soil systems

Article

Accumulation of Soil Metal(loids) in Fast-Growing Woody Plants of the Post-Mining Area of Freiberg, Germany

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Abstract: Soil pollution is a global threat that seriously affects biodiversity in (agro)ecosystems and may compromise water and food quality. Therefore, the ability of tree species (*Populus tremula*, *Salix caprea,* and *Betula pendula)* to accumulate and phytoextract specific toxic heavy metals from soil was investigated. The study was conducted in and near relict mining areas of Freiberg (Germany) and sampling sites selected according to their spatial location relative to potential sources of metal(loid)s. The concentrations of geogenic (P, Fe, Mn, Ca) and pollutant (Pb, Cd, Zn, As) elements in soil and the present trees were measured using ICP-MS. The highest total soil concentrations of As (8978 $\mu g\ g^{-1}$) were found within the Davidschaft mining area, and for soil Pb, both in the Davidschaft vicinity (328 $\mu g\ g^{-1}$) and mining area (302 $\mu g\ g^{-1}$). Unexpectedly, the highest soil Zn (0.64 mg g^{-1}) and Cd (3.5 mg g^{-1}) concentrations were found in Freiberg city Forest. The lowest soil concentrations of pollutants (As, Cd, Pb, and Zn) were recorded for Seifersdorf. Total soil P was highest in Colmnitz, but Ca, Mn, and Fe concentrations were very similar across all sites. The available concentration of all measured toxic elements in the soil generally decreased in the order Davidschaft > Davidschaft vicinity, Colmnitz > Seifersdorf = Freiberg city forest. All studied tree species had higher concentrations of the essential elements in leaves than in branches. Generally, higher values of bioaccumulation coefficients (especially for Cd) were found for *Salix caprea* compared with *Populus tremula* and *Betula pendula*.

Keywords: contaminated soil; heavy metals; trees compartment; phytoremediation; bioaccumulation

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1. Introduction

Soil pollution is a global threat that seriously affects biodiversity in (agro-) ecosystems and may compromise water and food quality [1]. Most contaminants in soil originate from human activities such as industrial processes and mining, poor waste management, unsustainable farming practices, and related accidents [2]. The soils in the area around Freiberg (Saxony, Germany) are heavily impacted by past mining activities. Besides the already natural high geological background content of certain toxic trace elements, such as zinc (Zn), arsenic (As) cadmium (Cd), and lead (Pb), the local emissions from metal smelting plants and tailing sites that occur widespread in the area [3,4] lead to topsoil pollution with these metals and metalloids. One of the earliest and most important centers of medieval mining of silver ore in Europe is the 'dump-fields' in Freiberg (Saxony, Germany) [5]. Today, mining is no longer carried out here, but the consequences caused by long-term operations in this region are significant. Indeed, historically, over more than 800 years, one of the primary sources of pollution was the Muldenhütten mine smelter complex and the smelter Hohe Esse, which released metal(loid) containing fumes that entered the environment and led to soil contamination even in remote areas further away. Additionally, in this area, numerous tailing sites where sandy remains of flotation processes were deposited have contributed to the pollution of adjacent soils by the emission of dust and leachates, of which especially the recent Davidschacht (DV) tailing site is still an environmental threat. The DV is located on the northeastern outskirts of Freiberg on the valley slope to the Freiberger Mulde. The Davidschacht mining complex has an area of approximately 6.3 hectares, operated until 1964, and the respective tailing site deposits more than 760,000 m^3 of Arsenic (As), Cadmium (Cd), Zinc (Zn), and lead (Pb) containing tailing materials. Nowadays, DV represents the main source of the leaching of Cd in the Freiberger Mulde river and the Elbe River [6]. Furthermore, there are polluting elements, such as As, Pd, and Cd ions, present in its soils and draining waters, which are not essential, but on the contrary, are toxic to plant and animal organisms [7].

The presence of such metal(loid) pollutants on potentially accessible lands calls for complex engineering, technical, and agrotechnical technologies focused on the development of protective, meliorative plantings that, under specific conditions, may also have an economic meaning. There is an urgent demand to better understand the uptake of toxic metals in plants from contaminated soil, to allow us to introduce methods to newly or more effectively mitigate against it [8,9].

Different plants can show specific individual sensitivity/resistance to certain toxic elements, which is a genetically fixed feature. This fact is used to establish their potential phytoremedial role, as well as to obtain information about the ability to participate in phytoremediation processes under certain soil and environmental conditions [10]. The success of any phytoremediation technique depends upon the identification of suitable plant species that hyperaccumulate trace metals and produce large amounts of biomass [11,12]. Woody species, especially fast-growing trees as common aspen (*Populus* spp.), willows (*Salix* spp.), and birches (*Betula* spp.), have a high potential for phytoextraction, regarding the accumulation of heavy metals and nutrients, and they are known to be resilient to metal toxicity [13,14].

In this study, we quantified: (i) the total plant and soil concentrations and bioavailability of dominant geogenic, i.e., phosphorus (P), calcium (Ca), iron (Fe) and manganese (Mn) and locally main pollutant elements (As, Pb, Cd, Zn) present in different forest sites in Freiberg area. Through establishing the concentrations of the aforementioned elements in the various trees in the region, we could also identify the optimal tree species for phytoremediation and phytomining research.

2. Materials and Methods

2.1. Study Area and Selection of Sampling Sites

The study area was situated in the Freiberg area (Central Saxony) (GPS 50°54′46″ North, lat. 13°20′29″ East, long.), covering approximately 1000 km^2 in the southern part of the district of Central Saxony (Figure 1). Freiberg lies on the northern declivity of the Ore Mountains. Most of the region is located to the west of the Eastern part of the Freiberger Mulde river. Some parts of the city are in the valleys of the Münzbach and Goldbach streams. The center has an altitude of about 412 m above sea level. Across this area, the sampling sites were selected according to their spatial locations relative to potential emission sources for metal(loid)s, the Davidschacht tailing site and the Muldenhütten mine smelter complex, respectively, to determine the present level of anthropogenic load and degree of pollution. The Davidschaft mine tailing (DV) is in Freiberg's municipal area. It is located near the Freiberger Mulde River (westerly) and on the eastern edge of the city (GPS 50°55′34″ N 13°22′8″). The DV area covers approximately 72,500 m^2 [15,16] and entails the DV company that operated from 1951–1964 for depositing tailing sands.

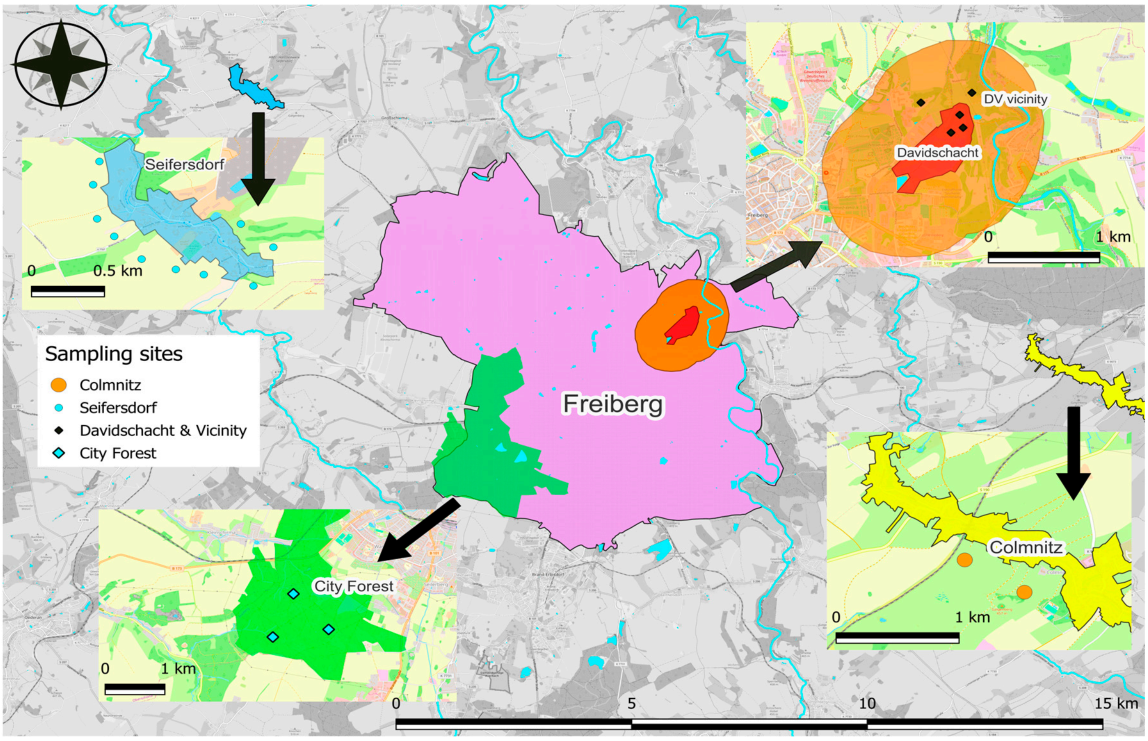

Figure 1. The study area within the Freiberg region: Davidschacht mine tailing, Davidschacht tailing vicinity, village Colmnitz, village Seifersdorf, vicinity of the Freiberg City Forest. Markers in the insert Figures indicate the number of sample locations at each site.

The Davidschacht mine tailing is broadly unremediated and contains approximately 760,000 m^3 of silphidic tailing sands that contain considerable concentrations of As, Cd, Pb, and Zn [15]. The elements are permanently leached by the infiltration of rainwater into the neighboring soils and the Freiberger Mulde river or enter the neighboring soils (Davidschacht tailing vicinity) through the aeolian dust emission. In contrast to the soil pollution originating from the tailing site, pollution by fumes of the Muldenhütten ore smelter complex led to element deposition in soils with west-wind drift and reached remote areas where Colmnitz is situated. Based on data on possible emission paths, geochemical soil maps, data from vegetation mapping, CIR data, and data from previous studies [3,4], we selected in total 20 sampling sites across the study area characterized by forest vegetation or smaller patches of trees. Three sampling sites were equally distributed on the Davidschacht mine tailing (DV), two sampling sites were situated in small forest patches in the vicinity of the Davidschacht tailing (DVV), two sites were in the village of Colmnitz (COL), ten sampling sites were selected in the village of Seifersdorf (SEI), and three sites were in the Freiberg City Forest (FCF).

2.2. Collection of Soil and Plant Samples

The occurrence of natural tree vegetation was recorded during field observations in each of the 20 sampling locations. Within each allocated rectangular area (50 × 50 m), all present tree species were recorded. *Populus tremula* (common aspen) and *Salix caprea* (pussy willow) were present in all sampling locations and were therefore selected for the latter comparison of element accumulation depending on soil properties. In addition, *Betula pendula* (silver birch) occurred at all sampling sites within the Freiberg City Forest. Thus, *B. pendula* was selected to evaluate the species-specific accumulation behavior within this study area, whereas location-dependent differences in element accumulation were evaluated based on a comparison of element concentrations in *P. tremula* and *S. caprea* across the sampling locations. The selected trees were roughly of a similar age and were quite young. They had a stem diameter at breast height (DBH) between 6 and 8 cm. Given that DBH correlates with tree height and age, this ensured that within a tree species, we collected samples from comparable individuals.

In each of the sampling locations, five equally distributed soil samples (n = 60) were taken from a soil depth of 30 cm using a 3 cm diameter steel auger. The replicate samples were mixed and homogenized to obtain one composite sample per sampling location. Additionally, for each sampling location, leaves and branches samples from the top and middle of at least four tree individuals, the dominant species *S. caprea, P. tremula,* and occasionally also *B. pendula,* were collected. Replicate samples of two individuals were pooled to obtain pooled duplicate samples per sampling location. In total, 104 individual plant samples from *S. caprea* (40), *P. tremula* (40), and *B. pendula* (24) were collected. The field sampling campaign was conducted in August 2022, at the time of the most developed aboveground compartments of trees and shortly before leaf senescence. The soil samples were dried at 105 °C for 24 h. The plant biomass was separated into leaves and dried at 60 °C for 48 h. All samples were stored in plastic tubes at 4 °C until being analyzed.

2.3. Analysis of Soil and Plant Sampling

The soil samples were ground in a boron carbide mortar. Then, 500 mg of the powder was weighed in a nickel crucible and mixed with 1 g of Na_2CO_3 and 1 g K_2CO_3 [3]. The soil samples were melted for 30 min in a muffle furnace at 900 °C. The decanted samples were dissolved in 50 mL of 2 M HNO_3 and 0.5 M citric acid. Soil samples were extracted according to a five-step sequential leaching procedure; we accordingly obtained five fractions. Fraction 1 (mobile/exchangeable elements) was extracted by shaking with 1 M ammonium acetate (pH 7) for 24 h. Fraction 2 (acid-soluble elements) was obtained by shaking with ammonium acetate buffered to pH 5 for 5 h. Fraction 3 (elements bound to oxidizable matter) was obtained by gently heating with 20 mL H_2O_2 for 5 h in an ammonium acetate buffer solution. Non-crystalline components, predominantly Fe, Mn, and Al-oxides, were isolated by selective dissolution with 0.2 M ammonium oxalate (pH 3.2) in the dark conditions (Fraction 4). Then the solid and supernatant were separated by centrifugation. The element's concentrations in the supernatant of all mentioned fractions were measured using the ICP-MS (inductively coupled plasma mass-spectrometry). The total concentration of investigated elements is calculated as the sum of all five isolated fractions, and the plant's bioavailable fraction is calculated as the sum of Fractions 1–4.

The dried plant biomass was ground to a fine powder using a centrifugation mill equipped with a titanium rotor (type ZM1000, Retsch, Germany). Further, microwave-assisted digestion (Ethos plus 2, Milestone Srl., Sorisole, Italy) was performed with 100 mg of plant material taken from the ground biomass (duplicates). Samples were mixed with 1.6 mL of nitric acid (65% or higher) and 0.6 mL of hydrofluoric acid (4.9%) and heated to 220 °C in a microwave oven [4,17]. Concentrations of elements of geogenic (P, Fe, Mn, Ca,) and pollutant (Pb, Cd, Zn, As) groups from the diluted digestion solutions were determined by ICP-MS (model X Series 2, Thermo Fisher Scientific, Dreieich, Germany) using 10 $\mu g\ L^{-1}$ rhodium and rhenium as internal standards. Calibration solutions (0.01–100 $\mu g \cdot L^{-1}$) were prepared by appropriate dilution of a multi-element stock standard solution. Accuracy was checked by analysis of the certified reference standards GBW07407, NCS ZC73032, and NCS ZC73030 (China National Analysis Center for Iron and Steel 2014) [3]; all results deviated by less than 12% from certified values.

2.4. Data Processing and Statistical Analysis

All element concentrations were calculated on a dry weight basis. The results of the obtained data, namely the calculation of the total concentrations and the percentage of the content of individual fractions of the studied elements, were processed by using Statgraphics Centurion 19. Differences in total concentrations of investigated elements between the woody plants, their part compartments, and between the study sites were identified by a multivariate analysis of variance (MANOVA). Homogeneity of variances was tested using Levene's test. In case of samples with unequal variances, Kruskal–Wallis tests were used.

3. Results

3.1. Total and Potentially Plant Available Concentrations in Soil

The overall bioavailability and general mobility of elements in soil depend on several factors, including soil pH, redox potential, organic matter content, clay mineralogy, texture, microbial activity, and irrigation water (Table S1). From the elements we studied, five were considered essential (P, Fe, Ca, Mn, Zn), while the other three (As, Pb, Cd) do not have any functional significance for plants and are considered toxic when present in high concentrations. Note that Zn, when present in a concentration that is high enough in soil (prevalent in acidic and sludge-amended soils), will become a toxic element for plants in its own right, similar to Fe and Mn [17]. The category of plant macronutrients included P and Ca, whereas Fe, Mn, and Zn are micronutrient elements. The main functions of essential elements for plants are structural (P, Ca), catalytic (Fe, Mn, Zn), and regulatory (e.g., Ca). The total soil concentrations of calcium (Ca), manganese (Mn), and iron (Fe) were very similar and not significantly ($p > 0.05$) different across all study sites (Table S2). Soils in COL were characterized by the highest P concentrations being significantly ($p < 0.05$) higher than DVV and the FCF (Table S2). The highest total soil As concentrations were found in the DV substrate and were significantly ($p < 0.05$) higher than all other sites. The concentration of As in soil was 143 and 230 times higher compared to FCF and SEI, respectively. The COL and DVV showed ~99% lower As concentrations than DV. However, their concentrations were still 2.8 and 2.6 times higher than in FCF and SEI soils. The most significantly ($p < 0.05$) elevated concentrations of soil Pb were in DV and DVV (Table S2), and the lowest in SEI. Surprisingly, the highest soil concentrations of Zn and Cd were found in FCF and, less unexpectedly, in DV. The lowest concentrations of soil Cd and Zn were observed in SEI, ca. 80–90% lower than DV and FCF ($p < 0.05$ and $p < 0.01$, respectively). There were no significant differences in total soil Cd and Zn concentrations in COL, DVV, or DV (Table S2).

The DV and DVV contained the highest soil available concentrations of As, Cd, Zn, and Pb, equivalent to >83% for Cd and Pb, 33–61% for Zn, and 12–35% for As of their total concentrations. The concentrations of all four fractions, which made up the total available concentration (Table S2), generally decreased in the order DV > DVV, COL > SEI = FSF. However, Pb and As were more bioavailable in the FSF soils than in SEI, whereas As availability in FSF was similar to DVV. Available As was ~30 to 180 times higher in DVV than all other sites ($p < 0.01$). Available Zn and Pb were also significantly higher in DV and DVV than all other site locations ($p < 0.01$). (Table S2). Soil in COL had the highest available P concentrations of all sites ($p < 0.05$). Available Fe and Ca concentrations were similar for all sites ($p < 0.05$). However, available Mn and Cd were the highest at the DVV, i.e., 67% and 85% higher for Cd and Mn compared to the FSF soils ($p < 0.05$). Furthermore, Mn was less available in FSF than in COL and SEI soils (Table S2).

3.2. Tree Element Concentration

Small letters in Figures 2 and 3 present significant differences between the plant parts (leaves, branches), whereas the capital letters demonstrate significant differences between the concentrations of these elements depending on the study sites. All species exhibited similar concentrations of P, Ca, Fe, Mn, and Zn in branches, and there was no significant difference in the concentrations of As and Pb (Figures 2 and 3).

There were also no significant differences in P, Ca, Fe, Mn, and Zn in the leaves and branches of the three species *B. pendula, P. tremula,* and *S. caprea* growing in FSF ($p > 0.05$). There were also no differences in the concentrations of As and Pb ($p > 0.05$). The leaves and branches of *P. tremula* and *S. caprea* contained significantly higher Cd concentrations ($p < 0.01$). Furthermore, *S. caprea* exhibited the highest Cd concentrations (Figure 3).

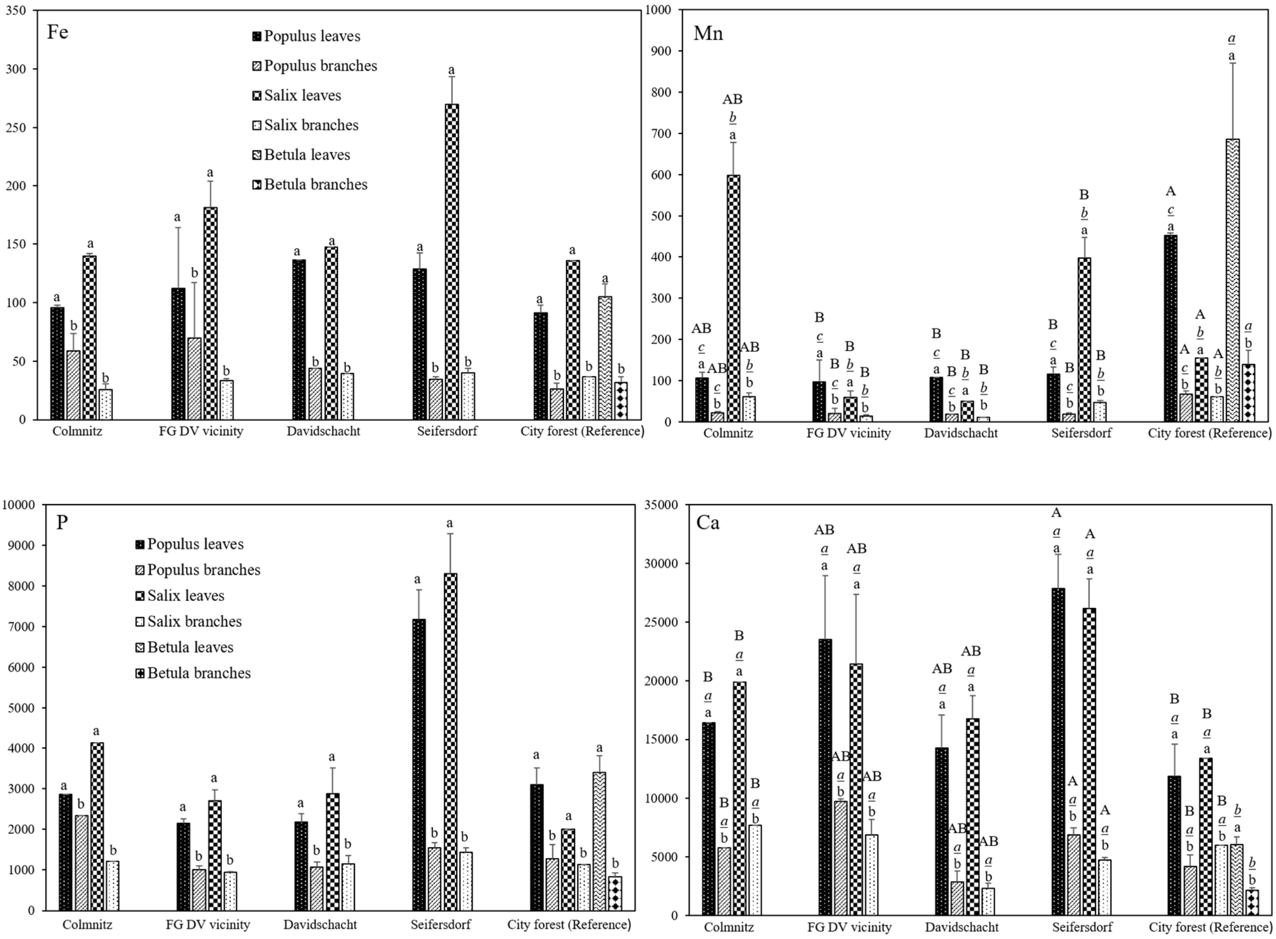

Figure 2. Total concentrations of geogenic elements (µg g^{-1} dw) in the leaves and branches of *Populus tremula*, *Salix caprea,* and *Betula pendula*. The values used on ordinate axis correspond to decimal place convention. Significant differences were determined by a multivariate analysis of variance (MANOVA). Each bar represents the mean concentration plus standard error. Small letters demonstrate significant differences between the part compartments. Capital letters—between the study sites, and italicized letters—demonstrate significant differences between the species ($p = 0.05$).

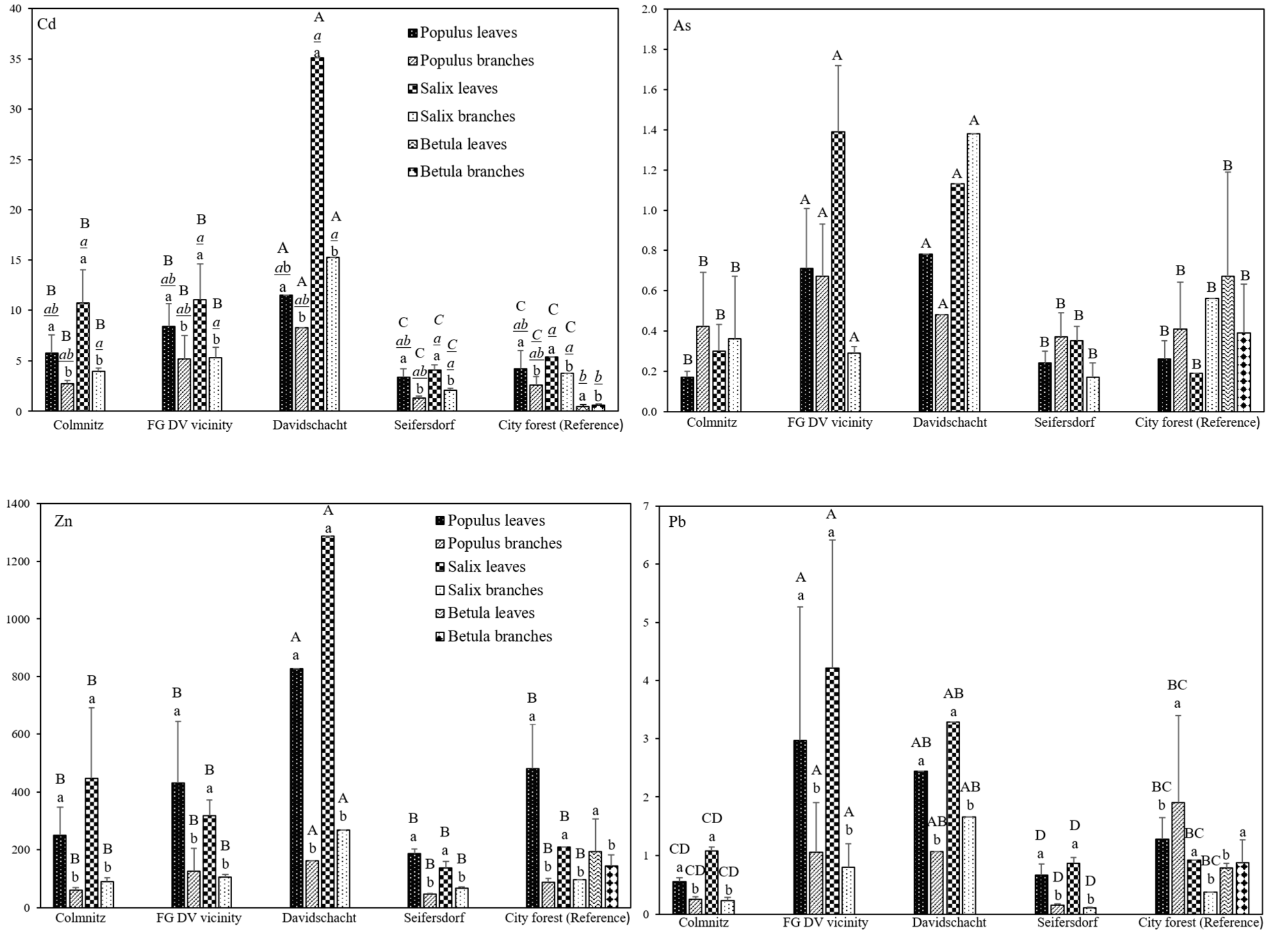

Figure 3. Total concentrations of Cd, As, Zn, Pb (μg g^{-1} dw) in the leaves and branches of *Populus tremula*, *Salix caprea*, and *Betula pendula*. Significant differences were determined by a multivariate analysis of variance (MANOVA). Each bar represents the mean concentration plus standard error. Small letters demonstrate significant differences between the part compartments, capital letters—between the study sites, and italicized letters—demonstrate significant differences between the species ($p = 0.05$).

There were generally no significant differences between the plant species with regard to any of the studied leaf nutrients (Figures 2 and 3), except the leaf concentrations of *S. caprea* and *P. tremula*, which exhibited higher Cd concentrations than *B. pendula*. The concentrations of essential elements were generally higher in leaves than in the branches.

The *S. caprea* exhibited 77–278%, *P. tremula* 44–573%, and *B. pendula* exhibited 181–396% higher concentrations. Three factors (plant part, study site, and species) were found to affect cadmium (Cd), calcium (Ca), and manganese (Mn). Almost all the elements (P, Ca, Mn, Fe, Zn, Cd, Pb) are accumulated in leaves. The relationships between different geogenic and toxic elements are indicated in Table S2. In the leaves, the negative relationship trends were found in the cases when Cd, Pb, and As depend on P; As depends on Ca; Cd and As depend on Mn; Pb depends on Fe (Table S3). In other cases, there were positive relationships. Almost the same we can see in the branches.

Among the more geogenic elements, there were only significant overall differences in the tree species between the study sites for Ca and Mn ($p < 0.01$). The highest P, Ca, and Fe essential nutrient concentrations were determined in tree leaves sampled in SEI. The leaves of birch sampled only in the city forest accumulated the highest amount of Mn. The accumulation of the micronutrient Zn and the elements from the toxic pollutant group (As, Cd, and Pb) in the plant materials significantly differed between study sites.

The calculated indices of plant–soil bioaccumulation in the plant compartments indicate a more 'expected' bioaccumulation (range ~ 1–9), coefficients for essential metals P, Ca, and Zn. However, a comparable or even higher range was observed for the toxic metal Cd (~1–14), especially for the polluted DV site. Overall, generally higher values were found in *Salix* than in *Populus* (Table S1). The bioaccumulation coefficients for the other metals did not exceed the value of 1, which, accordingly, indicates a higher soil content than measured in the tree tissues and points to a lack of bioaccumulation. The lowest ranges (<0.01) for heavy metals were found for Fe, As, and to a lesser extent Pb, which suggests high natural abundance (e.g., Fe) or potentially high local levels of soil pollution (As, Pb). Note that Al also has low values like As and Fe, suggesting that it is also 'less preferred' by the studied woody plants (i.e., has potential toxic properties).

4. Discussion

4.1. Soil Element Concentration

Investigated essential elements, i.e., P, Ca, Fe, Zn, and Mn (Table S2), are not anthropogenic pollutants in the Freiberg region, as they have never been mined or processed here, unlike the toxic pollutants As, Pb, and Cd. Thus, it can be generally assumed that the origins of these metals in the soils are geochemical (geogenic/natural). There were also statistically significant differences between both the total and bioavailable concentrations of Zn, As, Cd, and Pb depending on the study sites (Table S2), which points to their anthropogenic origin [3,4]. These elements, therefore, come from the weathering of the bedrock typical of the Freiberg region, which is orthogneis in the whole study area [18–20] and is also contained in the process residues dumped at the DV site. Given that phosphates are widely used as fertilizers in agriculture [21] it is reasonable that the higher concentrations in the rather small forests patches in COL and SEI have their origin from adjacent agricultural sites, whereas P in the tailing material and mining affected soils in the vicinity of the DV where agriculture is restricted, is most probably geogenic [3,4].

As and Pb are the metals that exhibit toxic effects. These are two metals-genotoxicants, or elements that, in excess or under the wrong conditions, can cause errors in the genetic information system. Arsenic is a weak mutagen but a potential carcinogen [22]; it is primarily found as the anions, arsenate and arsenite, under oxidized and reduced conditions, respectively. Arsenic may form insoluble compounds with Fe and Al oxides or may be adsorbed to organic matter or hydroxyl groups on clay minerals [23]. Being one of the main and powerful sources of environmental contamination with As in Freiberg, DV likely significantly influenced COL, thereby elevating both the total (111 $\mu g\ g^{-1}$) and bioavailable (39 $\mu g\ g^{-1}$) concentrations of As. The high mobile concentrations of Zn and Cd were determined in the samples from DV (Zn: 0.17 $\mu g\ g^{-1}$, 33% of the total; Cd: 2.61 $\mu g\ g^{-1}$, 88% of the total), DVV (Zn: 0.17 $\mu g\ g^{-1}$, 61% of the total; Cd: 1.51 $\mu g\ g^{-1}$, 85% of the total), and COL (Zn: 0.09 $\mu g\ g^{-1}$, 47% of the total; Cd: 1.23 $\mu g\ g^{-1}$, 49% of the total). The minimum concentrations of Cd and Zn were at SEI. The highest total concentrations of Zn and Cd were found in the FCF soil, while the concentrations of these metals in available Fractions 1–4 were low. As previously determined, bioavailability is a product of an element's geoavailability, physical dispersion, and chemical mobility, as well as the organism's exposure, biological characteristics, and individual sensitivity [24,25]. Here, the bioavailable content of Zn and Cd was only 8% and 11% of the totals, respectively. Bioavailability is a limiting factor for phytoextraction [26,27], and a low percentage of these metals in the bioavailable form in the soil can indicate a significant limitation of the intake of these metals into plants. We did not measure pH in our soil sampling as we focused on the interactions between potential available (labile) elements in the soil (sequential extraction) and concentrations in plants. Typically, the portion of labile elements governs plant uptake of elements. However, the distribution of elements in different labile soil fractions is not only affected by pH but also integrates other physicochemical soil properties (texture, SOM, etc.). Some related data on the soil pH of the site exist. The mine dump site was found to be highly acidic (pH 4–5) [4]. The other areas are expected to have a soil pH of around 6, as these soils are quite young and are derived from gneiss, which is an acidic metamorphic rock.

Redox reactions link the geochemical cycles of various elements [28]. Fe is the most widespread transition metal in the Earth's crust, accounting for 5.1% of its mass [29]. Under natural conditions, Fe exists mainly in the form of Fe (II) and Fe (III). Due to its higher solubility, Fe (II) is more bioavailable than Fe (III) [30]. Fe always coexists in various forms with Mn in various surface and near-surface environments (e.g., waters, soils, and sediments). The redox cycling of Fe and Mn functions as a 'pump' for elemental cycling and energy flow and plays a special role in the dynamics of ecological systems [29]. Furthermore, a growing body of research shows that the coupled redox process between Fe and Mn can bi-directionally influence the crystallisation and transformation of Fe and Mn (oxyhydro)oxides, which are among the most abundant nano-minerals and mineral nanoparticles in these environments [29,30]. We assume that in our research, the main part of the investigated metals was bound to crystalline Fe, Mn oxides, and refractory silicates. This indicates their geochemical origin in the FCF soil. Zn and Cd have strong chemical affinity, and both are maintained in soil exchangeable sites as divalent ions [31,32].

For the data we obtained for the soils of the Freiberg region, the presence of significant correlations was found in the pairs Zn-Cd ($r = 0.86$, $p < 0.001$), As-Pb ($r = 0.515$, $p < 0.01$), and As-Zn ($r = 0.450$, $p < 0.05$). The mobility and accessibility of Pb results from a sequence of several processes [33], such as the formation of silver–lead alloys. The area of Freiberg, where our research was conducted, is known primarily for the past mining of silver ore. The results we obtained showed the presence of a significant amount of Pb in the soil environment (Table S2) at all the studied sites. Its highest content is noted for DV, with an excess of metal concentration compared to the COL, FCF, and SEI in 8.2, 3.3, and 16.1 times. The search for correlative relationships with other elements in soil also revealed the presence of correlation in such pairs as Pb-Zn ($r = 0.892$, $p < 0.001$), Pb-Fe ($r = 0.470$, $p < 0.05$), and Pb-Cd ($r = 0.464$, $p = 0.05$). As can be seen from these results, the strongest correlation in the soil is recorded in the case of the interaction of Pb with Zn. The positive relationship ($r = 0.562$, $p < 0.05$) between Pb and Zn was also found by another research work [34]. Trace elements can be bound by organic matter in stable complexes. In addition, organic matter represents an exchanger surface and can bind cations in a non-specific, easily mobilizable form [35]. As previously found in the investigated areas, the pH values at the Davidschacht tailings dam were in the strongly acidic to acidic range (3.7 to 5.5) [36]. This can be attributed to the oxidation of sulphide ores, which leads to soil acidification [37]. Overall, this suggests that local soil conditions in our studied areas are adequate for the transfer of non-essential toxic elements, for instance, Pb, into plant tissues. Furthermore, there was a positive correlation between Pb and Ca in the soil ($r = 0.480$, $p < 0.05$). However, our observations contrasted with those obtained by Andráš et al. (2018), who described negative correlations between some metals in soils, including Pb with Ca, and the associated limitations on the transfer of heavy metals to plant organs [38].

4.2. Plant Element Concentration

Some woody plant species are already recognized as being promising for phytoremediation [39,40]. Among the woody plants, hyperaccumulators are noted, including *Betula* L., *Populus* L., and *Salix* L. [14,41]. It is known that the bioavailability of elements essential for plants primarily depends on soil parameters such as pH, salt content, the content of different forms of water in the soil, the content and properties of cation exchange, microbiological conditions, etc. [42–44]. When bound to solid soil particles, metals are usually immobile and unavailable to plants [45].

In this turn, it has been proven that the accumulation of substances necessary for plants, such as the total content of N and P, is facilitated by the presence of organic acids in the soil, which accelerates the transition of P and N from the non-rhizosphere layer to the rhizosphere layer [46]. High concentrations of Pb in the soil lower the soil pH, which can increase the availability of P to plants. This effect is possibly related to the root activity of plants that release organic acids in the soil, which leads to increased accumulation of soil P in plant tissues [47]. P can also increase glutathione levels and prevent membrane damage, potentially increasing plant tolerance. In turn, as shown by other authors, increased P uptake in plants was observed at low As [48]. As^{3+} is the most toxic form of As, as it has a better affinity for proteins and lipids, leading to intensive uptake by plants [49,50]. Phosphates and organic matter in the rhizosphere can bind As, reducing its bioavailability, but can also promote microbial activity that affects As transformation. Organic acids can also change the form of Cd and improve its bioavailability, effectively activating the solid heavy metals adsorbed on the surface [10]. On the other hand, there are data about the increase in P content in the soil that was correlated with Cd in plant roots, but a negative correlation of this element with cadmium in plant shoots was recorded. We also found negative significant correlations of Cd with P both in leaves ($r = -0.423$, $p < 0.05$) and in branches ($r = -0.456$, $p < 0.05$) in *Populus* plants and in leaves of *Salix* plants ($r = -0.389$, $p < 0.05$). Other authors note the same negative correlations in the Cd/P pair in their works [51]. Therefore, with an increase in the mineral content in the soil substrate, the bioavailability of Cd in plant compartments becomes limited. In other words, a decrease in the content of P in the soil promotes the accumulation of Cd in aboveground plant organs. One of the reasons for this, as noted by Huang et al. (2021), is that organic acids can significantly reduce Cd migration from roots to shoots [51].

In our investigations, we found that the relative bioaccumulation of essential nutrients (P, Ca, Zn) was generally higher than for toxic elements (As and Pb), especially for SEI and DVV (Figures 2 and 3; Table S4). Meanwhile, Mn and particularly Fe were more comparable to the latter toxic elements. The lowest amounts of the essential element Fe were observed within DV and COL, while Mn showed the lowest levels on the DV plot. For the toxic elements, the lowest uptake of As and Pb in plants was found in SEI and COL. According to some authors, Pb and As are characterized by lower transfer factors (0.01 to 0.1) than Zn and Cd (1.0 to 10) [52]. For this reason, Cd would be most easily and effectively absorbed by the plant. Cd accumulates widely in leaves and branches of the fast-growing woody plants, clearest for DV and COL, similar to or above that of P and Ca (Table S4).

Bioavailability of Cd in soil is an important factor affecting Cd uptake by plants, and exchangeable and carbonate forms are its main forms [53,54]. The efficiency of phytoextraction is related to the ability of plants to accumulate the toxicant, and there are significant differences in the remediation of heavy metals among different plants [55,56]. In our investigation, we found that compared with soil samples, Cd content was 1.5–5.6 times higher in leaves of *Populus* and 1.7–13.9 times higher in leaves of *Salix*. In the branches, both species' accumulation of Cd occurred not as intensively compared with leaves, with a maximum of 5.2 times (*Salix* samples within DV).

A relatively high correlation coefficient of bioavailable Cd in the soil with that input to plant compartments of Salix plants Cd was noted ($r = 0.563$, $p < 0.01$). Cd is known to be taken up by plant cells, inter alia, through transporters belonging to ZIP and Nramp, which also transport Zn [57]. As can be seen from the above results, bioavailable Cd elements are well correlated with Zn ($r = 0.510$, $p < 0.001$). Similarities in the accumulation patterns of Cd and Zn indicate common transport mechanisms, which play a significant role in the distribution of elements in plant tissues [52]. A reliable positive correlation can also be explained by the fact that these two elements have similar indicators of subcellular localization, as was particularly found in the leaves of some plants [58].

Uptake of Cd and Zn in plants can also have an antagonistic effect because the similarity of the two metals leads to competition for binding sites [52]. Although plants distinguish between Cd and Zn, they produce ligands that are particularly specific to one of these elements. The data we obtained do not agree with the results of the above-mentioned authors for representatives of Salix. On the other hand, a positive correlation of the Cd/Zn pair for both leaves and shoots is noted for the other studied species of Populus.

In contrast to Zn, another essential metal, Fe, has a negative correlation with Cd ions ($r = -0.640$, $p < 0.001$). Our data agrees with other plant studies, as it is well known that Cd effectively competes with Fe transport [55]. Some publications have shown that Fe deficiency leads to intensive accumulation of Cd in plants [59]. In this study, it was found that along with a significant Fe deficiency, the accumulation coefficient of Cd in all variants of the plant samples studied is high. The highest index of the bioaccumulation coefficient is indicated for willow plants in the DV area, which may indicate iron deficiency in the soil at this site.

Our data obtained for the *Populus* leaves demonstrated a significant relationship between soil As and plant Zn ($r = 0.472$, $p < 0.05$) and Fe ($r = 0.376$, $p < 0.05$). Additionally, a correlation of soil As with plant Zn ($r = 0.482$, $p < 0.01$), leaf Ca ($r = 0.482$, $p < 0.01$) was noted for branches of *Populus*. This indicates that the presence of As in our soils did not prevent plant uptake of the two essential elements Fe and Ca. No significant correlations of As with other elements were found in *Salix* leaves, but similarly to *Populus tremula*, a correlation of the bioavailable fraction of this metalloid with Ca ($r = 0.427$, $p < 0.05$) and Pb ($r = 0.473$, $p < 0.05$) was recorded for its branches.

Observations of patterns of distribution and accumulation of Cd revealed that this element does not accumulate in the soil, regardless of the place of sampling. Compared to the soil, plant tissues accumulate this metal, and to a greater extent, this is applied to plant leaves compared to branches. It was found in the largest quantity on the territory of DV, as well as in COL. From the data we obtained, both studied tree species can be hyperaccumulators of such an element as Cd, which is also in line with the data of other authors [60,61]. Mineral fertilization into the nutrient substrate will, however, cause a negative effect on cadmium accumulation, which is evidenced by the presence of antagonistic relationships between the elements. In general, the relatively low concentrations in plants at the DV may be the result of the low availability of elements for plants. It should be noted that total element concentrations often correlate only to a limited extent with plant concentrations. Rather, the availability of elements to plants in soil occurs only when the elements are present in dissolved form and in bound forms that can be taken up by plant roots [3].

5. Conclusions

The maximum soil concentrations of total As and Pb were generally in the Davidschacht mining area or its vicinity. Unexpectedly, the highest soil Zn and Cd concentrations were found in the Freiberg city Forest region. The lowest concentrations of four soil pollutants (As, Cd, Pb, and Zn) were observed in Seifersdorf. Total soil P was highest in Colmnitz, but Ca, Mn, and Fe concentrations were very similar across all study sites. The concentrations of the available fractions in soil decreased in the order DV > DVV, COL > SEI = FSF. There is a stronger accumulation of elements in the tree leaves than in the branches. The bioaccumulation of Cd in *Salix caprea* (willow) branches was the most significant among the non-essential elements. For *Populus tremula* (common aspen), Cd was significantly correlated with Zn and Fe, whilst for willow, a correlation between As and Ca was recorded, in both cases, only for the woody (branches) plant parts. Critically, willow accumulates Cd better than common aspen and silver birch (*Betula Pendula*). We conclude that among fast-growing woody plants, willow is a suitable bioindicator for soil Cd contamination.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/soilsystems9020056/s1. Table S1. Studied elements, their properties and roles in plants. Table S2. Total and bioavailable concentrations of major and trace elements in the soils in the different sites of Freiberg area (means ± sd). Table S3. The relationships between essential and toxic elements in plants organs. Table S4. Bioaccumulation coefficients for the leaves and branches of *Populus* and *Salix*. References [50,62–68] are cited in the Supplementary Materials.

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