriads of processes and interactions between a plant root, soil and the associated microbes take place influencing pH, redoxpotential and chemistry through release of C-compounds in the vicinity of the roots (Wiche et al., 2016a; Wiche & Heilmeier, 2016). In phytoremediation and phytomining research numerous methods to enhance phytoextraction efficiency have been proposed including the use of chemical soil amendments such as chelating agents of organic and mineral acids (e.g. citric acid) elemental sulfur and ammonium fertilizers (Mahar et al., 2016; Wiche et al., 2017). The application of synthetic chelating agents such as ethylene diamine tetraacetic acid (EDTA) are potentially acidifying agents enhancing the phytoextraction of Ni, Cu, Cd, Pb and Zn (Evangelou et al., 2007; Mahar et al., 2016). Robinson et al., (1996) has shown that soil acidification increases the solubility of metals in ultramafic soils which in turn can increase metal uptake by the plants. Damian et al. (2018) investigated the effects of organo-zeolitic material as soil amendment on the efficiency of phytoremediation using a substrate from a copper mining waste dump in Slovakia. They could demonstrate that the addition of organic zeolites decreases the available heavy metal content in the mining dump material and improved the nutritional conditions leading to enhanced plant growth. Previously, Damian et al. (2013) found similar effects of natural zeolite on the immobilization of Pb, Cd, Zn and Cu in soil under greenhouse conditions.

However, application of these soil additives in phytoremediation and phytomining practice often suffers from their high costs and their restriction to small soil volumes and sites without connection to waterbodies, since the chemicals are expensive and may have hazardous environmental side-effects. Besides inorganic soil additives the use of organic soil amendments and fertilizers such as manure and fermentation residues represent a promising chance to improve phytoextraction efficiency. The use of organic soil amendments influences microbiology, bring in organic compounds which may increase solubility of target elements (Davranche et al., 2015), affect pH, redox potential and nutritional state of the plant through input of nutrients (Vamerali et al., 2014). Generally the effect of organic soil amendments on the availability of target elements can be dual: On the one hand it may increase the concentration of labile element pools through increase of the cation exchange capacity and on the other hand it may increase the solubility of elements in soil solution through changes in soil pH and input of dissolved organic ligands fostering the formation of soluble chelate-complexes (Warren & Haack, 2001; Basta et al., 2005; Sheoran et al., 2016) . While literature on effect of soil organic matter on the availability of heavy metals and plant nutrients is extensive (Macclean 1976; Bolan & Duraisamy 2003; Herencia et al., 2008; Wiszniewska et al., 2016) until today there still is a lack of knowledge in if and how the use of organic soil amendment influences the availability of Ge and REEs in soils. Therefore, in the present study we investigated the effect of the use of compost as soil amendment and soil pH on the concentrations of P, Mn, Zn, Fe, Ge, REEs, As, Pb, Cd in soil solution and the uptake in *Phalaris arundinacea* (reed canary grass), a novel bioenergy plant. In this study *Phalaris arundinacea* was used, because it is a highly expansive, fast growing and high-biomass producing plant species, showing a high capacity of trace element bioaccumulation, particularly of Ge and rare earth elements (REEs) (Polechońska & Klink 2014; Wiche & Heilmeier 2016; Wiche et al., 2017). Therefore, the present study not only elucidates the effects of organic compost amendment on the mobility of target elements in soil but also reports novel results on soil-associated factors on the availability of the elements to plants.

2. MATERIAL AND METHODS

2.1 The field experiment

The field experiment was carried out in a semi-lysimeter consisting of a concrete basin with an area of 400 m^2 and a depth of 1.8 m at the recycling and remediation center of Bauer Umwelt Company in Hirschfeld (Saxony, Germany). The basin was filled with two different homogenized top soils (300 m^3 each) (for details see Wiche & Heilmeier 2016). The first soil from a road construction site (hereafter referred to soil A) was a silty loam with a pH (H_2O) 7.8, CEC 13.6 cmol kg^{-1} and organic matter content of C_{org} 6.8%. The second soil from a mining affected area near Freiberg (hereafter referred to soil B) was a silty loam with a pH (H_2O) 6.6, CEC 9.1 cmol kg^{-1} and organic matter content of C_{org} 5.9%. Element concentrations in the two different substrates before fertilizer application (compost) and concentrations of elements in the compost are shown in Table 1. Initial plant available nutrient concentrations of the substrate A (before fertilizer application) were 83 µg g^{-1} N, 25 µg g^{-1} P, 289 µg g^{-1} K, 956 µg g^{-1} Ca, 224 µg g^{-1} Mg and 95 µg g^{-1} N, 30 µg g^{-1} P, 374 µg g^{-1} K, 357 µg g^{-1} Ca and 118 µg g^{-1} Mg for substrate B (before fertilizer application). The elements K, Mg, and P were extracted by calcium acetate lactate (CAL) (Schüller 1969) and measured with ICP-MS. Ca was extracted with NH_4acetate buffered to pH=5 For the analysis of mineral N (N_{min}), NH_4^+ and NO_3^- were extracted from soil samples with 1M KCL or rather with deionized water and photometrically determined according to Bolleter et al., (1961) and Hartley & Asai (1963). The plant available N (mineral) in soil was calculated as the sum of NH_4^+-N and NO_3^-—N.

At the beginning of the vegetation period in 2017 5 l m^{-2} of compost from leaves and grass cuttings were spread out on half of the total area of each of the two substrates in order to investigate the effect of compost amendment separately for each soil pH.

2.2 Plant growth

Plants of different *Phalaris arundinacea* genotypes were obtained from Deutsche Saatveredelung AG, Lippstadt, Germany. To test the effect of soil properties on the availability of trace elements in soils and concentrations in shoots of *Phalaris arundinacea*, on each of the four substrates 10 different genotypes of *Phalaris arundinacea* were cultivated on 80 plots with an area of 4 m^2 each. On each of the substrates each *Phalaris arundinacea* genotype was cultivated with two replicates. Surrounding each plot, a 0.5 buffer zone was kept without vegetation to prevent interactions between neighbouring plots. The planting was finished at the end of June 2017. The field experiment was carried out from summer 2017 until autumn 2018. During this time, the plant individuals of the perennial grass species *Phalaris arundinacea* were allowed to establish closed stands.

2.3 Sampling of soil solution

For the sampling of soil solution plastic suction cups (Company: ecotech, Bonn, Germany) were installed at a soil depth of approximately 20 cm in the middle of each of the plots. The arrangement of the suction cups allowed a continuous and non-destructive collection of soil solution from the main rooting horizon per plot. After installation of the suction cups

Table 1. Total element concentrations of the two different substrates and the compost used in the experiment. The element concentrations were measured according to Wiche and Heilmeier (2016). Results are means of 15 replications for each substrate. Total concentrations of REEs were calculated as sums of all 16 rare earth elements (La–Lu, including Sc and Y)

Substrat	P	Mn	Fe	Zn	As	Pb	Cd	Ge	REEs
	µg g^{-1}								
A	1103	694	18328	439	1.24	137	324	1.33	177
B	1155	727	21013	291	2.46	172	376	1.53	136
compost	2578	317	5465	297	0.32	448	40	0.76	47

a negative pressure of 60 kPa was immediately applied and maintained over the whole vegetation period. The received soil solution was continuously collected in sorption free polypropylene bottles, that were buried in soil on the field site to protect the solution from sunlight and drastic changes of temperature. From these bottles, soil solution was sampled monthly in Mai, June, July and August 2018. The first sample solution after installation of suction cups and planting of *Phalaris arundinaneca* (Mai 2018) was discarded to minimize the effect of installation on the chemistry of the first soil solution sample. Due to a longer drought period in June and July 2017, in these months sampling of soil solution was not possible. Therefore, the presented data focusses on the soil solution sampled in August 2017. The sampled soil solution was stabilized by acidifying to pH < 2 with nitric acid and stored at 4°C until being analysed by ICP-MS.

2.4 Harvesting and element analysis

All plants were harvested at the end of the vegetation period in late autumn 2018. The shoots of all plants were cut 10 cm above the soil surface. Only the shoots in the inner square meter of each plot were used for further chemical analysis to exclude plants who might be influenced by edge effects (e.g. root interactions with plants on neighbour plots, changes in transpiration through differences in climatic conditions). After harvest the shoots of each plot were dried at 70°C, weighed and grounded to a fine powder prior to trace element analysis. A microwave digestion with nitric acid and hydroflouric acid was performed with a subsample (100 mg) of the plant material according to Krachler et al., (2002) and Wiche & Heilmeier (2016) . Concentrations of Ge, REEs, P, Fe, Mn, Zn, As, Pb and Cd in shoots were measured by ICP-MS with 10 µg/l rhodium and rhenium as internal standard. Accuracy was checked by analysis of the certified reference material NCS ZC73032 (China National Analysis Center for Iron and Steel 2014); all results deviated by less than 10% from certified values.

2.5 Statistical Analysis

Differences in element concentrations in the shoots of genotypes of *Phalaris arundinacea* and soil solution concentrations were identified by one-way analysis of variance ANOVA using Statgraphics Centurion XV. For each of the analysis residuals were tested for homogeneity of variances by using Levene’s test a. In case of equal variances (at p = 0.05) significant differences between groups were identified by a Fisher LSD post-hoc test at $\alpha = 0.05$. In case of unequal variances, a non-parametric Kruskall-Wallis test was used.

3. RESULTS AND DISCUSSION

3.1 Effect of compost amendment on the availability of P, Mn, Fe, Zn in soil

Addition of compost to the soil significantly affected the mobility and availability of all considered plant nutrients except of Zn and this effect was clearly dependent on the initial pH of the soil (see Fig. 1 and 2). In this study most effects of the compost amendment on the availability of nutrients were observed on the slightly acidic substrate B suggesting a number of biogeochemical interactions between the organic matter and the initial element binding forms within the soil. Specifically, addition of compost significantly decreased the concentrations of P in soil solution of the slightly acidic substrate B (B1: 324 – 118 µg l^{-1} and 161 – 46 µg l^{-1} on B2), while there was no effect on substrat A. For P the decreasing mobility could be explained by specific sorption of phosphate to humate surfaces through the formation of sparingly soluble humate Fe(Al)P complexes under acidic soil conditions (Mengel et al., 2001). In contrast, we observed a significant increase in the soil solution concentrations of Fe (p = 0.0046) and Mn **(**p = 0.026**)** on substrate B when compost was added. Here, the concentrations in soil solution increased from 78.8 µg l^{-1} to 18430 µg l^{-1} for Mn and from 10 µg l^{-1} to up to 2811 µg l^{-1} for Fe. In soil Fe and Mn are mostly present in the form of sparingly soluble Fe-oxihydroxides or Mn-oxides which form the largest potential plant available “labile” pool for these elements (Marschner 1995). Most probably for these elements, the input of chelating compounds such as humic acids and low molecular weight organic acids with the compost and, therefore, the formation of dissolved chelate complexes may have led to these results. However, in the present study, the increased concentrations of Fe and Mn in soil solution where only observable under slightly acidic conditions which could be due to a strong readsorption of Fe and Mn under alkaline conditions favouring the presence of these elements in particulate soil fractions. Concomitantly we observed significantly higher concentrations of the abovementioned elements in plants. On substrate B addition of compost significantly increased the concentrations of Fe and Mn in the shoot biomass of *Phalaris arundinacea* by a factor of 5 (see Fig. 1), while there was no significant effect on Zn and P in the plants. Possibly, availability of these elements to plants depends on processes in the rhizosphere rather than slight changes in bulk soil chemistry. In the rhizosphere plants are able to influence availability of nutrient through release of protons, enzymes and chelating compounds (Hinsinger et al., 2009; Lambers et al., 2015) and can buffer changes in bulk soil chemistry (Hinsinger et al., 2009). From this, it would be interesting to investigate effects of compost amendment on chemical changes in rhizosphere of the plants. However, since we did not expect these results our data obtained from this field experiment do not allow further interpretation and the elucidation of the processes involved remains field for future research.

3.2 Effect of compost on the availability of heavy metals, Ge and REEs in soil

Compared to plants cultivated on the slightly alkaline substrate A, plant shoots of *Phalaris arundinacea* cultivated on the slightly acidic substrate B were characterized by significantly higher concentrations of all investigated elements except of Ge (at $\alpha = 0.05$) (Fig. 1). Concentrations of elements in the plants considering all substrates ranged from 0.24 µg g^{-1} to 0.9 µg g^{-1} for Ge, 0.1 – 2.5 µg g^{-1} for REEs, 0.6 – 4.7 µg g^{-1} for As, 0.01 -0.2 µg g^{-1} for Cd and 0.2 -7.7 µg g^{-1} for Pb (Fig. 1). Amendment of the soil with compost further increased the shoot concentrations of As, Cd, Pb and REEs, while there was no effect on Ge (Fig. 1e). The concentrations for As increase from 0.7 to 4.7 µg g^{-1}, for Cd from 0.02 to 0.2 µg g^{-1}, for Pb from 0.7 up to 7.7 µg g^{-1} and for the REEs from 0.1 µg g^{-1} to 2.5 µg g^{-1} on the slightly acidic soil with compost (Fig. 1). Similar to the investigated nutrients it appears reasonable that this increase in plant concentrations may derive from an increased mobility of the elements in soil allowing them to move towards the plant roots where they are subsequently taken up. Effects of dissolved organic compounds on the mobility of Pb, Cd and REEs are extensively reported in the literature (Harter 1983; Pourret et al., 2007) and predominantly derive from the formation of dissolved complexes. However, in this study concentrations of elements significantly decreased in case of Pb, Cd, Ge and REEs following the soil amendment with compost, or remained constant in case of As (Fig. 2). For these elements it appears reasonable, that the uptake of the elements by the plant roots led to a depletion of the mobile element fraction pool as already pointed out by (Wiche et al., 2016) and Hecht et al., (2017). Decreasing concentrations of Ge in soil solution may result from an increasing adsorption of Ge on soil organic compounds (Wiche et al., 2018) and the Ge that was initially mobile was removed from soil solution and no longer available for plant uptake (Wiche et al., 2018). Overall, these results clearly show that

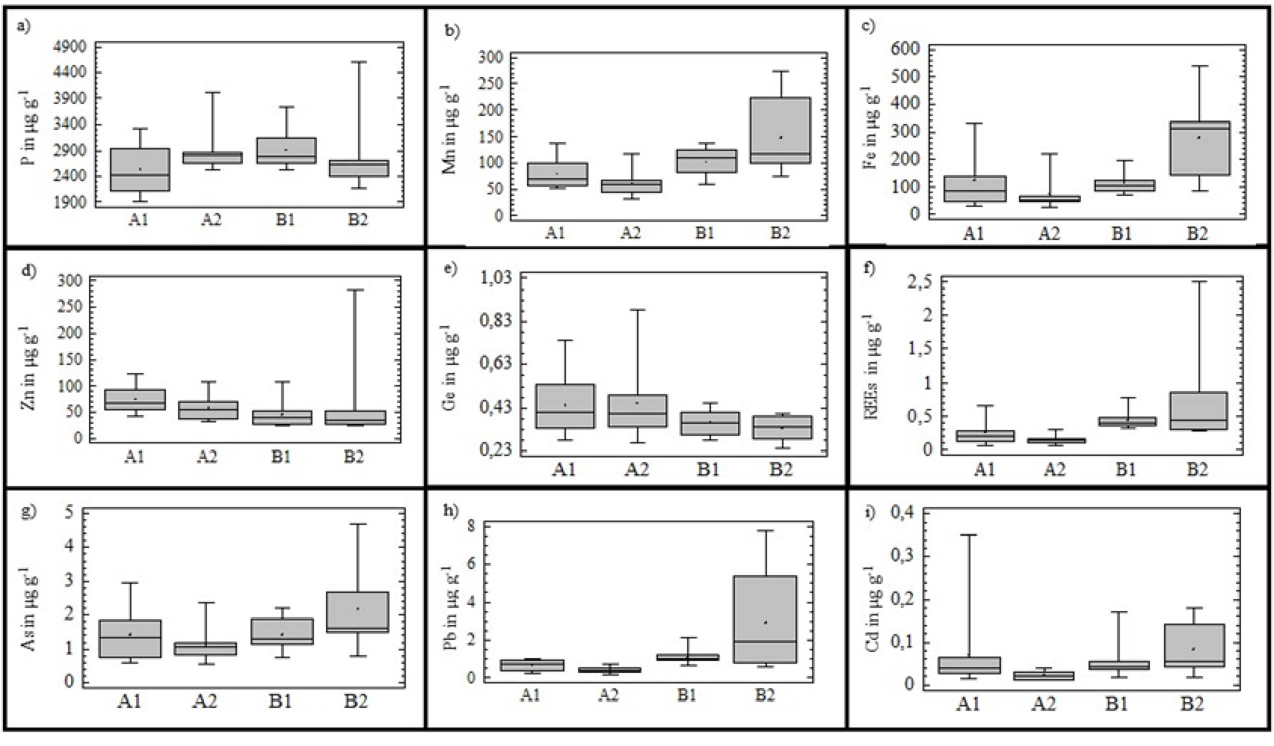

Figure 1. Concentrations of essential a) P, b) Mn, c) Fe, d) Zn and non-essential elements e) Ge and f) REEs as sum of all REEs, g) As, h) Pb and i) Cd in shoots of *Phalaris arundinacea* growing on an alkaline (A) and an acidic substrate (B) with compost (A2: pH 7.8, B2: pH 6.6) and without compost (A1: pH 7.8, B1: pH 6.6).

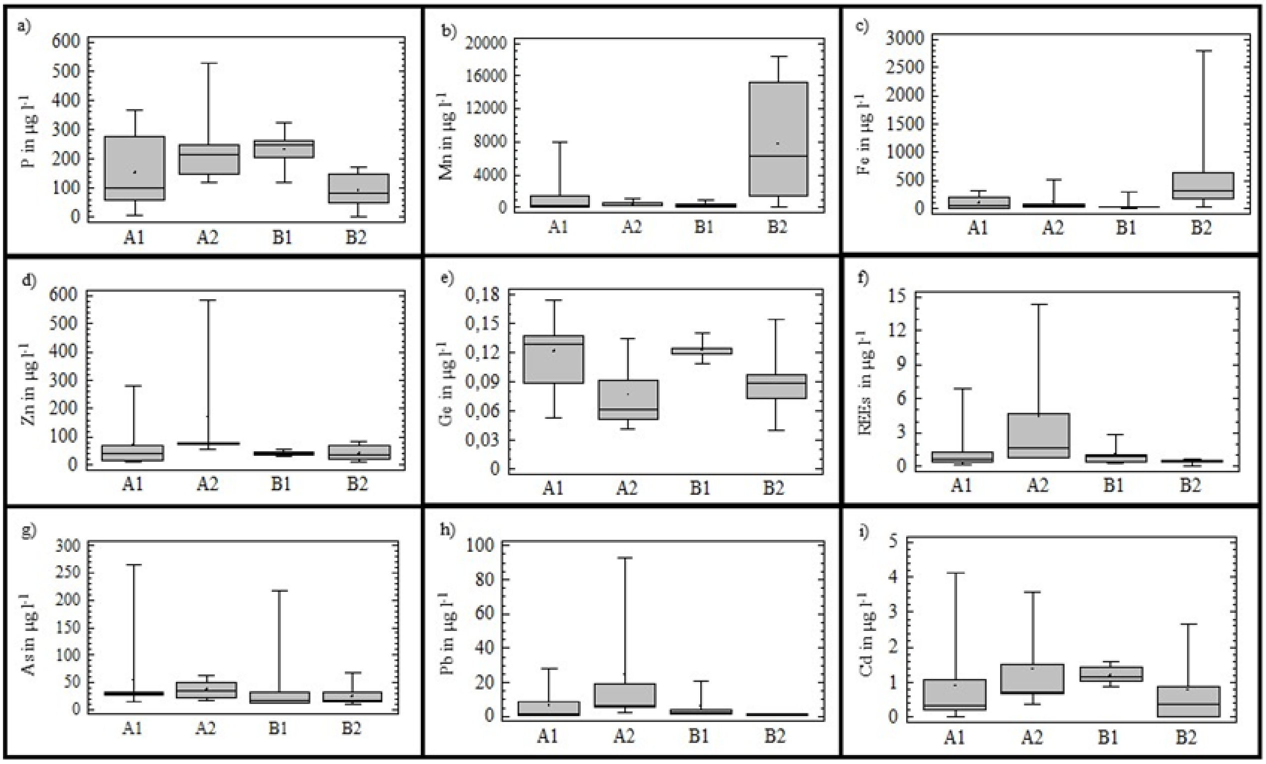

Figure 2: Concentration of soil solution of essential a) P, b) Mn, c) Fe, d) Zn and non-essential elements e) Ge and f) REEs as sum of all REEs, g) As, h) Pb and i) Cd on an alkaline (A) and an acidic substrate (B) with compost (A2: pH 7.8, B2: pH 6.6) and without compost (A1: pH 7.8, B1: pH 6.6).

amendment with compost has a high potential for the enhancement of the phytoextraction efficiency of a number of target elements in phytoremediation and phytomining research enhancing the mobility of the target elements in soil hence fostering soil-plant transfer. However, the processes behind these results remain unclear and need further research. In our study we observed a high variability in the element concentrations within the plants although all plants were cultivated on homogenized soil within each substrate (Fig. 1). This variability might be an effect of an intraspecific variation in element acquisition and uptake among the different genotypes used in this study (Kalisz et al., 2019). Therefore, major objectives of future experiments will be to evaluate the genotypic variability in element accumulation among the genotypes and elucidate related processes in the rhizosphere.

4. CONCLUSION

We could demonstrate under field conditions that both, the initial soil pH as well as the amendment of soil with compost significantly affects the availability of a number of target elements in phytoremediation and phytomining research (Mn, Fe, REEs, As, Cd, Pb), except of Ge. Under slightly acidic conditions amendment with compost significantly increased the uptake of Mn, Fe, REEs, Pb and Cd in shoots of *Phalaris arundinacea*. In soil solution only concentrations of Fe and Mn significantly increased while we observed decreasing concentrations for Ge, REEs, Cd and Pb). Decreasing concentrations in soil solution may indicate increased interactions of the elements with the soil matrix as well as enhanced uptake of the elements by plants. This clearly shows that amendment of soil with compost represents a powerful tool to enhance phytomining of REEs and the remediation of polluted soils. However, the processes remain enigmatic and remain field for further research.

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