Concentration and bioavailability of toxic trace elements, germanium, and rare earth elements in contaminated areas of the Davidschacht dump-field in Freiberg (Saxony)

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Konzentration und Bioverfügbarkeit von Schwermetallen, Germanium und Seltenen Erdmetallen in kontaminierten Substraten der Spülhalde Davidschacht in Freiberg (Sachsen)

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Summary: The presented research is focused on the geochemical characterization of substrates of the Davidschacht dump-field in order to elucidate plant available concentrations of selected toxic trace elements (As, Zn, Cd, Pb), Ge, and rare earth elements (La, Nd, Gd). In total, 12 sampling sites with different composition of plant species were selected. Soil samples from a depth of 10 cm and samples of plant material were taken at each of these sites. The soil samples were analyzed for total concentrations of elements, pH (H_2O) and element concentrations in four operationally defined soil fractions. Element concentrations in soil extracts and plant digests were measured by ICP-MS. Our results show that besides high concentrations of toxic trace elements, the substrates are characterized by high concentrations of Ge (up to 8 mg kg^{-1}), but only moderate concentrations of REEs. The pH of the substrates correlated significantly positively with the total concentrations of all investigated elements, except of As and Pb. Potentially plant available concentrations decreased in the order Cd > Zn > As > Pb > >REEs > Ge. However, highest concentrations of Ge were found in *Phragmites australis* (0.63 mg kg^{-1} Ge) and *Phalaris arundinacea* (0.57 mg kg^{-1} Ge), whereas *Populus tremula*, *Tanacetum vulgare*, *Lotus corniculatus* and *Agrostis capillaris* showed high concentrations of toxic trace elements and rare earth elements.

Keywords: flotation tailing, rare earth elements, germanium, bioavailability / Spülhalde, Seltene Erden, Germanium, Bioverfügbarkeit

1. Introduction

Mining presents a massive country-changing anthropogenic activity. The mining waste, deposited in country enclaves (dump-fields) often contains a complex composition of the residual mining material and chemical substances from ore processing. Thus, dump-fields are of particular environmental concern since they can be a source of toxic metals or chemicals that are released through leaching by infiltration of rainwater into the substrate. The presence of those enclaves mechanically and chemically affects the environment, and thus cause ecological stress.

Very recently, however, mine dumps are of increasing interest for the recovery of economically valuable elements through “urban mining”. Urban mining means the recovery of raw materials from secondary resources, for instance from dump material (Brunner 2011). In times of concerns for long-term availability of natural resources, elements in mine dumps represent often overlooked reservoirs that might offer an opportunity for more sustainable development (Bergbäck et al. 1997; Krook et al. 2011; Krook & Baas 2013). Among these elements germanium (Ge) and rare earth elements (REEs) might be of particular interest, since policies for the transition to a low-carbon economy and a non-toxic environment have reshaped the global raw material demand patterns to those elements used for high-tech devices and engineered systems (Erdmann & Graedel 2011). Ge and REEs are important raw materials with a growing demand for the production of electric automobiles, infrared optics, fiber-optic technologies, displays and micro-electronics (Wiche & Heilmeier 2016). Unfortunately, worldwide only a few deposits exist that contain workable concentrations of REEs (Kumari et al. 2015). Moreover, primary deposits of germanium are lacking. Until today germanium is only gathered as a co-product of the Zn ore processing (Rosenberg 2007). However, these elements are actually not rare but occur widely dispersed in the Earth`s crust. The average concentration of Ge in Earth`s crust is estimated at 1.6 mg kg^{-1} (Rosenberg 2007). The group of REEs is commonly defined as the 15 elements comprising the Lanthanide series, sometimes scandium (Sc) and yttrium (Y) are included as well (Tyler 2002). REEs are prevalent in the Earth`s crust with average concentrations that vary from 66 µg g^{-1} for cerium (Ce 9, 40 µg g^{-1} for Nd, 35 µg g^{-1} for La to 6.1 µg g^{-1} to 0.8 µg g^{-1} for Lu (Tyler 2002). Sulfide ores such as sphalerite (ZnS) are often enriched in Ge (Bernstein 1985; Liang et al. 2009) and consequently we hypothesize that mine dumps in the polymetallic mineralization area of Freiberg might be promising spots for urban mining. In this study, the Davidschacht dump-field ("Spülhalde Davidschacht") in Freiberg (Saxony, Germany) was selected as the study area, due to its age, position, geochemical character and environmental impact, caused by toxic trace elements such as Zn, Cd, Pb, and As (see Fritz & Jahns 2017). The estimation of tailing material volume is approx. 1.3 Mt. The average of metal content in the dump-heap was estimated to be 0.25 wt.% Pb and 0.24 wt.% Zn, whereas the content of S refers to 5.57 wt.%. The waste material is covered by a thin layer of coarse sand and topsoil (Redwan et al. 2012). Besides traditional mining techniques, phytomining might be a particularly suitable technique to extract the elements from those mine dumps. Phytomining represents an environmental friendly, advanced technique of phytoremediation that uses plants to extract elements economically viable from soils or ore bodies with sub-economical mineralization, for instance from mine tailings (Heilmeier et al. 2016; Wiche & Heilmeier 2016). Concomitantly, during the accumulation of economically valuable elements some plant species also accumulate toxic trace elements in their plant tissues and give possibilities for the remediation of these sites. However, only little is known about the mineralization and plant available concentrations of Ge and REEs in the dump material in the Freiberg region (Wiche et al. 2017).

The aim of the present study was to (a) establish the total concentrations of Ge, REEs and selected toxic trace elements (As, Pb, Cd, Zn) in the dump material of the Davidschacht tailing, (b) evaluate the plant availability of the elements in the substrate, and (c) investigate the concentrations of the aforementioned elements in the present dump vegetation, in order to identify potentially promising plant species for phytoremediation and phytomining research.

2. Study area

The mine-dump of Davidschacht is located within the municipality area of Freiberg (Saxony). It is situated next to Freiberger Mulde river (in western direction) and at the eastern margin of the city (GPS 50˚55′34″N 13˚22′8″). The area of study consists of app. 72,500 m^2 and its elevation is within the limits of 25 – 30 m (Fritz & Jahns 2017, Richert et al. 2017a).

The mining activity in Freiberg was focused on Ag, Cu, Pb, As (1168 – 1915) and later on Zn and pyrite (end of 19th century – 1968). The geological base of Freiberg is formed by two hydrothermal mineralization events: Late-Variscian and Post-Variscian. The Late-Variscian event is mainly characterized by followed minerals: pyrite, sphalerite, arsenopyrite, galena and quartz. The Post-Variscian mineralization event consists mainly of galena (PbS) pyrite (FeS_2), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and marcasite (FeS_2) as well as quartz (SiO_2), barite ($BaSO_4$), fluorite (CaF_2) and carbonates (Baumann et al. 2000; Junghans & Tichomirowa 2009). The waste rock material of dumps in the locality and its surroundings consists mainly of the hard rock gneiss dome of Freiberg. Typical mineral constituents of this biotite gneiss are quartz, feldspar and biotite (Baumann et al. 2000; Stockmann et al. 2012).

The dump exists since the third decade of 20th century and represents the waste of the main mining activity of Davidschacht (see Fritz & Jahns 2017). Until the end of mining activity, approximately 760,000 m^3 of waste was cumulated at the heap, which has an artificial dam downslope at North and East (Fig. 1). In order to extract the materials of interest, the flotation technique was used. Thus, the significant part of the tailings consists of flotation residues (Redwan et al. 2012). During the following years, the dump was used as a deposit for communal and building waste.

The substrate composition of the dump-field is heterogeneous. The western slope of the heap is formed by fine-grained sand, whereas the rest of the dump plateau is partly covered by clay with an explicit mould horizon. The communal and building waste is located in small deposits at the northern and southern parts of the study area. The eastern part of the dump-field is specific by significant mould top layer. This area was probably recultivated by covering the tailing material with a backfill. Today the dump-field shows a mosaic of open and woody vegetation (Richert et al. 2017a) and represents a specific habitat for plants and animals (see Erler et al. 2017, Funke et al. 2017, Richert et al. 2017b).

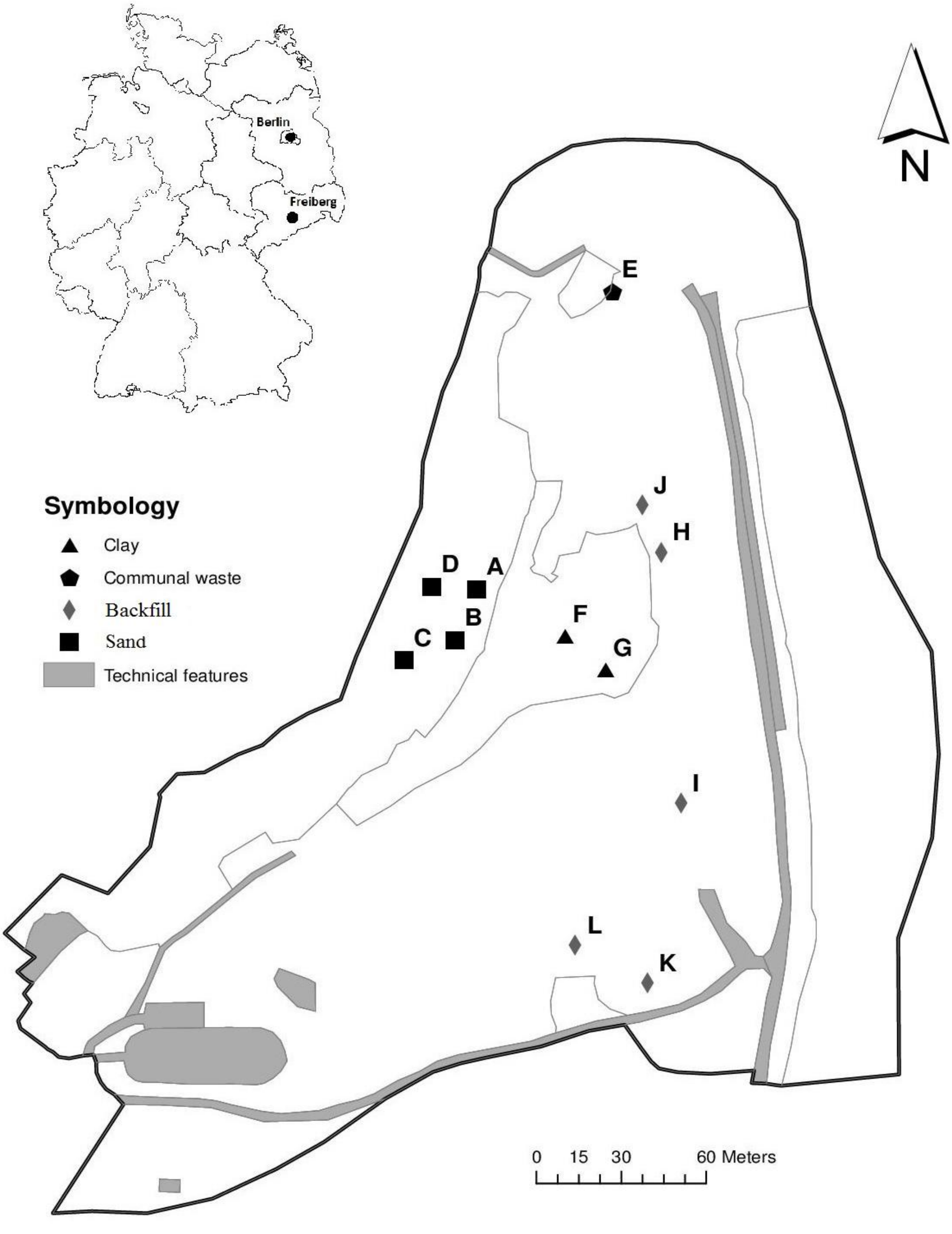

Fig. 1: The study area of the Davidschacht dump, showing the sampling sites (capital letters) with the specification of top soil layers, where backfill represents the sites, where the top-layer seems to contain a big amount of organic matter which reached deeper than 12 cm.

Abb. 1: Das Untersuchungsgebiet der Spülhalde Davidschacht mit den Beprobungsstellen (Buchstaben) und Angaben zur Substratbeschaffenheit.

3. Material and Methods

3.1 Sampling of soil and plant material

In total, 12 sampling sites were selected on the study area (Fig. 1). The selection includes all significant soil types, found on the dump-field. The sampling itself was realized in summer of 2015, during a sunny and dry weather period. The analyses took a place in the laboratories of the Institute of Biosciences at the Technische Universität Bergakademie Freiberg. The soil samples were taken from the depth of 10 cm (main rooting horizon). Deep soil pits were realized at the sites B, G, H, I (Fig. 1) in the order to examine the proximate geochemical character of the whole dump area (see also Wiese 2015). At each sampling place, 3-fold soil composite samples were taken, using steel spade. All samples were stored in plastic bags at 4 °C before being analyzed.

The plants were collected from the same sites as the soil samples. Collected plant material consisted of 35 representatives of grass, herb and woody species. The most frequent species collected was *Agrostis capillaris*, which is unevenly distributed at the whole area and represents a typical plant species of the local grassland vegetation. The plant samples consisted of all parts of the plant body (roots, stalks and leaves/needles). The leaves and tillers were dried at 80 °C for one day and weighted.

3.2 Analysis of soil and plant material

For the assessment of the total trace element concentrations, a split of the soil substrate samples was dried over night by 105 °C and pulverized in a boron carbide mortar. 500 mg of powder was weighed in a nickel crucible and mixed with 2 g of Na_2CO_3/K_2CO_3 to perform a melting digestion procedure according to Alfassi and Wai (1992). The soil was roasted in a muffle furnace for 30 min at 900 °C. Then the samples were cooled and dissolved in 50 ml of a 2 M HNO_3 and 0.5 M citric acid solution and subsequently measured by inductively coupled plasma mass spectrometry (xseries 2, Thermo scientific).

For the identification of potential plant available element pools in the soil substrate, a sequential extraction procedure according to Wiche et al. (2016) was performed. A split of the substrate samples was dried at 60 °C for 24 h. 1 g of each sample was placed in a 50 ml falcon tube and extracted with four extraction solutions in sequence: Mobile/exchangeable elements by shaking with 1 M ammonium acetate (pH 7) for 24 h (Fraction I.), acid soluble elements by shaking with ammonium acetate buffered to pH 5 for 5 h (Fraction II.), elements bound to oxidizable matter by gently heating with 10 ml H_2O_2 for 5 h in an ammonium acetate buffer solution (Fraction III.). Non-crystalline components, predominantly Fe, Mn and Al-oxides were isolated by selective dissolution with acidic 0.2 M ammonium oxalate (pH 3.2) in the dark (Fraction IV.). After each step, the solid and supernatant was separated by centrifugation and the concentration of the elements in the supernatant was measured by inductively coupled plasma mass-spectrometry (ICP-MS).

The total concentrations in the soil samples and the bioavailable fractions of elements were correlated with two physiochemical soil parameters – pH and soil organic matter. The soil reaction (pH) was measured according to Sobek et al. (1978). 10 g of fresh soil samples were mixed with 100 ml distilled water into a suspension and shaken for 1 h. The pH values were measured directly from the centrifuged solutions. In the order to define the organic matter content, a specific amount of soil sample was weighted and consequently heated to 550 °C for 2 hours. The percentage of humus was calculated from the combustion residues.

The dry plant samples were ground to a fine powder. A subsample of 100 mg of plant material was used for microwave digestion (Ethos plus 2, MLS) with nitric and hydrofluoric acid according to Krachler et al. (2002).

3.3 Statistical Analyses

Statistical analyses were performed by univariate analysis of variance (ANOVA), followed by a LSD post-hoc test (in case of equal variances). In case of unequal variances Kruskal-Wallis tests were used. Spearman's rank correlation coefficients were calculated in order to identify significant relationships between two numerical parameters. Results with p-values < 0,1 were considered as statistically significant.

4. Results and Discussion

4.1 Concentrations of trace elements in the substrates

4.1.1 General characteristics of the sampling sites

At sites A, B, C and D, representing the western part of the dump, the soil formation was insufficient and the profiles showed a sandy tailing material (Fig. 1). A surface horizon with significant content of communal waste was found at site E. Sites H, I, J, K and L represented soils with partly developed mould horizons. The sites G and F were situated at the highest part of the dump-relief (407.1 m). At these sites, the colour and structure diversity of layers showed remarkably differences and a high variability of metal contents (Table 1). Site I represents a specific moist grassland habitat. The mean values of pH and the contents of organic matter (humus) for the whole study area are presented in Table 1. The average pH value, analyzed in the technogenic sediment indicates acid conditions throughout the whole study area: mean pH 4.9 (min. pH 3.8, max. pH 5.6). The lowest pH values were determined at sites G and F situated at the top of the dump-relief (Fig. 1). At these sites the substrates are characterized by a fine-grained clayey texture and partly grey-coloured reduction zones, indicating that the oxidation of sulfide minerals is still in progress, even in thesurface layers. The near neutral pH values were found at sites K and L, on the southern slope of the dump (Fig.1) where no tailing material was noticed in the sampled depth. Most probably, recultivation measures included the application of soil in order to cover the tailing material. Surprisingly, at these sites the humus content was not significantly different in comparison to the other sites (Table 1), except sites A, B, C and D which were situated on tailing material with sandy texture without vegetation cover (Fig. 1).

4.1.2 Total concentrations of toxic trace elements, Ge and REEs in surface substrates

High concentrations of trace elements (especially Zn, As, Cd and Pb) in the surface layers of the dump material, as reported in Table 1, derived most probably from the residues of the sulfide ore minerals sphalerite (ZnS), galenite (PbS) and arsenopyrite (FeAsS). The highest concentrations were found for As (average 3328 mg kg^{-1}) (Table 1). The mean concentrations of Zn at different sampling locations range from 149 to 2888 mg kg^{-1}. The highest Zn content was found at site E in a layer of communal waste that was used to cover the tailing material, whereas the highest content of As was measured at sites A, B, C and D characterized by fine-grained sandy tailing material without vegetation cover. Moreover, site E was characterized by high concentration of Cd (10.2 mg kg^{-1}) and Pb (2211 mg kg^{-1}) and high contents of organic matter (SOM) which might have immobilized these elements in exchangeable element pools (Sheoran et al. 2016). Considering all sampling locations, the mean concentration of Ge was calculated at 2.7 mg kg^{-1}, which is approximately two times higher than the average content in the Earth`s crust (Rosenberg 2007). High concentrations of Ge probably derived from Ge-bearing sphalerite (Andráš et al. 1991; Frenzel et al. 2015). In contrast, the average contents of REEs were roughly a factor of two lower compared to the mean contents in the Earth`s crust and the world soil average (Kabata-Pendias 2001). Fig. 2 shows a significant positive correlation ($p < 0.1$) between the pH of the substrates and all investigated elements, except of Pb and As, indicating increasing concentrations with increasing pH of the substrates.

Is has to be noted that all investigated elements with the exception of Pb and As can be easily mobilized with decreasing pH (Tyler & Olsson 2001) what might have led to a depletion of sites with highly acidic tailing material. In contrast, mobilization of Pb requires pH values < 4 (Scheffer & Schachtschabel 2010), while As is more mobile under alkaline conditions (Tyler & Olsson 2001). However, lowest concentrations of both Pb and As were found in the recultivation substrates characterized by near neutral pH values, high organic matter contents and consequently high buffer and cation exchange capacities (see Scheffer & Schachtschabel 2010).

Table 1: The mean values of pH, soil organic matter (SOM), selected trace elements, REEs and Germanium in the dump material at the particular sampling sites.

Tabelle 1: Konzentrationen ausgewählter Spurenelemente, Seltene Erden und Germanium in den Substraten der Versuchsflächen. Zusätzlich sind die mittleren pH-Werte und Gehalte von organischem Material (SOM) dargestellt.

Site	pH(H_2O)	SOM	Zn	As	Cd	Pb	Ge	La	Nd	Gd	∑ REEs
		%					mg kg^{-1}				
A	4.4	2.7	436	5502	5.1	463	1.55	14.5	15.9	4.16	86.3
B	5.7	2.2	879	5109	11.5	468	1.50	21.3	19.4	4.81	114.0
C	4.0	3.8	435	5811	3.4	913	1.64	14.9	14.2	3.31	78.6
D	4.2	3.8	271	5698	2.5	678	1.51	14.6	14.9	3.68	81.6
E	5.6	14.3	2888	2014	10.2	2211	2.95	25.5	23.7	5.13	126.8
F	3.9	7.2	225	7421	1.7	2550	1.46	11.0	10.5	2.25	57.4
G	4.2	11.2	149	3543	2.3	1725	1.36	13.2	10.5	2.21	62.1
H	4.3	21.0	1083	1018	4.8	2844	2.21	23.7	21.3	4.58	115.1
I	5.7	7.8	573	1172	5.2	432	1.32	15.9	14.1	3.18	78.3
J	4.8	27.6	1703	875	4.2	3209	3.18	27.6	25.2	5.42	135.8
K	6.1	8.3	971	1002	7.2	1258	5.84	24.2	21.3	4.45	118.7
L	5.7	10.2	1150	767	8.3	1414	7.91	25.5	22.1	4.68	124.8

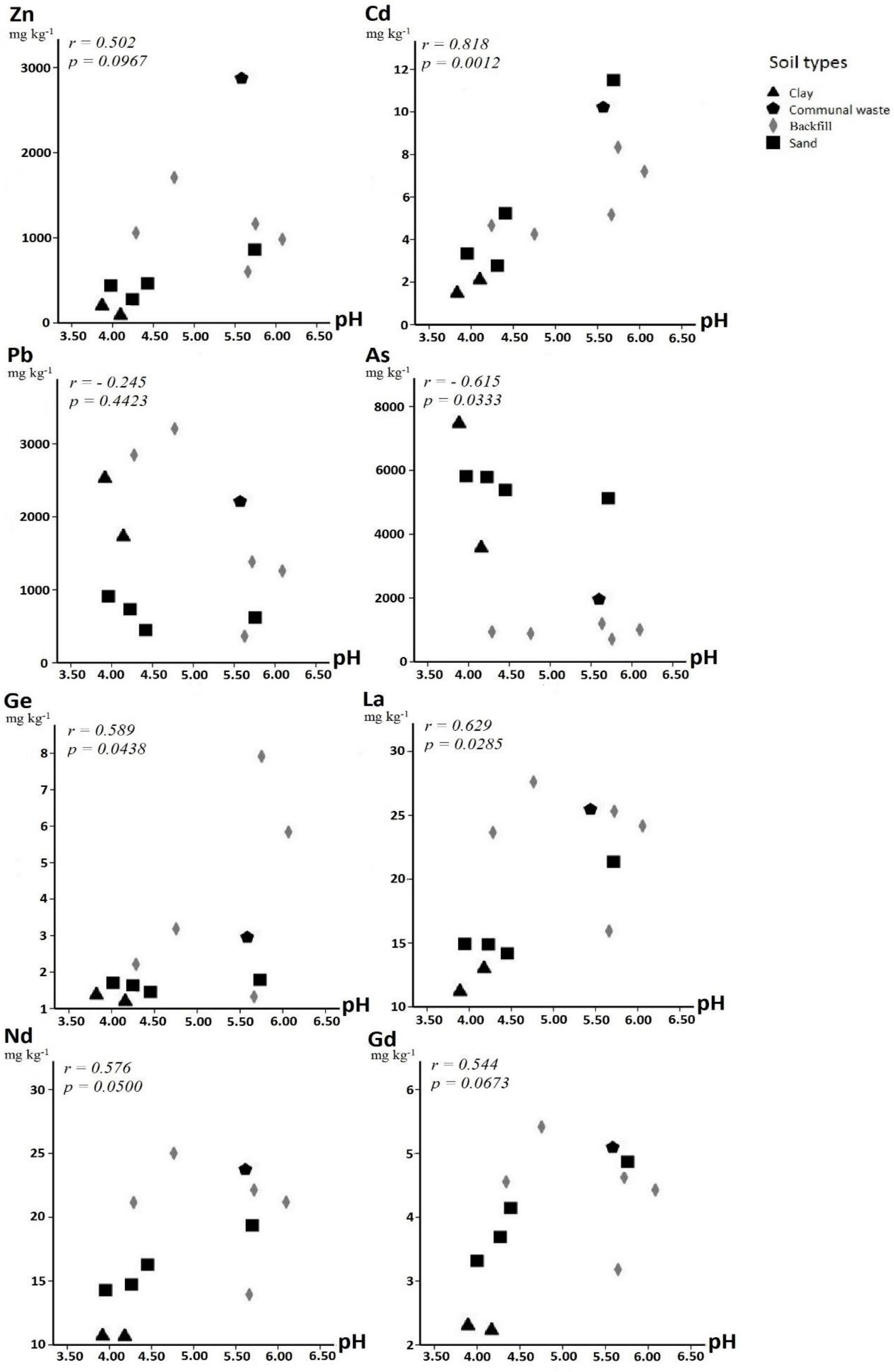

Fig. 2: Spearman rank correlations of concentrations of selected elements and the pH values of the substrates at the different sites (all sampling sites considered).

Abb. 2: Spearman-Rangkorrelationen zwischen den Konzentrationen ausgewählter Elemente und den pH-Werten der Substrate (alle Flächen berücksichtigt).

4.1.2 Toxic trace elements, Ge and REEs in potentially plant available fractions

The results of the sequential extraction show that only minor amounts of the selected elements were present in the, potentially plant available, fractions I–IV (Fig. 3). Among all investigated elements Cd was most abundant in these fractions (25% of total concentrations), followed by Zn > As > Pb (Fig. 3). As and Pb were mostly found in Fraction IV, indicating that they were present in easily reducible forms such as Fe/Mn-oxides (Wiche et al. 2017). With regard to the economically valuable elements, potentially plant available Ge represented 1.8% of the total Ge contents (Table 1 and 2). The highest portion of Ge was detected in Fraction IV with only low concentrations in exchangeable and acid soluble fractions (Fig. 3). In Fraction IV, the investigated REEs represented roughly 3% of the total contents of the substrate. Compared to Ge, all investigated REEs were found with high percentages in Fractions II and III (Fig. 3) indicating high amounts of REEs bound into organic matter and acid soluble pools such as REE-containing sulfates and phosphates (Johannesson et al. 1995; Davranche et al. 2015). Surprisingly, high concentrations of potentially plant available elements were found on sites E, J, K and L (Table 2). These sites are characterized by recultivation measures and consequently showed a layer of allochthonous soil substrates, such as communal waste and organic rich topsoil from the area of Freiberg (see Fig. 1). According to Wiche et al. (2017), SOM is playing a substantial role in the plant availability of Ge and REEs to soil-grown plants. Based on the results of the SOM contents (Table 1) it seems that sites with high contents of organic matter tend to have higher concentrations of all elements in potentially plant available fractions I–IV. However, some of the sandy sites with low SOM contents and without vegetation (sites A, B, D) are characterized by high concentrations, particularly of REEs. It has to be noted that in this study we did not investigate soil but mine-tailings and their recultivation layers. From this it would be interesting to know the origin of the soil material used for the recultivation of the different areas of the dump. Possibly, these substrates were initially characterized by high element contents or the element contents originate from the tailing material through accumulation in secondary soil minerals and adsorption into SOM over time. Unfortunately our experimental design does not allow further interpretations.

Table 2: Potentially plant available concentrations (mg kg^{-1}) in substrates at the different sampling sites calculated as the sum of elements in Fractions I–IV.

Tabelle 2: Potentiell pflanzenverfügbare Elementkonzentrationen (berechnet als Summen der Fraktionen I–IV) in Substraten der verschiedenen Untersuchungsflächen.

Site	Zn	As	Cd	Pb	Ge	La	Nd	Gd
				mg kg^{-1}				
A	34.8	490	0.4	51.6	0.01	0.35	0.39	0.18
B	127.4	390	1.82	55.2	0.01	0.45	0.53	0.22
C	7.6	325	0.08	11.5	<0.01	0.1	0.16	0.11
D	20.8	530	0.21	43.9	0.01	0.28	0.32	0.16
E	439.9	183	4.25	183.4	0.12	0.59	0.65	0.23
F	10.1	433	0.16	25.9	0.01	0.02	0.03	0.04
G	8.5	212	0.05	12.4	<0.01	0.04	0.05	0.03
H	77.1	69	2.88	204.6	0.03	0.3	0.33	0.19
I	53.3	130	0.83	56.4	0.01	0.11	0.11	0.09
J	170.9	84	5.51	213.6	0.05	0.22	0.24	0.19
K	128.0	54	1.86	109.1	0.1	0.47	0.47	0.19
L	163.1	79	2.47	111.9	0.12	0.44	0.45	0.18

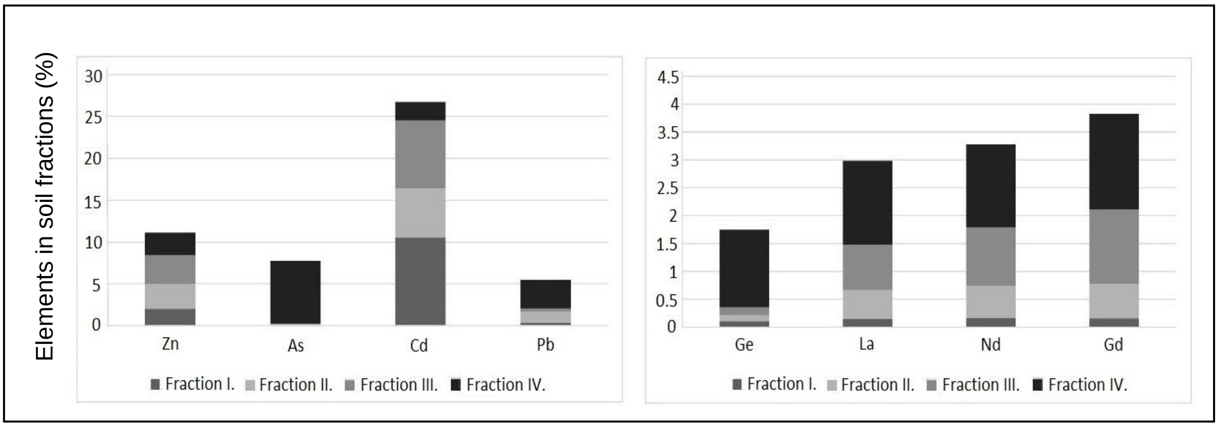

Fig. 3: Percentages of selected elements in the investigated fractions. Fraction I: mobile/exchangeable, Fraction II: acid soluble, Fraction III: bound into organic and oxidizable matter, Fraction IV: bound to easily reducible soil constituents.

Abb. 3: Prozentuale Anteile ausgewählter Elemente in den untersuchten Bodenfraktionen. Fraktion I: Mobil/austauschbar, Fraktion II: Säurelöslich, Fraktion III: Gebunden in organischem und oxidierbarem Material, Fraktion IV: Gebunden an leicht reduzierbare Bodenbestandteile.

4.2 Accumulation of trace elements in different plant species

The plant material taken from the study area consisted of 15 vascular plant species, which represent the natural occurring vegetation of the dump. The analyzed material consists of *Agrostis capillaris*, *Betula pendula*, *Calamagrostis epigejos*, *Fallopia japonica*, *Lotus corniculatus*, *Phalaris arundinacea*, *Phragmites australis*, *Pinus sylvestris*, *Populus tremula*, *Quercus robur*, *Salix caprea*, *Silene vulgaris*, *Spirea douglasii*, *Tanacetum vulgare*, and *Tussilago farfara*. Mean concentrations of selected elements in these plant species are shown in Table 3. In the plant species, the lowest concentrations among the selected elements were measured at sites F and G, whereas the highest were found at site E that was characterized by high contents of all investigated elements in potentially plant available fractions. The highest variability among the most investigated metals (except Cd and Ge) was found in the grass species *Agrostis capillaris* and *Calamagrostis epigejos.* Despite low concentrations of Ge in plant available fractions, grass species such as *Phragmites australis* (collected from site I) and *Phalaris arundinacea* (collected from site H) showed a high accumulation potential for Ge (Table 3).

Table 3: Mean concentrations of toxic trace elements, Ge and REEs in selected plant species.

Tabelle 3: Konzentrationen von Spurenelementen, Ge und Seltenen Erden in ausgewählten Pflanzenarten

Plant species	Zn	As	Pb	Cd	Ge	La	Nd	Gd
				mg kg^{-1}				
Agrostis capillaris	94.9	66.0	20.2	1.5	0.17	0.37	0.35	0.12
Betula pendula	522.5	3.2	7.9	4.7	0.06	0.13	0.13	0.07
Calamagrostis epigejos	115.7	50.1	13.1	1.5	0.12	0.31	0.29	0.11
Lotus corniculatus	145.8	124.2	28.4	0.7	0.07	0.69	0.62	0.18
Phalaris arundinacea	67.3	1.2	2.2	0.5	0.57	0.08	0.09	0.07
Phragmites australis	125.1	0.4	0.5	0.2	0.63	0.07	0.07	0.06
Pinus sylvestris	84.8	55.9	14.0	1.1	0.07	0.36	0.35	0.13
Populus tremula	709.1	20.6	22.2	5.2	0.07	0.42	0.40	0.15
Quercus robur	78.9	4.7	6.3	0.4	0.08	0.17	0.17	0.08
Fallopia japonica	116.5	0.7	3.2	0.8	0.06	0.13	0.12	0.07
Salix caprea	178.6	0.9	1.4	0.03	0.27	0.08	0.09	0.06
Silene vulgaris	204.8	0.8	1.1	1.3	0.06	0.08	0.08	0.06
Spiraea douglasii	280.8	1.7	1.4	8.2	0.05	0.10	0.10	0.06
Tanacetum vulgare	398.9	4.0	3.6	10.2	0.19	0.13	0.12	0.07
Tussilago farfara	445.7	27.4	27.0	4.8	0.08	0.32	0.30	0.12

Grasses typically accumulate high levels of Si, while dicots are unable to accumulate Si in shoots (Ma & Yamaji 2006). Since Ge is taken up by the roots in the form of ($Ge(OH)_4$), similar to silicic acid ($Si(OH)_4$), species with high accumulation of Si typically show high contents of Ge (Wiche & Heilmeier 2016). In contrast, the investigated forbs such as *Lotus corniculatus* and *Tanacetum vulgare* showed a high phytoaccumulation ability of toxic trace elements and REEs. Unfortunately, we could not collect all plant species on all sites what makes it difficult to judge whether these concentrations of plant species result from physiological traits or substrate properties. However, the phytoaccumulation results among the woody species show that *Pinus sylvestris* accumulated all elements with no observable differences between sites, while *Betula pendula* has a surprisingly high accumulation potential at site G. High concentrations of Ge were found in *Salix caprea* at site L, with the highest value in potentially plant available fractions (0.12 mg kg^{-1}). Kabata-Pendias (2001) proposed the following values as critical loads for toxic trace elements in soil, causing phytotoxic effects in plants: Pb = 3.0 mg kg^{-1}; Cd = 0.5 mg kg^{-1}; Zn = 10 mg kg^{-1}. This classification is based on the lowest contents in leaf tissues in plants that are neither highly sensitive nor tolerant. With regard to these values, the phytocoenoses of vascular plants of the Davidschacht dump-field can be considered as highly tolerant, most probably due to the development of specific ecotypes.

6. Conclusions

Besides a high contamination by toxic trace elements (Zn, As, Pb, Cd), surface substrates of the Davidschacht mine tailing are characterized by high concentrations of Ge that are roughly a factor of two higher than the average concentration in soils. In contrast, compared to the world soils average (Kabata-Pendias 2001), concentrations of REEs in the tailing substrates were not significantly enriched. Plant availability of elements is strongly depended on the mobility of trace elements in soil solution, which is particularly affected by the pH. Sites with near neutral pH were characterized by the highest total concentrations of all investigated elements except of Pb and As. The results of sequential extraction show that potentially plant available concentrations of elements decreased in the order Cd > Zn > As > Pb > >REEs > Ge. *Phragmites australis* (0.63 mg kg^{-1} Ge) and *Phalaris arundinacea* (0.57 mg kg^{-1} Ge) were characterized by high concentrations of Ge, while *Populus tremula*, *Tanacetum vulgare*, *Lotus corniculatus* and *Agrostis capillaris* were characterized by high concentrations of Zn, Cd, Pb and REEs.

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7. Zusammenfassung

Konzentration und Bioverfügbarkeit von Schwermetallen, Germanium und Seltenen Erdmetallen in kontaminierten Substraten der Spülhalde Davidschacht in Freiberg (Sachsen): Das Ziel der Untersuchungen war die geochemische Charakterisierung der oberflächennahen Substratschichten auf der Spülhalde Davidschacht. Insbesondere sollten die Substrate hinsichtlich Gesamtelementkonzentrationen und Pflanzenverfügbarkeit von toxischen Spurenelementen (Zn, As, Cd, Pb), Germanium (Ge) und Seltenen Erden (La, Nd, Gd) untersucht werden. Dazu wurden an 12 Probenahmestellen Substratproben aus einer Tiefe von 10 cm sowie Pflanzenproben von dominanten Pflanzenarten entnommen und hinsichtlich ihrer Gesamtelementkonzentration mittels ICP-MS untersucht. Pflanzenverfügbare Konzentrationen wurden mittels einer vierstufigen sequentiellen Extraktion erfasst. Die Ergebnisse zeigten, dass die Substrate der Spülhalde, neben hohen Gehalten an Zn, As, Cd und Pb, auch erhöhte Ge-Konzentrationen (bis zu 8 mg kg^{-1}) aufweisen. Im Gegensatz dazu waren die untersuchten Seltenen Erden im Vergleich zur mittleren Konzentration in Böden der Umgebung Freibergs nicht signifikant erhöht. In allen untersuchten Substraten sanken die potentiell pflanzenverfügbaren Elementkonzentrationen in der Reihenfolge Cd > Zn > As > Pb > >REEs > Ge. Trotzdem waren einige Pflanzenarten, insbesondere die Gräser *Phragmites australis* (0.63 mg kg^{-1} Ge) und *Phalaris arundinacea* (0.57 mg kg^{-1} Ge) durch vergleichsweise hohe Konzentrationen an Ge gekennzeichnet. Einige der untersuchten Kräuter und Gehölzarten (*Populus tremula*, *Tanacetum vulgare*, *Lotus corniculatus* and *Agrostis capillaris*) zeigten hohe Konzentrationen an Cd, Zn, Pb und Seltenen Erden.

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Appendix

Table A1: Concentrations of toxic trace elements, germanium and rare earth elements in different fractions of substrates from different sampling sites. n. a. represents values < 0.001.

Tabelle A1: Konzentrationen von Spurenelementen, Germanium und Seltenen Erden in verschiedenen Bodenfraktionen

Sample	Fraction	Zn	As	Cd	Pb	Ge	La	Nd	Gd
					mg kg^{-1}				
A	1	1.58	1.97	0.07	0.18	n. a.	0.04	0.03	0.01
B	1	18.18	2.92	0.48	0.54	n. a.	0.05	0.04	0.01
C	1	0.37	1.32	0.01	0.03	n. a.	0.01	0.01	n. a.
D	1	0.70	2.28	0.03	0.09	n. a.	0.03	0.02	0.01
E	1	82.81	1.34	1.75	12.17	n. a.	0.06	0.07	0.01
F	1	0.43	0.48	0.01	0.13	n. a.	0.00	0.00	n. a.
G	1	0.94	0.51	0.01	0.08	n. a.	0.01	0.01	n. a.
H	1	14.91	1.05	1.22	23.03	n. a.	0.05	0.05	0.01
I	1	12.09	1.55	0.39	1.62	n. a.	0.02	0.01	n. a.
J	1	34.43	0.86	2.35	20.17	n. a.	0.04	0.04	0.01
K	1	23.34	0.33	0.75	10.41	n. a.	0.02	0.02	n. a.
L	1	37.97	0.55	1.10	12.09	n. a.	0.02	0.02	n. a.
A	2	3.36	9.43	0.05	2.75	n. a.	0.15	0.13	0.03
B	2	26.98	11.48	0.29	6.44	n. a.	0.20	0.17	0.04
C	2	0.94	8.42	0.01	0.21	n. a.	0.04	0.06	0.02
D	2	1.23	11.78	0.02	1.19	n. a.	0.09	0.08	0.02
E	2	152.26	5.21	1.10	54.04	n. a.	0.21	0.23	0.05
F	2	1.60	4.62	0.02	1.70	n. a.	0.02	0.03	0.01
G	2	1.88	2.95	0.01	0.67	n. a.	0.03	0.04	0.01
H	2	22.90	3.68	0.65	71.06	n. a.	0.16	0.16	0.04
I	2	14.11	4.90	0.20	12.16	n. a.	0.06	0.06	0.01
J	2	63.46	3.33	1.54	60.37	n. a.	0.15	0.15	0.04
K	2	25.61	1.47	0.38	25.35	n. a.	0.06	0.06	0.02
L	2	30.31	1.99	0.46	26.12	n. a.	0.06	0.07	0.02
A	3	12.32	2.33	0.23	0.39	n. a.	0.16	0.23	0.08
B	3	52.76	1.93	0.95	0.21	n. a.	0.20	0.32	0.10
C	3	2.96	1.61	0.05	0.06	n. a.	0.05	0.09	0.04
D	3	7.61	2.91	0.13	0.38	n. a.	0.16	0.22	0.08
E	3	108.49	1.08	1.13	13.42	n. a.	0.32	0.35	0.07
F	3	1.35	0.01	0.10	0.01	n. a.	0.00	0.00	n. a.
G	3	0.71	1.21	0.01	0.05	n. a.	0.00	0,00	n. a.
H	3	12.22	0.63	0.63	12.25	n. a.	0.09	0.12	0.03
I	3	10.12	1.26	0.17	1.36	n. a.	0.03	0.04	0.01
J	3	17.24	0.53	0.81	6.93	n. a.	0.03	0.05	0.01
K	3	59.93	0.33	0.66	14.92	0.01	0.39	0.39	0.09
L	3	71.41	0.33	0.83	17.87	0.01	0.36	0.36	0.09
A	4	17.54	476.47	0.05	48.27	0.01	0,21	0,20	0.06
B	4	29.47	373.70	0.10	48.02	0.01	0,32	0,25	0.07
C	4	3.30	314.30	0.01	11.18	n. a.	0,10	0,14	0.05
D	4	11.27	513.33	0.03	42.30	0.01	0,18	0,19	0.05
E	4	96.38	176.20	0.27	103.77	0.12	0,52	0,46	0.10
F	4	6.71	428.80	0.03	24.01	0.01	0,09	0,12	0.03
G	4	4.96	208.03	0.02	11.58	n. a.	0,07	0,10	0.02
H	4	27.10	63.86	0.38	98.24	0.03	0,52	0,44	0.11
I	4	16.95	122.90	0.07	41.25	0.01	0,31	0,28	0.07
J	4	55.79	79.11	0.81	126.10	0.05	0,55	0,45	0.13
K	4	19.15	51.78	0.07	58.38	0.09	0,42	0,36	0.08
L	4	23.40	75.78	0.08	55.84	0.11	0,36	0,30	0.07