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Accumulation of elements in vegetation spontaneously developing on self-heating waste dumps in the Upper Silesia area (Poland)

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Accumulation of 34 trace and major elements was analysed in 9 plant species (*Tussilago farfara, Arctium tomentosum, Solidago canadensis, Populus* L.*, Eupatorium cannabinum, Verbascum* sp.*, Solanum nigrum*, *Rumex crispus* L., *Betula pendula*) and one fungus (*Schizophyllum commune*) collected from coal, PbZn-smelting, and mixed-type waste heaps in Upper Silesia (Poland). The most persistent and extreme enrichment was found in the burnt bark of *Betula pendula* from Bytom. Enrichment factors in relation to the geometric mean of elevated (PE) and hyperaccumulator (PH) plant contents show extreme values for elements toxic to vegetation, such as Zn (EF_{PE} up to 13, EF_{PH} up to 17), Pb (EF_{PH} up to 4, EF_{PE} up to 161), Tl (EF_{PE} up to 8), Cd (EF_{max} of 327), Hg (EF_{PH} up to 3), and Ag (maximum EF_{PE} of 14). Elevated are also V (EF_{PN} up to 13), Sc (EF_{PN} up to 14), Ni (EF_{PN} up to 17), Se (EF_{PN} up to 16), Fe (EF_{PN} up to 48), Co (EF_{PN} up to 23), Sb (EF_{PN} up to 31), and Bi (EF_{PN} up to 34). Although the levels of the elements studied were usually below potentially toxic levels, they were often above the normal ones. Furthermore, significant differences in the contents between different plant tissues were observed, as reflected in the translocation factor (TF). *Verbascum* sp. and *S. nigrum* accumulate such elements mostly in their above-ground tissues, and may thus be considered useful in phytoextraction of Zn, Pb and other elements. *Sl. canadensis* and *E. cannabinum* mostly display the opposite strategy, with element immobilization in their roots. Extreme Zn contents in *E. cannabinum,* peaking in its roots, suggest it to be a potential Zn phytostabilizer.

Key words: toxic metals, burning heaps, environment contamination, coal/smelting waste, plant hyperaccumulation, element translocation.

INTRODUCTION

BURNING COAL-MINING WASTE HEAP ENVIRONMENT

Long-term coal mining in Poland has led to significant landscape transformation, with settling ponds, perimeter ditches, and – most importantly – numerous waste heaps. The latter contain vast amounts of post-mining waste rocks (coal remnants, shales, and other sedimentary and minor non-sedimentary rock types) with masses reaching tens of millions of metric tons. Heap formation and their long-term existence are leading to substantial environmental disturbance. Many of the heaps are affected by fires (and are herein referred to as BCWHs, for burning coal-mining waste heaps). The fires are initiated by spontaneous coal combustion preceded by initial coal oxidation and self-heating. As a result, entire levels of the waste burn, often with multiple fire foci, in a process that may last for tens of years. Remediation of the BCWHs is very cost-consuming. This is especially true in the case of large heaps, of area often >100 ha (e.g., the BCWH in Czerwionka-Dębieńsko, Upper Silesian Coal Basin, or USCB) and height >100 m a.g.l. (e.g., 138, the "Szarlota" BCWH in Rydułtowy – the highest heap in Europe; PZPWŚ, 2004).

Self-heating, the causes and evolution of the component processes being characterized by Wagner (1980), Cebulak et al. (2005) and Sokol et al. (2005), triggers long-term waste rock transformation; the processes are grouped into high-temperature (~330–1200°C) pyrometamorphic, moderate-temperature (~up to 500–600°C) exhalative, and low-temperature (<50°C) supergene (e.g., Srebrodolskiy, 1989; Nasdala and Pekov, 1993; Stracher, 2007; Kruszewski et al., 2018, 2019, 2021; Kruszewski, 2013). Pyrometamorphism includes initial rock fusion, partial or complete melting, and partial (re)crystallization from locally formed melts, mainly governed by solid-phase physico-chemical transformations and gaseous matter transfer. The fire gas ascent is also related to exhalative processes: mineral crystallization directly from the gas phase (condensation, i.e., desublimation) or via gas-waste pneumatolytic/hydrothermal interaction, solution crystallization, and evaporation. The supergene processes are either low-temperature evaporative crystallization or weathering. Coal fire gas chemistry mainly

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comprises H_2O, CO_2, some CH_4 and CO, other hydrocarbons (aliphatics, aromatics, cycloalkanes, and their alkyl and halogenated derivatives), and, most likely, some (semi)metal and nonmetal hydroxides, carbonyls, nitrosyls, hydrides, and organo(semi)metallics. These gases and newly formed minerals are sources for local anomalies of ammonium, B, F, K, Na, Ca, Mg, Al, Ti, Cr, V, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Sr, REE, Mo, Ag, Cd, In, Sn, Sb, Te, I, Ba, Re, Au, Hg, Tl, Pb, Bi, Th, and U. The exhalative and supergene minerals that may influence local waters due to their unstable nature (including solubility), are mainly sulfates and halides (mainly chlorides, with minor fluorosilicates, fluoroaluminates, and fluorides) of NH_4, K, Mg, Fe, Al, Ca, and Na (Kruszewski et al., 2018, 2019, 2021). The list of the organic compounds deposited in the BCWH environment was further updated by Nádudvari et al. (2018).

SOURCES OF ELEMENTS IN THE BCWHs

Coal's organic matter is well-known to fix many elements via ligand coordination (e.g., Montross et al., 2020). This phenomenon was largely addressed by Ketris and Yudovich (2009), who reported Coal Clarkes (average worldwide coal contents), of mainly trace elements (TEs). They also report the Coal Affinity Index (CAI) for the particular TEs. Seredin and Finkelman (2008) delivered a detailed review of extreme TE contents in coals. Their reported maximum levels, in ppm, are 100 for Ag, 32000 for As, 15 for Au, 9000 for B, 22000 for Ba, 330 for Be, 170 for Cd, 1185 for Ce, 932 for Co, 3200 for Cr, 75 for Cs, 7000 for Cu, 198 for Ga, 2116 for Ge, 45 for Hf, 1000 for Hg, 2685 for La, 747 for Li, 3200 for Mo, 300 for Nb, 3490 for Ni, 1900 for Pb, 6.1 for Pd, >10 for Pt, 408 for Rb, 46 for Re, 5800 for Sb, 700 for Sc, 2900 for Se, 2800 for Sr, 500 for Th, 420 for Tl, 14100 for U, 10600 for V, 2800 for W, 1400 for Y, 19000 for Zn and 1852 for Zr. As much as 8.1 ppm Bi, 0.14 ppm In, 168 ppm Se, and 0.08 ppm Te was found in coal nanotubes from the Ruth Mullins coal fire site (Silva et al., 2012). The listed values are much higher than typical contents in both the Earth's crust (e.g., Parker, 1967), and plants (e.g., Kabata-Pendias and Pendias, 2001). Indeed, some coal deposits are mined for rare elements – especially Ge, but also Sb and Cs – that are often recognized as critical or strategic materials. This matter is worth a closer look when addressing vegetation, especially since plants have been suggested by some authors as a potential industrial source of such materials (e.g., Liu et al., 2020; Vural, 2017; Novo et al., 2015).

VEGETATION OF THE HEAP HABITATS

Geochemically extreme conditions in the heaps lead to the development of habitats where a small number of plant species are able to survive (especially on sterile heaps; Bârlea and Ardelean, 2009) or where distinctive fauna and flora flourish. Such extreme sites may be related to anomalous toxic metal concentrations, as exemplified by mercury in an extensively studied Wuda coal fire zone (Li et al., 2018). The vegetation structure of heaps is often simple and characterized by low species diversity. Anomalies in plant development are also observed (Alekseenko et al., 2018). Such extreme environments are thus especially attractive for studying the ecological tolerance of particular species and the influence of stressors on biological communities.

Studies of the diversity of spontaneously developing vegetation on heaps are especially important for proper planning of remediation. As noted by many authors, the identification of local species able to form populations and achieve reproductive success in such extreme habitats is important for the reduction of reclamation costs (Rostański, 2006). Plant species spontaneously expanding around post-industrial areas are excellent indicators of habitat conditions (Zając and Zarzycki, 2013), with some species being pioneers in this field.

The species composition of some of the Polish heaps is well known (e.g., Hanczaruk, 2017; Hanczaruk and Kompała-Bąba, 2019; Rostański and Woźniak, 2000). The last authors studied vegetation in 112 coal mine spoil heaps within the USCB. Recently, self-heating dumps have also attracted scientists to study their botanical composition. For instance, Abramowicz et al. (2020) showed a dominance of species from the Asteraceae family on two BCWHs in the USCB (Bytom and Ruda Śląska sites). They pointed out that the vegetation spreading in such an environment is affected by a range of factors, including heap shape, exposure, and thermal activity.

The relationship between soil type with its physicochemical properties and vegetation has also been addressed (Kompała-Bąba et al., 2019). Plants able to grow in such unfavorable conditions, e.g., the metalliferous areas of post-industrial sites, must have developed strategies for survival (Siwek et al., 2008; Hanczaruk and Kompała-Bąba, 2019). Although varying from species to species, toxic elements derived from the substrates have accumulated in most parts of the plants (Baker, 1981; Hanczaruk and Kompała-Bąba, 2019). Important sources of potential plant toxicity in the coal-mining industrial environment come from coal ash and PAHs deposited in local soils, as exemplified by a study by Atanassova et al. (2018). Furthermore, soils may be largely influenced by fires (coal fires, vegetation fires), e.g., by enrichment in organic nitrogen and carbon due to gaseous emissions, and changes in soil moisture content (Martinez and Ressler, 2001; Knicker, 2007; Tobin-Janzen et al., 2015). They act as scavengers of fire-derived pollution (Querol et al., 2011). Dump vegetation, in turn, not only causes variations in soil levels of biophilic elements and their particular forms (especially nitrate and ammonium nitrogen, due to mineralization processes), but may also influence the slope stability of heaps (Tripathi et al., 2012).

Concentration levels of heavy metals stored by plant tissues are often higher than in surrounding soils and are species- (Stefanowicz et al., 2016) and families-dependent (Hobbs and Streit, 1986). The ability of vegetation to accumulate elements may play an important role in matter transfer within heaps. Stefanowicz et al. (2016) studied concentrations of 9 metals in roots and shoots of plants from Zn-Pb metallurgical waste heaps and observed much higher levels of, e.g, Cd, Pb, Tl, and Zn in plant tissues than "values for a reference plant". Similar studies were made by Nadgórska-Socha et al. (2013, 2015). Most of these studies focus on a few (Pb, Zn) metallurgical waste heaps.

UPTAKE AND MIGRATION OF ELEMENTS IN PLANTS

Metals exist mainly in the soils in a form that is not bioavailable to plants. Releasing root exudates, however, plants may increase metal solubility by change of rhizosphere pH (Dalvi and Bhalerao, 2013). Subsequently, metal ions may enter into a plant shoot via two main mechanisms: passive diffusion (apoplastic pathway) and active transport (symplastic path) through the plasma membranes. Later, metals are complexed with chelators (Clemens, 2001; Hall, 2002) and mostly immobilized (Thakur et al., 2016; Yan et al., 2020). Retention in the roots is a resistance mechanism to toxic elements or high concentrations of metals, and thus the largest amount of metals are accumulated in the roots. However, some plants (hyperaccumulators) have an ability to translocate a high content of metals through the xylem by dint of a symplastic pathway (Thakur et al., 2016). However, plants adopt different strategies to cope with high concentrations of different metals. This means that the same plant species behave differently in relation to different elements: some elements may be accumulated in the roots, whereas others are transferred to the above-ground tissues. For instance, specimens of *Noccaea caerulescens* have a great ability to accumulate extreme concentrations of Zn in comparison to non-hyperaccumulators (Peer et al., 2006). Polymetallic accumulation also exists, e.g., *Thlaspi goesingense* accumulates Ni, Zn Co, and Mn (Baker et al., 2000).

Accordingly, vegetation in the heaps may play a dual role in element cycles. Despite extensive research regarding the content of specific elements in different plant tissues, there are still gaps in knowledge that are crucial to establishing a proper management strategy for polluted areas. Depending on the species strategy regarding element management, they may immobilize pollutants and may thus be useful in phytoremediation. Also, due to bioaccumulation in shoots, they may transfer particular elements to higher strata of the food chain, which poses a threat to human and wildlife health. Because of this environmental risk and the potential of vegetation for the recovery of rare elements, it is essential to know what kind of strategies are adopted by particular species towards particular elements. Therefore, the main goal of our research was to evaluate the potential of element accumulation by nine chosen plant species (*Solidago canadensis, Rumex crispus* L., *Arctium tomentosum, Verbascum* sp., *Populus* L., *Betula pendula, Tussilago farfara, Solanum nigrum, Eupatorium cannabinum*) and one fungus (*Schizophyllum commune*). These plant species were chosen because they constituted the dominant taxa of the plant community, whereas the fungus *Sc. commune* was selected due to its extensive and dense cover on *Populus* L.

To this purpose, the chemical composition of different parts of the plants was analysed. The data obtained are discussed in the context of enrichment in relation to Coal Clarkes, local coals, local shales, and plant concentrations (including mean, moderately elevated – potentially toxic, and hyperaccumulation levels). This comparison was to make preliminary assessment of potential environmental risks related to pollutant diffusion. Translocation factors were calculated for four species (*Verbascum* sp., *S. nigrum, E. cannabinum, Sl. canadensis*) to address their potential as hyperaccumulators. The results obtained will help plan further, more detailed, studies.

MATERIALS AND METHODS

STUDY AREA AND SAMPLING

The study area is located within the Upper Silesian Coal Basin, southern Poland (Fig. 1 and Appendix 1). Nine plant species (*Sl. canadensis, R. crispus* L., *A. tomentosum, Verbascum* sp., *Populus* L., *B. pendula, T. farfara, S. nigrum, E. cannabinum*), and one fungus species (*Sc. commune*), that are widespread in the heaps studied, were collected.

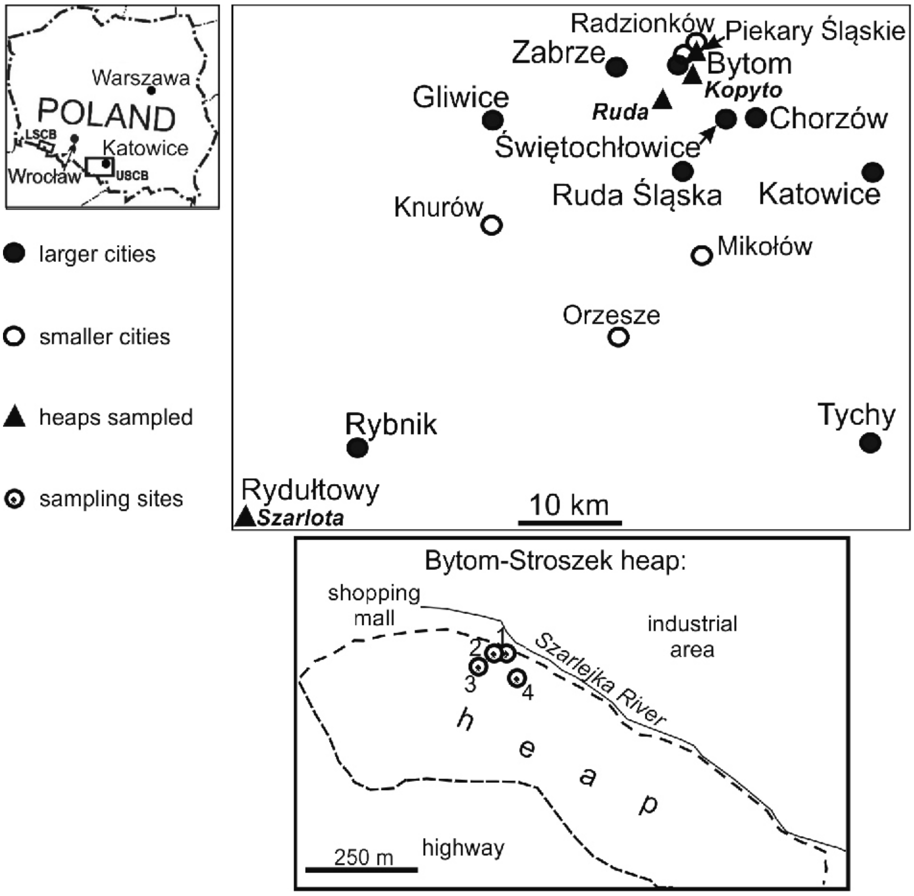

Fig. 1. Location map of the Upper Silesian Coal Basin (USCB) in Poland and the heaps sampled in the USCB

Sampling details on the Bytom-Stroszek heap inset: 1 – riverside, 2 – burning slope, 3 – plateau, 4 – smelting-waste part

Plant samples were collected especially from BCWH no. 4a in Bytom (Stroszek district, at the border with the Radzionków Nowy district of Radzionków). This heap is related to "Powstańców Śląskich" mine activity, and besides coal wastes, it also collects post-smelting PbZn(CdAgTl)-rich slags due to past PbZn mining in the area. This large (11.6 ha; Parusel, 2003) heap has been burning strongly since at least 2018; starting from about 2019, the fire has spread over a ridge-like pile of the heap, on the embankment of Szarlejka River (Fig. 2). Due to the mixed character of the waste and the vicinity of a fresh subsurface fire, the samples were collected in both coal- and slag-rich areas, close to the burning wall and fire front. The first collecting spot is directly at the river bank; here, samples of *Verbascum* sp. (mullein), *R. crispus* L. (curly dock), and *A. tomentosum* (wooly/downy burdock) were collected. In a zone above, i.e., immediately below the burning escarpment, burnt and unburnt branch fragments of *B. pendula* (birch) were collected. These were derived from trees once growing within the burning escarpment, and then fallen due to their roots being burnt out. The holes thus formed glowed at their bottoms, and the local gases were shown (via a portable *Fourier-Transform InfraRed* spectrometer) to be reduced, with methyl disulphide as a major component (unpublished results). Within the escarpment, a narrow area mineralized with greenockite (CdS), a Cd-Sb sulphide, native bismuth, and probably also locally enriched in Ni and Mo, with the surface temperature reaching 800°C, was once present (P. Kosałka pers. comm.; Ł.K. portable X-Ray Fluorescence study). The presence of greenockite with bismuth droplets has been confirmed by Nowak et. al. (2020). Most branches of *Populus* L. were covered by *Sc. commune* fungus. Riverfront, burnt slopes with *Populus* L. (poplar) trees still standing were also sampled. Another sample of *Verbascum*, and a sample of locally abundant *Sl. canadensis* (Canadian goldenrod) were collected from the top of the heap, close to the burning escarpment. The *Verbascum* sp. was growing by a thin fire-crack, the gases emitted being enriched in AsH_3 (~3 ppm). The final Bytom sample, of *T. farfara* (coltsfoot), was derived from slag wastes in the heap centre. In Zabrze, a sample of *S. nigrum* (black nightshade) was collected on the "Ruda" heap, Biskupice district. This heap, 35 ha in area, formed by the "Zabrze-Bielszowice" mine, has been burning since at least 2004 (Ł.K. field observations). Nowadays, the fire is still active even despite reclamation. *S. nigrum* was the only plant growing near the local fumarolic vents (not including some unidentifiable, burnt stems). The heap is located directly on the bank of Bytomka river, with very saline water (a mineralization of ~1500 mg/L was determined *in situ*, related to mine-derived brine dumping and brine-rich waste pore water – e.g., Pałys, 1966). The third sample of *Verbascum* sp. was collected from the large plateau of a strongly burning southern pile of the famous "Szarlota" (Ruch 1 cones) heap in Rydułtowy – the highest heap in Europe (~138 m high; 37.8 ha area; PZPWŚ, 2004), related to the "Rydułtowy-Anna" mine. A second sample – *E. cannabinum* (hemp-agrimony, holy rope) – was collected from slag wastes that come from the "Kopyto" heap (on the shores of the "Ajska" pond) of the former Guidotto smelter. This area is in the Lipinka River valley, part of which is a nature-landscape conservation area. The smelting-slag substrate was probed for comparison with the coal-waste one.

LABORATORY WORK AND CHEMICAL ANALYSIS OF THE PLANTS

At a laboratory, the collected samples were shorn of dead shoots and thoroughly washed with tap water followed by deionized water. The plants were split into roots and shoots, and, if possible, into flowers. They were then dried at 60°C for 48 h. In total, 9 shoots (*Verbascum* – 3 samples; *Solidago*, *Rumex*, *Arctium, Tussilago, Solanum, Eupatorium*), 4 roots (*Solidago, Verbascum, Solanum, Eupatorium*), 4 stems (*Solidago*, *Tussilago*, *Solanum*, *Eupatorium*), 2 flowers (*Solidago*, *Eupatorium*), 2 wood, 3 bark, and 1 pericarp samples were obtained, totalling 25 samples. The dried parts were ground, homogenized, and split into two subsamples. On the first subsamples the concentration of 34 elements (Al, Ca, Fe, K, Mg, P, S; As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Ga, Hg, La, Mn, Mo, Ni, Pb, Sb, Se, Sr, Te, Ti, Tl, U, V, W, Zn; rare earth elements, REEs: La, Sc, Th) were measured by Inductively Coupled Plasma Mass Spectrometry (ICPMS) at a commercial laboratory (Bureau Veritas, VG101 procedure). Additional elements – Be, Ce, Cs, Ge, Hf, In, Li, Nb, Pd, Pt, Rb, Re, Sn, Y, Ta, and Zr – were only measured in selected samples, within a reconnaissance for further, extended studies planned. One-gram sample aliquots were first dissolved in HNO_3 and then aqua regia digestion of raw materials (i.e., without ashing) was used due to suspected elevated amounts of As, Se, and Hg. Other subsamples were used to measure total nitrogen (TN), total organic carbon (TOC), and total hydrogen (TH). These elements were determined using the Vario MicroCUBE elemental analyzer at the Institute of Geological Sciences PAS in Warsaw. Sulfanilic acid was used as a standard for analysis, and the typical analytical error was smaller than 0.1%.

INITIAL DATA PROCESSING

The element concentrations obtained were compared to calculated geometrical means (M_g) of typical (normal, background) levels (PN), excess, potentially toxic levels, found in published data (see Table 1 for references), herein referred to as PE. Enrichment factors (EFs) were then calculated, by dividing our values by the M_g values (Table 1). The EFs are thus expressed as multiples. EFs were also calculated considering the M_g of extreme (hyperaccumulator) plant concentrations (PH), Coal Clarkes (CC, i.e., mean worldwide coal contents), local coal (LC), and local shale (LS) levels. EFs 2 were treated as anomalies. Although the means obtained were usually based on large datasets, the mean excess levels should be treated with care as they are only rough estimates. This is due to large discrepancies in the literature related to both the geochemical character of the local soils and the species-dependent behavior of the particular elements. Furthermore, translocation factors (TFs) were calculated for *Sl. canadensis*, *S. nigrum*, and *E. cannabinum*, to assess the potential of these plants as hyperaccumulators (McCutcheon and Schnoor, 2003; Wei et al., 2005; Sasmaz et al., 2021).

CORRELATION ANALYSIS

Correlation analysis was performed for further exploration of the chemical data. The normality of distribution was checked using the Shapiro-Wilk test. The Levene test was run to check the homoscedasticity of the dataset. Normality tests displayed a non-normal distribution of the data, while the Levene test pointed out heteroscedasticity of the data. Therefore, the Kendall Rank Correlation Coefficient was used to investigate relationships between the given chemical variables. Prior to these analyses, the data set was normalized by log ratio. All statistical calculations were performed using *R* software.

To avoid incorrect conclusions, the results of Li, Be, Ge, Rb, Y, Zr, Nb, Pd, In, Se, Ce, Hf, Ta, Re, Pt analysis were excluded from the statistical processing because of the small number (n = 4) of observations. Concentration values below detection limits composed <15 % of the whole dataset; therefore, they were included in further processing.

Table 1

Results of bulk ICP analyses of the vegetation samples collected in the waste heaps of the Upper Silesian Coal Basin

Sample	BST-VSc				BST-VRc	BST-VAt	BST-VV1	BST-VV2		RDT-VV	NRS-VV	BST-FSc	Typical / toxic level[2]
Plant part[1]	S	F	R	St	S	S	S	S	R	S	S		
Species	*Solidago canadensis*				*Rumex crispus* L.	*Arctium tomentosum*	*Verbascum* sp.					*Schizophyllum commune*	
Trace elements [ppm]													
B	212	80	46	55	31	30	26	45	21	37	21	8.0	60 / 47
Sc	0.40	0.40	0.60	0.30	0.20	0.40	0.20	0.20	0.20	0.30	0.20	1.1	0.08
V	2.0	<2.0	7.0	<2.0	<2.0	7.0	3.0	4.0	2.0	2.0	<2.0	<2.0	0.52 (7.5)
Cr	2.6	3.3	9.3	2.0	2.6	8.9	4.3	5.2	3.1	3.4	2.9	9.7	1.6 (1920)
Mn	65	56	140	21	47	128	125	254	111	108	62	59	134 (1178)
Co	1.4	0.94	2.6	0.43	0.16	1.1	1.0	0.96	0.57	0.33	0.45	1.1	0.14 (108)
Ni	3.2	2.5	7.0	1.5	4.0	10	2.8	4.5	6.2	19	2.1	5.0	1.1 (434)
Cu	21	19	30	15	17	28	53	**70**	**76**	14	16	28	6.3 (80)
Zn	200	173	290	233	146	**450**	362	**746**	**483**	39	42	280	43 (195)
Ga	<0.10	<0.10	0.50	<0.10	<0.10	0.60	0.30	0.30	0.20	0.40	0.10	0.90	2.2 (125)
As	<0.10	1.2	1.3	<0.10	1.4	**9.0**	1.7	3.8	2.4	0.90	<0.10	1.9	5.8 (72)
Se	**3.2**	**2.1**	**1.9**	**1.2**	0.60	0.50	0.90	0.90	0.80	**1.7**	0.60	0.70	0.24 (8.3)
Sr	54	39	75	43	15	68	48	44	25	21	15	31	48
Mo	0.50	0.35	0.73	0.33	**5.4**	**2.9**	0.61	**1.3**	**1.1**	0.66	0.30	0.49	0.62 (488)
Ag	0.15	0.15	0.15	0.04	0.15	**0.31**	**0.24**	**0.33**	**0.38**	**1.1**	**0.24**	**0.21**	0.50 (0.18)
Cd	**4.4**	**5.0**	**8.3**	**4.8**	0.78	2.5	2.4	**5.7**	**8.3**	0.25	0.10	**6.0**	0.11 (12)
Sb	0.21	0.56	**1.6**	0.54	0.17	**0.91**	**1.3**	**2.2**	**1.9**	0.37	0.10	**1.3**	0.16 (<0.20)
Te	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	<0.02	<0.02	0.03	0.03	0.07 (2.0)
Ba	9.4	7.4	30	8.1	38	641	20	33	23	8.9	12	21	121 (500)
La	0.18	0.16	1.3	0.01	0.18	2.3	0.73	0.82	0.37	0.78	0.25	2.1	0.13
W	<0.10	<0.10	<0.10	<0.10	<0.10	0.30	0.10	0.30	0.20	<0.10	<0.10	0.20	2? (36)
Au	0.002	0.003	0.001	0.001	**0.004**	**0.007**	0.001	**0.003**	**0.003**	**0.003**	**0.003**	0.002	0.004
Hg	**0.24**	**0.16**	0.06	0.02	0.03	0.06	0.18	0.10	0.06	0.08	0.04	0.08	0.002 (20)
Tl	0.06	0.06	0.19	0.12	**1.7**	**1.1**	0.34	**2.4**	**1.1**	0.07	<0.20	0.12	0.04 (0.45)
Pb	16	22	53	5.5	14	**122**	**77**	**178**	**132**	**428**	2.6	**55**	1.8 (5.5)
Bi	<0.02	<0.02	0.07	<0.02	<0.02	0.22	0.16	<0.02	<0.02	0.40	0.09	0.19	<0.02
Th	0.10	0.10	0.50	0.20	0.20	0.70	<0.10	0.30	0.20	0.30	<0.10	1.1	0.20 (35)
U	0.05	0.04	0.33	<0.01	<0.01	0.16	0.13	0.07	0.03	0.12	0.03	0.36	2.0
Main elements [wt.%]													
Na	0.019	0.022	0.02	0.039	**0.769**	0.115	0.05	0.055	0.027	0.049	0.04	0.018	3.28
Mg	0.487	0.395	0.28	0.197	**0.519**	0.308	0.40	0.504	0.308	0.222	0.20	0.189	0.40
Al	0.01	0.02	0.12	<0.01	0.02	0.19	0.06	0.08	0.04	0.06	0.03	0.17	0.007
P	0.117	0.181	0.053	0.083	**0.858**	0.349	0.24	0.236	0.292	0.165	0.24	0.31	0.08
S	0.82	0.69	0.23	0.30	0.56	0.40	0.59	0.24	0.16	0.19	0.22	0.40	0.21 (0.35)
K	0.96	1.61	0.79	1.65	**5.93**	**4.78**	1.3	**2.35**	1.46	**2.83**	1.2	0.33	0.90 (2.9)
Ca	1.63	1.08	1.73	0.67	0.44	1.46	1.3	1.46	0.44	0.65	0.83	0.63	1.90
Ti	0.0009	0.001	0.004	0.0004	0.002	0.007	0.002	0.003	0.001	0.002	0.001	0.005	0.001
Fe	0.074	0.075	0.326	0.018	0.056	0.374	0.31	0.216	0.094	0.106	0.05	0.432	0.02

Tab. 1 cont.

Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	S	St	S	St	R	S	R	F	St
Species	*Populus* L.		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Trace elements [ppm]														
B	7.0	28	13	14	36	43	40	34	32	20	99	12	53	17
Sc	0.20	0.20	0.20	0.20	0.60	0.80	0.20	0.30	0.20	0.10	0.30	0.30	0.30	<0.10
V	2.0	<2.0	<2.0	<2.0	5.0	5.0	<2.0	2.0	<2.0	<2.0	3.0	3.0	5.0	<2.0
Cr	3.4	2.8	1.9	3.6	4.6	5.6	2.5	3.0	2.4	3.0	4.0	4.5	8.4	1.7
Mn	6.0	27	15	50	147	715	163	663	326	172	210	216	129	27
Co	0.14	0.46	0.10	0.33	3.1	3.2	0.87	0.90	0.62	0.76	0.88	1.3	0.73	0.10
Ni	2.1	3.4	0.90	3.6	7.6	5.7	1.8	3.5	2.2	3.2	3.4	5.6	6.0	0.70
Cu	6.2	14	5.1	16	16	24	9.4	25	15	19	17	24	22	6.7
Zn	72	411	233	508	**1060**	**3150**	**976**	235	230	235	**1760**	**2640**	**1200**	305
Ga	4.9	4.6	<0.10	<0.10	0.60	0.50	0.10	0.20	<0.10	<0.10	0.30	0.50	0.30	<0.10
As	<0.10	0.30	<0.10	0.10	0.30	**23**	6.4	0.90	0.50	1.0	**81**	**140**	**58**	**9.7**
Se	0.30	0.80	<0.10	0.50	**3.8**	**1.6**	**1.3**	0.50	0.40	0.30	0.70	0.70	0.50	0.30
Sr	23	129	19	41	129	93	71	46	51	29	48	15	25	17
Mo	0.08	0.37	0.28	0.36	**1.4**	0.96	0.32	**1.6**	0.76	0.83	0.82	0.79	0.76	**1.0**
Ag	0.10	**0.26**	0.09	**0.34**	0.13	**1.0**	**0.30**	0.12	0.07	0.08	**2.6**	**4.0**	**1.2**	**0.31**
Cd	1.1	**6.3**	0.80	2.4	**29**	**31**	**12**	**8.7**	**5.6**	**4.4**	**36**	**18**	**15**	**24**
Sb	**1.7**	**1.5**	0.39	**2.1**	**12**	0.51	**1.5**	0.32	**1.4**	**1.4**	**1.8**	**2.9**	**1.9**	**1.1**
Te	<0.02	<0.02	<0.02	0.04	**0.12**	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	3.2	17	17	50	66	19	8.4	44	51	27	36	58	27	5.3
La	0.03	0.14	<0.01	0.20	1.2	1.2	0.24	0.42	0.14	0.09	0.48	0.66	0.33	0.01
W	<0.10	<0.10	<0.10	0.10	0.30	0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Au	0.0007	**0.004**	**0.001**	0.0005	0.0008	**0.01**	**0.002**	**0.002**	0.0002	0.0002	0.0009	0.0005	0.0004	0.0003
Hg	0.01	0.03	0.01	0.12	**0.44**	0.05	0.009	0.03	0.007	0.004	0.04	0.01	0.02	0.007
Tl	<0.20	0.10	0.07	0.17	**0.49**	**8.2**	**16**	0.37	0.41	**0.49**	0.16	0.41	0.15	0.06
Pb	1.7	32	3.7	**43**	**100**	**428**	**197**	7.5	6.5	7.9	**467**	**884**	**398**	**71**
Bi	<0.02	0.02	<0.02	0.10	**0.68**	0.13	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	<0.02	<0.02
Th	<0.10	0.20	<0.10	<0.10	0.40	1.2	0.10	0.20	<0.10	0.10	0.10	0.20	0.10	0.10
U	<0.01	<0.01	<0.01	0.03	**0.79**	0.35	0.10	0.03	0.01	<0.01	0.09	0.12	0.05	<0.01
Main elements [wt.%]														
Na	0.02	0.014	0.003	0.01	0.01	0.023	0.031	0.041	0.033	0.031	0.02	0.004	0.011	0.009
Mg	0.048	0.168	0.04	0.10	0.17	**1.72**	**0.82**	0.346	0.25	0.181	0.24	0.164	0.168	0.071
Al	0.12	0.01	<0.01	0.02	0.16	0.13	0.02	0.05	0.01	0.01	0.06	0.06	0.03	1.3
P	0.31	0.052	0.03	0.07	0.04	0.112	0.097	0.428	0.262	0.198	0.11	0.093	0.171	0.043
S	<0.05	0.21	0.17	0.21	**1.30**	**4.39**	**2.79**	0.67	0.38	0.37	**2.48**	0.35	0.40	0.26
K	0.06	0.11	0.05	0.19	0.04	**4.01**	**7.27**	**4.35**	**4.88**	**5.40**	1.58	0.99	0.92	1.3
Ca	0.39	**3.19**	0.35	0.88	**5.40**	**6.46**	**2.54**	1.50	1.01	0.46	3.57	0.67	1.40	0.90
Ti	0.0002	0.0005	0.0001	0.0007	0.003	0.003	0.0007	0.002	0.001	0.0007	0.003	0.003	0.002	0.0002
Fe	0.01	0.066	0.01	0.07	**0.22**	**0.959**	0.215	0.089	0.035	0.024	0.559	0.908	0.356	0.056

[1] – V – plant vegetation, F in the sample name – fungi, W – wood, Bn – normal bark, Bb – burnt bark, S – shoots, St – stem, R – roots, F – flowers; detailed samples description is available in the Appendix 1; [2] – geometric means calculated based on Welch et al. (1973), Chaudhry et al. (1977, 1997), Cowgill (1988), Kabata-Pendias and Pendias (1989), Patra and Sharma (2000), Mengel and Kirkby (2001), Shtangeeva and Ayrault (2004), Shtangeeva et al. (2004), Tyler (2004), Wierzbicka et al. (2004), Shtangeeva (2005, 2008), Broadley et al. (2007), Chen et al. (2009), Menzies (2009), Tschan et al. (2009), Yruela (2009), Millaleo et al. (2010), Ahmad and Ashraf (2011), Bergqvist (2011), Wei et al. (2011), Adamakis et al. (2012), Lamb et al. (2013), Pé-Leve Santos et al. (2013), Lutgen (2015), Farooq et al. (2016), Karbowska (2016), Koca et al. (2016), Lange et al. (2016), Noubissie et al. (2016), Li et al. (2017), Lyu et al. (2017), Wiche et al. (2017), Vural (2017), Abbas et al. (2018), Gupta and Walter (2018), Ismael et al. (2018), Jensen et al. (2018), Ma et al. (2018), Tang et al. (2018), IPNI (2019), Brdar-Jokanović (2020), Jasinskas et al. (2020), Ray et al. (2020) ; normal content with excess (potentially toxic) content in parentheses; concentrations highly elevated as compared to both the typical/toxic levels and other samples studied are in bold; the excess levels are approximate – see the main text for details

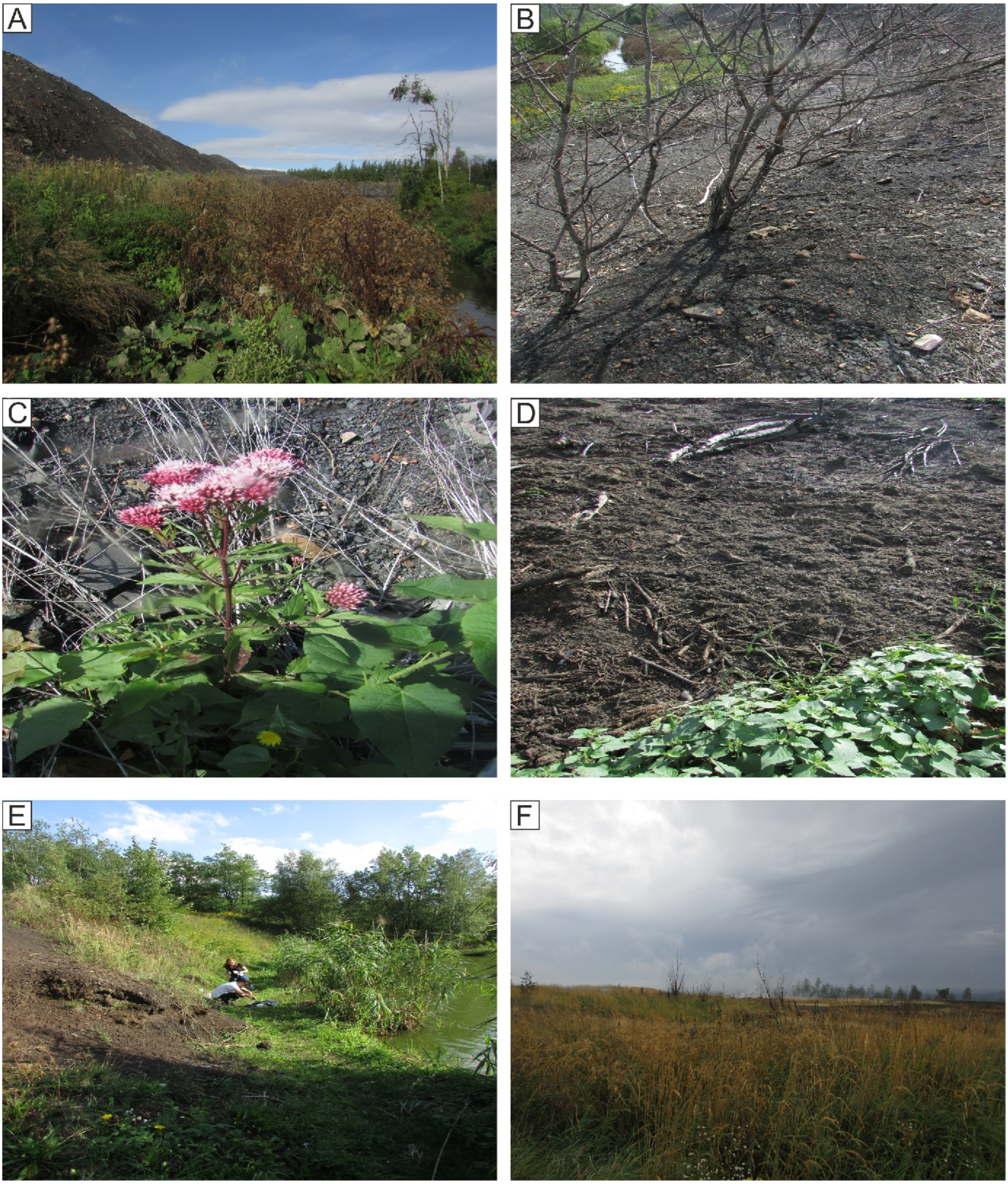

Fig. 2. Field images of the habitats and plant specimens analysed

A – riverside habitat with burning slope in the background; **B** – dead *Populus* trees on the burning slope; **C** – *Eupatorium cannabinum* (pink flowers) and *Tussilago farfara* in the smelting-waste zone (yellow flower), A–C – Bytom-Stroszek heap; **D** – Zabrze-Biskupice (Ruda heap) habitat, dominated by *Solanum nigra*, on the burning slope; **E** – Świętochłowice-Chropaczów smelting heap (Kopyto) lakeside habitat; **F** – Rydułtowy (Szarlota) plateau habitat with prominent *Verbascum* specimens in the middle

RESULTS

CONCENTRATION OF ELEMENTS IN THE VEGETATION

The ICP analysis results for both trace (and minor) and main elements are collected in Table 1. The CHN analysis results are given in Appendix 2. The element concentrations in the tissues of the vegetation samples studied vary with the type of element and plant species. The elements analysed, therefore, are characterized by high intra-sample variability. Calculated coefficients of variation (CVs) show that most of the elements determined were characterized by strong (45–100%; B, Sc, Cr, Co, Ni, Cu, Se, Sr, P, K, Ca, and Ti) or very strong (>100%; Mo, Ag, Cd, Sb, Ba, La, Au, Hg, Tl, Pb, Th, U, Na, Mg, Al, Ga, As, Mn, Fe, and Zn; Appendix 3) dispersion within the data set. Many of these elements reach high contents in the plant tissues, that exceed toxic levels (Table 1). For instance, vegetation samples from the Bytom heap accumulated a significant amount of Zn, which in most cases exceeds the toxic level of 195 ppm. Extreme values of Zn were noted in parts of *T. farfara* (up to 3150 ppm) and *E. cannabinum* (up to 2640 ppm). A high content of zinc was also noted in the burnt bark of *B. pendula* (up to 1060 ppm) and in *Verbascum* sp. (up to 746 ppm; Table 1), and in the tissues of *Verbascum* sp. from another heap (Rydułtowy). In most of the samples, enrichment to toxic levels was also observed for Sb and Pb. The concentration of Pb in several samples has extreme values ranging from 428 (*Verbascum* sp., *T. farfara*) to 884 ppm (*E. cannabinum*). Harmful contents of As and Ba were found, respectively, for *E. cannabinum* (up to 140 ppm in the roots, Świętochłowice heap), and *A. tomentosum* (641 ppm, Bytom heap). In addition, toxic concentrations of Cd were found in some samples (Table 1). Although the toxic levels of the elements studied were not frequently exceeded, the concentrations were often higher than those typically reported for plants in general. For instance, in most of the samples the contents of Sc, Cr, Co, Ni, Zn, Se Cd, Sb, Te, La, Hg, Al, P, and Fe were above the normal plant values.

Contents of the main biophilic elements such as C and N varied relatively strongly (Appendix 2). Carbon ranged from 39.85 wt.% in the roots of *Verbascum* sp. to 51.83 wt.% in the *Populus* L. bark. In the case of nitrogen, a high content (>6 wt.%) was found in the shoots of *R. crispus* L. and *S. nigrum,* while *Sl. canadensis* and all the tissue types of the *Verbascum* sp. and *E. cannabinum* studied were poor in N. Hydrogen content ranged from 2.46 wt.% (*T. farfara* shoots*)* to 5.78 wt.% (*Sl. canadensis* shoots). Results of the reconnaissance additional-element analyses are given in Appendix 4. These additional analyses were run for 3 samples of *B. pendula* and 1 sample of *Verbascum* sp. shoots from the Bytom heap. A wide range of values was noted for Rb (1.6–14 ppm) and Li (0.04–0.93 ppm). The minimum and maximum contents of Rb and Li, as well G, Rb, Y, Cs, and Ce, concern *B. pendula* wood and *Verbascum* sp., respectively.

ENRICHMENT FACTORS

EFs based on the calculated M_g and considering CC, LC, and LS levels are listed in Appendix 5. Corresponding factors relating our results to PN, PE, and PH levels are shown in Appendix 6.

In total, 142 anomalous EFs were found. Three elements showed extreme enrichment, based on EFs calculated by referring to PH levels (EF_{PH}). These are zinc, mercury, and lead. A single uranium anomaly of this kind was also found. Meaningful EF_{PE} is mainly found for Zn, Pb, Ag, S, Tl and Cd. Scandium, V, Co, Ni, Cu, Zn, As, Se, Cd, Sb, Hg and Tl (all samples), Pb, Al, P, S, Bi, Fe, Ti, K, and more rarely N, Mo, La, Th, K, Ag, Sr, B, Au, Te, Ba and Mg show anomalous EFs, i.e., 2, compared to normal plant levels (EF_{PN}). Maximum and average (M_g) EF_{PH} for Zn, Hg, and Pb are as follows: 13 and 3.7 (n = 12); 2.9 and 4 (n = 4); and 2.3 and 4 (n = 5). The corresponding data for EF_{PE} is: 19 and 161 for Pb (n = 18); 4.4 and 13 for Zn (n = 12); 4.1 and 22 for Ag (n = 11); 6.1 and 38 for Tl (n = 6); 2.4 and 3 and for Cd (n = 5). The highest EF_{PN} for Hg, Tl, Cd, Pb, Zn and Ag are 491, 220, 400, 327, 220, 73, and 22, respectively. Enrichment depicted by EF_{PN} is also shown in the case of V (M_g = 5.2, n = 26), Sc (M_g = 4.2, n = 24), Ni (M_g = 3.8, n = 23), Cu (M_g = 3.6, n = 22), Se (M_g = 4, n = 22), Fe (M_g = 8.3, n = 22), Al (M_g = 9.7, n = 20), Co (M_g = 6.1, n = 17), La (M_g = 5, n = 16), S (M_g = 3.7, n = 15), Sb (M_g = 9, n = 14), P (M_g = 3.3, n = 14), Ti (M_g = 2.9, n = 13), K (M_g = 3.7, n = 12) and Bi (M_g = 9.1, n = 9).

The burnt bark of *B. pendula* from Bytom is the most geochemically anomalous material studied. Two anomalies related to PH, 3 for PE, 12 for PN, 5 for LS, and 5 for LC (26 in total) were found in the specimen. It shows most of the maximum levels observed – for Bi, Ca, Co, Hg, Se, Sr, Sb, Te, U and W – while being second for the largest number of anomalous EFs. When compared to unburnt, normal bark, the EFs are 26 for U, 12 for Cd, 9 for Co, 8 for Se and Al, 7 for Bi, 6 for Ga, La and Sb, 4 for Mo and Th, 3 for B, Sc, V, Mn, As, Sr, Te, Hg and Tl, and 2 for Ni, Zn, Au and Pb. This enrichment clearly reflects the local mineralogy/geochemistry (Cd-Sb-Mo enrichment). Compared to the BpBb sample, the normal bark only shows 2 anomalies (PE basis), with elevated Ag and Pb.

T. farfara from Bytom's heap smelter waste area showed the record number of EFs anomalies, 30 in total, with 2 for PH, 5 for PE, 12 for PN, 5 for LS, and 6 for LC anomalies. Its shoots show maxima for Zn, Pb, Cd, but also elements not necessarily derived from this type of waste: Co, Au, Th, Mn, S, Fe, Mg and Ca. It also has clearly elevated Ag, Tl, Sc and V. The stem (12 anomalies: 5 for PE, 3 for PN, 2 for LS, and 2 for LC) has the highest-observed levels of Tl and K, and elevated Zn, Ag, Pb and S.

A. tomentosum (14 anomalies: 2 for PE, 6 for PN, 4 for LS, and 1 for CC) collected at a riverbank, within the essentially coal-waste-dominant part, has its shoots richest in Ba, La, Ti and N, and has elevated Ag, Tl, V, Ni, W, Co, Na, P and N. *R. crispus* L. from the same habitat (12 anomalies: 3 for PE, 4 for PN, 3 for LS, and 2 for LC) is the specimen richest in Mo, Na, K, and P, and has elevated Tl, Pb, S, and N. The shoots of the heap-top *Sl. canadensis* (10 anomalies: 1 for PH, 3 for PE, 4 for PN, 1 for LS, and 1 for LC) show very high B and Hg, and elevated Pb, Se, S and Co. Roots (6 anomalies) have the highest V levels, elevated Co, Ni, Pb and, to a lesser extent, also Cu. A single boron anomaly was found in its flowers. The bark of *Populus* L. (4 anomalies) from the coal-fire zone in Bytom is richest in Sr and has elevated Pb. The *Sc. commune* fungus (6 anomalies) growing on it shows the highest Sc levels and anomalous La, Th, Pb, W and Co.

The plants from the heaps in Bytom and Świętochłowice showed the highest contents of many elements. The shoots of *E. cannabinum* (14 anomalies: 2 for PH, 4 for PE, 4 for PN) show maxima for B, Cd, As, and have anomalous Pb, Zn, Ca, Ag and S. Roots of this plant (17 anomalies: 2 for PH, 3 for PE, 6 for PN, 3 for LS, and 3 for LC) show maxima for Pb, As, Ag, Fe, and have elevated Co, the latter suggesting a possible source from the nearby coal-waste heap. Its stem (3 anomalies) has the highest observed Al content. Six anomalies concern its flowers, with very high As, and elevated Zn, Cd, Pb and V.

The Rydułtowy *Verbascum* sp. shoots (5 anomalies) have the highest Ni, and elevated Ag, Pb and Bi, while the specimen from Bytom riverside (VV2; 8 anomalies) has the highest Cu (also in its roots). The latter sample is also enriched in Ag, Tl, Pb, Zn and W. The VV1 specimen from the heap top (5 anomalies) has elevated W, Cu, Pb, and S. The highest Mn and elevated S and N - possibly related to native sulfur, S_8, and salammoniac, NH_4Cl, observed in the nearby fumaroles – were found in the shoots of *S. nigrum* from Zabrze (5 anomalies).

The most frequent anomalies (*n* >100) concern zinc. Its CAI is quite low at 3.3. Zn enrichment is expressed even when juxtaposing our measurements with PH (12 records, M_g = 2, max = 13). Almost 100 anomalies were also found for cadmium, >20 of which are related to PN, CC, LC, and LS. Furthermore, >50 anomalies characterize, in decreasing order, Pb, Sn, B, Tl, Se, Ag, and Au. A significant number of anomalies (*n* >10) were also observed for Hg, As, V, Mo, Cu, Sc, Co, Ni, and Sr. Anomalous major element levels (especially P, S, and K) concern substrate-to-plant vegetation transfer.

ROOT/SHOOT RATIOS AND TRANSLOCATION FACTORS

The distribution of element content varies significantly between different parts of the following plant species: *Sl. canadensis, S. nigrum, Verbascum* sp.*,* and *E. cannabinum*. The highest values of most components in *Verbascum* sp. and *S. nigrum* were concentrated in shoots, which is reflected in their translocation factor TF >1. Eleven and thirteen elements displayed maximum concentrations in the shoots of *Sl. canadensis* and *E. cannabinum,* respectively. The lowest number of TF >1 concerns *Sl. canadensis*. The translocation factors of B and Hg are above 1 in all plant species (Table 2). Extremely high values of translocation factor were noted for Au (TF = 10) in S. *nigrum* and B (TF = 8.3) in *E. cannabinum.*

STATISTICAL ANALYSIS

Relationships between the measured physicochemical parameters of plant and fungi samples are shown by the correlation coefficients. The Kendall's tau coefficients (Fig. 3) point to numerous correlations between the elements studied, with statistical significance at the *p* <0.05 level. A strong positive correlation (>0.8) occurs between La and Ti. The correlation analysis also reveals a high positive correlation (>0.6) between U and Sc, Cr, Co, La, Fe and Ti; La with Th, Al, Fe, Ni and Cr; Ti and Cr, Ni and Fe; Pb and As, Ag and Fe; Sr and Ca; and in the Ni-Th system. Moreover, many positive correlations with moderate dependence (in the 0.4–0.6 range) are found. Most of the correlations with between 0.4–0.6 were found for several groups of elements, i.e., Cr with Sc, Co, Ni, Cu, Ga, Hg, Th, Al and Fe; Co and Ni, Cu, Se, Sr, La, Na, Ca, Ti and Fe; Ti with Mn, Sc, Ga, As, Pb, Mo, Ba, Th and Al; Zn and As, Ag, Cd, Sb, Pb, Ca, Fe. Negative correlations were found between C-Na, C-Mn, and C-K. Among the toxic elements positive correlations also characterize the following systems: Ni with Pb, Mo, U and Pb; As with Al, Cd and Ag; and Hg with Sc.

DISCUSSION

RELATIONSHIP BETWEEN THE ELEMENTS STUDIED

The strongest positive correlation found between Ti and La results from their elevated accumulation usually within the same vegetation (sub)samples (roots of *Solidago canadensis*, and in *Schizophyllum commune*). Both La and Ti may show a beneficial influence on plant growth. Low concentrations of La may result in an enhanced photosynthetic rate, root growth, and nutrient uptake (de Oliveira et al., 2015). Titanium, absorbed via roots and shoots, plays a similar role (Lyu et al., 2017). It was shown that a low Ti amount may have a similar beneficial effect to La. According to the study of Lyu et al. (2017), optimal concentrations of La and Ti are up to 1.4 ppm and 50 ppm, respectively – levels similar to these reported by us, of 1–2.3 and 50 ppm.

Recently, it was proposed that the positive role of Ti results mainly from its interactions with other nutrients, especially Fe. However, the link between Ti and Fe may be synergistic and antagonistic. The relationship between Ti and Fe was also revealed herein by Kendall's correlation analysis. As already noted, there is a confirmed dependence between these elements. This may be demonstrated, for instance by Ti supporting Fe uptake and utilization. In the case of elevated Fe, the role of Ti is variable and it may actually be phytotoxic (Lyu et al., 2017). Concentrations of Fe reported within this study were mostly above the typical level in plants (>0.02 ppm) and the highest values positively correlate with Ti.

Apart from those elements, several low-level heavy metals are beneficial for plants, too. This group of metallic nutrients encompasses Cr, Cu, Co, Mn, Mo, Mg, Ni, Se and Zn (Alloway, 2013). Two metals from this group – Cr and Ni – were found to be highly positively correlated with Ti within our dataset. Chromium and nickel also actively participate in oxidation-reduction reactions and are included in various cellular enzymes (Emamverdian et al., 2015). These elements, therefore, may positively influence plant development. This also seems to be true for our specimens, especially since their reported concentrations exceed the PN levels, while still being below the toxic threshold. The Ti correlation with Fe, and also with La, Cr, and Ni, may suggest the existence of other element pairs that are in an analogous relation. This assumption, however, is far-reaching and should definitely be tested first. More likely, these above-mentioned correlations with Ti are related to local anomalies in the soils, as demonstrated by (1) gas exhalations and newly formed mineral contents of Ni, Fe and Ti, and (2) the ability of some plant species to enable selective uptake and accumulation. This explanation may be also applied to the remaining groups of correlated elements. In the case of the alkaline metals Sr and Ca, the correlation may also result from their similar geochemical behaviour.

The observed positive correlation of actinides (U and Th) with REE (La and Sc) may arise from two causes. Firstly, these elements have similar ionic radii. As such, they often substitute each other in mineral structures (diadochy). However, due to the correlation being positive, it is rather a demonstration of parallel adsorption by plant tissues that is reminiscent of the behavior of these elements in the lithosphere: La, Sc and Th (part of the REEs) often coexist with U. All these elements show lithophile behaviour, being co-deposited as oxides, phosphates, carbonates, and – more rarely – silicates. Although these elements are not essential for plants, they may be adsorbed and accumulated in the course of soil-to-vegetation transfer not only governed by active transport but also by passive processes (Findenegg and Broda, 1965). The availability of these elements to the local vegetation may also be related to an observation by Kruszewski et al. (2021), who studied the geochemistry of some Upper Silesian BCWH soils. They found that Th, La, Sc, (the high field strength elements, of HFSE), but also Al, K, and some other elements were correlated with S and N. Aluminium and potassium, together with ammonium-contained nitrogen, are major components of usually water-soluble sulfate minerals deposited in BCWHs due to both exhalative

Table 2

Translocation factor (shoot-root quotient) of the studied elements calculated for *Solidago canadensis*, *Verbascum* sp., *Solanum nigrum* and *Eupatorium cannabinum*

Elements	Plant species			
	Solidago canadensis	*Verbascum* sp.	*Solanum nigrum*	*Eupatorium cannabinum*
C	1.09	1.11	1.10	1.01
H	1.25	1.03	1.31	0.93
S	2.65	0.13	**1.46**	8.25
B	4.61	2.14	1.70	8.25
Sc	0.67	1.00	**3.00**	1.00
V	0.29	**2.00**	1.00	1.00
Cr	0.28	**1.68**	1.00	0.89
Mn	0.46	**2.29**	3.85	0.97
Co	0.54	**1.68**	1.18	0.68
Ni	0.46	0.73	**1.09**	0.61
Cu	0.70	0.92	**1.32**	0.71
Zn	0.69	**1.54**	1.00	0.67
Ga	0.20	**1.50**	2.00	0.60
As	0.08	**1.58**	0.90	0.58
Se	1.68	1.13	1.67	1.00
Sr	0.72	**1.76**	1.59	3.20
Mo	0.68	**1.18**	1.93	1.04
Ag	1.00	0.87	**1.50**	0.65
Cd	0.53	0.69	**1.98**	2.00
Sb	0.13	**1.16**	0.23	0.62
Te	1.00	1.00	1.00	1.00
Ba	0.31	**1.43**	1.63	0.62
La	0.14	**2.22**	4.67	0.87
W	1.00	**1.50**	1.00	1.00
Au	2.00	1.00	**10.00**	1.80
Hg	4.00	1.67	7.50	4.00
Tl	0.32	**2.18**	0.76	0.39
Pb	0.30	**1.35**	0.95	0.53
Bi	0.29	1.00	1.00	1.00
Th	0.20	**1.50**	2.00	0.50
U	0.15	**2.33**	3.00	0.75
Na	0.95	**2.04**	1.32	5.00
Mg	1.74	1.64	1.91	1.46
Al	0.08	**2.00**	5.00	1.00
P	2.21	0.81	**2.16**	1.18
S	3.57	1.50	1.81	7.09
K	1.22	1.61	0.81	**1.60**
Ca	0.94	**3.32**	3.26	5.33
Ti	0.23	**3.00**	2.86	1.00
Fe	0.23	**2.30**	3.71	0.62

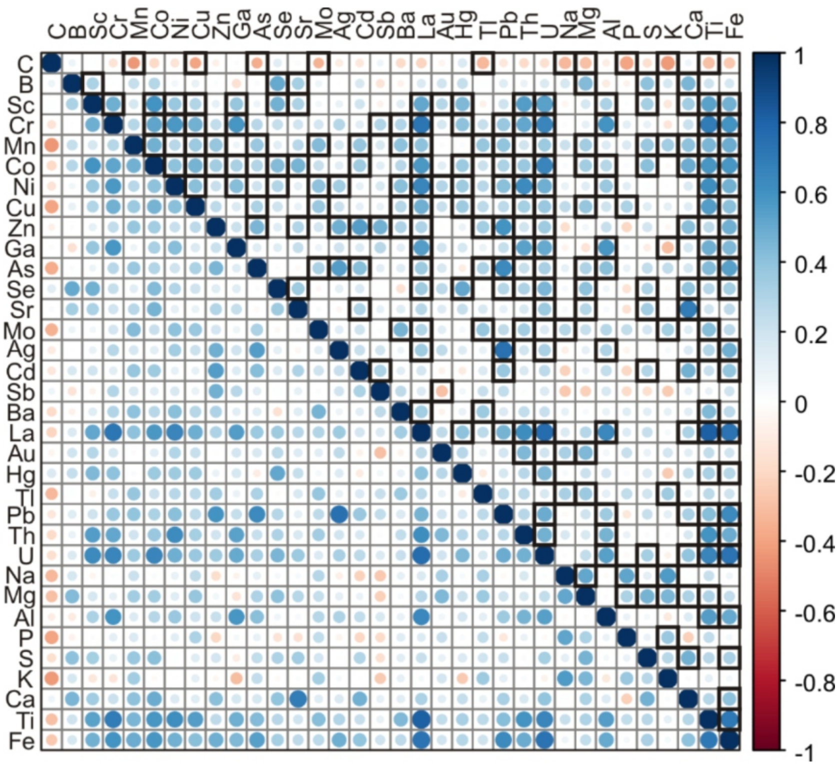

Fig. 3. Results of Kendall's tau correlation analysis

Correlations with *p* values <0.05 given in bold

and supergene processes. This suggests the occurrence of water-soluble REE (and possibly also U, e.g., due to its enrichment within moderately soluble gypsum, $CaSO_4 \cdot 2H_2O$) species, possibly sulfates and/or nitrates, in the BCWHs.

ANOMALOUS CONCENTRATION OF ELEMENTS AS A POTENTIAL ENVIRONMENTAL RISK

The calculated enrichment factors for the plant samples studied display a significant level of pollution severity. Enormous concentrations of several elements indicate their availability to the local vegetation and the possibility of their accumulation at significant levels. This, in turn, allows further transport within local biocenoses and constitutes a significant environmental issue.

Elevated concentration and enrichment factors in relation to both potentially toxic and hyperaccumulator plant contents were found for Zn, Hg and Pb. The origin of these anomalies is related to the type of the wastes and original (i.e., protolith) concentrations exceeding normal crustal contents. These findings show that toxic elements are constantly being released into the local environment, despite these being old heaps (>60–80 yr). This is especially dangerous because the toxicity of these elements has deleterious effects on humans, animals, and also plants. Zinc, as long as it is in its optimal range, plays an important role in plant metabolic processes. However, its excess is noxious for plants and causes deterioration of photosynthesis and reduction of respiratory rate and plant growth (Kaur and Garg, 2021). Despite its toxic threshold level being exceeded in most studied samples, the local vegetation was able to successfully colonize the study sites.

Mercury, in contrast to zinc, is redundant for plants and its high level is phytotoxic. The toxic effect of Hg is manifested, for instance, in reducing the ability of plants to take up water, loss of crucial elements (K, Ca), and accumulation of Fe (Pastricha et al., 2021). However, all the herein-reported concentrations of Hg were above the typical values noted in plants. The highest values were reported in the shoots, which contradicts the belief that this metal is mostly accumulated by roots. Li et al. (2018) however, stressed the possibility of mercury accumulation in shoots via translocation and absorption of its vapor form. This is especially interesting in the context of the heaps studied, where gas exhalations take place due to coal combustion. While the calculated TF displayed the possibility to accumulate Hg by translocation of its soluble form, the extent to which plants may absorb Hg^0 vapors in such an environment is notable. The occurrence of metallic mercury vapors within the coal fire gases of a BCWH within the USCB (in the Rybnik Coal Area) was confirmed by Kruszewski et al. (2018) and is consistent with observations of emissive Hg flux into soils over the Wuda coalfield fires in China (Li et al., 2018). Addressing this issue could have a significant role in the phytoremediation of the BCWHs. High Hg levels were not only noted in the burnt bark of *B. pendula* (where numerous other elements were found to be extremely enriched), but also in *Sl. canadensis* from the same heap. This suggests the presence of a diffuse, but rather evident and constant, source of Hg in the environment, likely connected with coal-fire-gas emanations within local fumaroles. Indeed, most of the exhalative mineral samples from the USCB BCWHs studied had >50 ppm Hg, and some gaseous Hg species other than Hg^0, such as $(HgH)_2$ or SiH_3HgH, were initially detected by *in situ* FTIR gas spectrometry (Kruszewski et al., 2018). Recent studies by Nádudvari et al. (2022) confirmed the presence of high concentrations of HgS and MeHg in the Bytom heap, which may represent a source of Hg-enrichment in plant tissues. This poses a serious problem for the local environment and society. Severe environmental risks related to wastes accumulated in this heap have also been stressed by Nádudvari et al. (2022).

Along with the highest contents of mercury, high values of Zn, Pb, Bi, U and Tl were also observed. Special attention must be paid to the latter element, Tl, due to its extreme toxicity and high contents noted. Furthermore, information about Tl contents is especially valuable due to the paucity of such data. As in the case of Hg, Tl does not show any role in the metabolic processes in plants. Its toxicity to plants is demonstrated, e.g., by negative influence on photosynthesis and triggering oxidative stress (Mazur et al., 2016). The reported Tl levels are several times higher than the toxic levels in plants but much lower than the lethal value of Tl for humans (12–15 ppm; Ferguson, 2012). However, the environmental risk results not only from the toxicity of Tl but also because it is a cumulative poison that can be absorbed through the skin and respiratory system. Environmental exposure of people at low levels causes sleep disorders, headaches, muscle pains, and tiredness. Such symptoms were observed in a population from a contaminated area in Germany (Kazantzis, 2000). In other places, e.g., Olkusz PbZn(Ag) mining area, close to the USCB, high contents of Tl were reported in some mammal and plant tissues. This means the problem has a regional significance (Dmowski, 2000; Wierzbicka et al., 2004). Elevated concentrations of thallium were reported in three plant species from different parts of the Bytom BCWH but were much lower than those reported by Wierzbicka et al. (2004). The size of these anomalies is related to the type of waste locally deposited, e.g., PbZn(CdAgTl)-rich slags. Noteworthy, a high concentration of Tl was reported in plants collected on the riverside of the heap which means that there is a risk not only related with local gas emissions, but also via leaching out of the heap area due to its contact with surface waters.

DISTRIBUTION OF ELEMENTS IN THE PLANTS AND (HYPER)ACCUMULATION POTENTIAL

The elemental concentrations differ among plant tissues. Ionic forms of elements are mostly absorbed from soil solutions by roots and then complexed by chelating agents and chaperones (proteins). Further, the ions are transported into different organelles where they are transformed, used by metabolic processes, or accumulated (Clemens, 2001; Hall, 2002). Metallic ions may also be included in long-distance transport and transferred to above-ground parts like shoots and flowers (Pend and Gong, 2014).

The distribution of element content varies significantly between different parts of the studied plant species: *Sl. canadensis, S. nigrum, Verbascum* sp., and *E. cannabinum*. The highest values of most components in *S. nigrum* and *Verbascum* sp. are concentrated in the shoots. This displays their potential to be hyperaccumulators of many elements. The opposite situation concerns *Sl. canadensis* and *E. cannabinum,* which have higher concentrations of the most studied elements in their roots.

Until now, many plant species have been described as accumulators that co-occur with some trace elements. Concentrations of inorganic elements in such plants are intermediate and are in the range between the usual concentration and hyperaccumulation (Reeves and Baker, 2000). A unique sink of elements comprises hyperaccumulators that have the ability to absorb large amounts of metals, up to thousands of times greater than the norm (Reeves, 2003) in their aboveground tissues.

As of 2017, 721 hyperaccumulator species were known. Such species may be indicative of mineralization and contamination processes. It is generally accepted that the threshold of hyperaccumulators for most trace elements is 0.1 wt.%. On the other hand, it varies by element, and in the case of Tl, Se and Cd equals 0.01 wt.%, Co and Cu – 0.03 wt.%, Pb, As, and Ni – 0.1 wt.%, Zn – 0.3 wt.%, and Mn – 1 wt.% (Reeves et al., 2018). In our dataset, the quantities detected of these elements did not exceed the thresholds. The exception is *T. farfara* for which 3150 ppm (~0.32 wt.%) of zinc was reported in the shoot samples from Bytom's heap smelter waste (Table 2).

The potential of *T. farfara* to absorb metallic elements has been recently described based on materials from Serbia (Jakovljević et al., 2019). However, these authors could not define *T. farfara* as a (hyper)accumulator of Zn because of the low values (< 500 ppm) recorded. Thus, they doubted its potential in phytoextraction. Hence, the data presented herein provide preliminary evidence for the potential of this species as a hyperaccumulator according to the criterion of Reeves et al. (2018).

Elevated concentrations of Zn, close to the threshold value, were also noted in the roots of *E. cannabinum* (2640 ppm) from the smelter heap in Świętochłowice. However, in the shoots, flowers, and stem of this plant, the content of Zn was much lower and varied between 305 and 1760 ppm, with the minimum in the stem. Such a distribution of metal concentrations in plants may indicate a strategy for their tolerance based on exclusion that is confirmed by a translocation factor (TF) of 0.67 (Boularbah et al., 2006). Despite the extremely high content of Zn in the waste deposits (from 7300 to 171790 ppm), low levels of Zn have been found in the shoots of *E. cannabinum* from other Zn-Pb heaps in Poland (Wójcik et al., 2014). The maximum value recorded in the shoots (276.9 ppm) by these authors was almost 10 times lower than those reported herein. The reason may be related to differences in the available Zn levels in the substrate, its bioavailability, and the share of its mobile fraction (Rieuwerts et al., 1998). The slags from the Świętochłowice heap comprise 0.32 to 47.26 wt.% ZnO (Bril et al., 2008). Plant species growing on substrates with variable metal contents may be either accumulators or excluders. After exceeding the critical content of metals in the substrate, the exclusion mechanism may break down, resulting in unlimited transport (Baker, 1981). However, despite the elevated concentration of Zn in the shoots of the Świętochłowice *E. cannabinum* the related TF suggests that this species is rather an excluder over a wide range of ground-Zn concentrations. To test this, further study is needed.

Plant species' behaviour towards various metals is diverse (Baker, 1981). Thus, the exclusion strategy by particular species with respect to a particular metal does not exclude this species as an accumulator of another element. Our data for *E. cannabinum* suggests consideration of this species as a potential accumulator of various elements. A TF >1 was in this very case recorded for B, Sr, Mo, Cd, Au, and Hg. A particularly high TF (8.25) was recorded for B, which suggests the potential of *E. cannabinum* as a boron hyperaccumulator. A similar conclusion was drawn recently by Sasmaz et al. (2021) who pointed out the usefulness of this plant for environmental decontamination or rehabilitation. On the other hand, boron is known to be an essential plant nutrient (e.g., Nejad and Etassami, 2020). Wang et al. (2015) pointed out a higher B demand for woody plants due to their body size and in relation to their expected deficiency (as compared to herbaceous plants). Interestingly, this may be confirmed by our studies, as the M_g boron content in our woody plant samples (17 ppm) is half as great as in the herbaceous plants.

The *E. cannabinum* studied displays an opposite behaviour in relation to As than in the case of B. The highest content of As was reported in its roots, as reflected by a TF <1. At the same time, the maximum value for *E. cannabinum* was almost twice as high as the toxic level. This, alongside the previous findings, could suggest the potential of *E. cannabinum* for phytostabilization of polluted soils. This finding intersects with the conclusion drawn by González et al. (2019) that the species can tolerate significant levels of As without any symptoms of toxicity. The highest contents were found by them in the roots, which coincides with our findings. They also concluded that As uptake and accumulation in the roots both increase in a basic pH and its concentration in the plant tissues may exceed 3500 ppm. In a remediation strategy, therefore, optimization of pH would assist its efficacity.

Several species of *Verbascum* have been identified as accumulators and hyperaccumulators of different elements. For instance, *Verbascum densiflora* has been recognized as a hyperaccumulator of barium (Kowalska et al., 2012). Data from Turkey shows the great ability of *Verbascum cheiranthifolium* Boiss to accumulate Ag, As, Cd, Cu, Mo, Zn and Pb (Sagiroglu et al., 2006). Those observations are in part consistent with our data. The TFs reported herein for Ag, Cd, and Cu suggest the opposite situation. However, this may be due to species-related differences. The calculated TFs allowed us to infer the great potential of *Verbascum* specimens as an accumulator of many other elements. This taxon was found to accumulate more elements in its shoots than in its roots. These elements, listed in descending order of TF, are U, Fe, Mn, La, Tl, B, V, Sr, Cr, Co, Hg, As, W, Ca, Th, Ba, Sb and Se.

Other plants that could be classified as excluders, based on the TFs in relation to given metals, may be potentially useful in the immobilization of pollutants (phytostabilization; Yoon et al., 2006). Within this study, it was found that *Sl. canadensis* and *E. cannabinum* had the highest contents of most elements in their roots. The TFs of numerous elements calculated for the former were below 1. This plant species has recently attracted the attention of environmental scientists due to its ability to colonize highly contaminated areas. Bielecka and Królak (2019a) found that it may be useful as a phytostabilizer of Zn and Pb, and for phytoextraction of the former. The maximum content of Zn in plant tissues reported by Bielecka and Królak (2019a) was above 2000 ppm while herein the highest reported content in *Sl. canadensis* was much lower (290 ppm). There is, however, another interesting finding for *Sl. canadensis*. The calculated TFs suggest the potential of this species also as phytostabilizer of numerous elements. For instance. TF <1 was also noted for Mn and Cu which are consistent with the findings of Bielecka and Królak (2019b). However, the Cu content found within this study was slightly higher (30 ppm), which alongside TF<1 provides additional evidence that this species could be useful as a Cu phytostabilizer.

Considering both the TF and PE-related anomalies, *E. cannabinum, Verbascum* sp., *Sl. canadensis* and *S. nigrum* may have potential in phytostabilization and phytoextraction. For instance, the content of As, Ag, Pb, and Cd in *E. cannabinum* exceeded the potentially toxic levels while the TFs suggest excluder strategies in relation to the first three elements and accumulation of Cd in the above-ground tissues. The element uptake is also a function of the soil content; thus, further studies should be designed. For plants to be classed as hyperaccumulators, three criteria must be met: (1) abnormal concentrations in any aboveground part of the plant (above the hyperaccumulator threshold), (2) the translocation factor (shoot/root quotient) must be larger than 1, and, (3) a bioconcentration factor (soil/shoot quotient) must also exceed 1. Despite lacking data herein about soil element contents, our analysis points to further research directions in characterizing potential plants-element relationships.

CONCLUSIONS

Post-mining areas include waste heaps that constitute potential sources of major, minor, and trace elements. This study evaluates the extent to which numerous elements, including potentially toxic ones, may be accumulated by specific plant species growing on burning coal- and mixed-waste heaps. The elements studied usually displayed high variability between the samples (CV >100%). Many correlated element pairs and groups are likely associated with their local anomalies in soils and the capacity of some plant species to selectively take up specific elements. The strongest correlation was found between Ti and La which may result from their similar beneficial effect on the plants. In our study, the highest content of these elements were associated with specimens of *Sl. canadensis* and *Sc. commune*.

The most frequent anomalies concerned Zn, Pb, and Hg, and resulted from the type of wastes deposited locally. There was significant accumulation of Hg in the shoots of *Sl. canadensis*, the high concentrations being likely related to absorption of Hg^0 vapors originating within fumaroles. Furthermore, together with the high Hg levels, elevated amounts of Zn, Pb, Bi, U and Tl were found. The high content of Tl, from the presence of the PbZn(CdAgT)l-rich slags, is especially alarming due to its toxicity and cumulative character. The data assembled here indicate the high environmental risks of the wastes of the Bytom heap, which agrees with another, recently published study.

Furthermore, differences in the contents of selected elements between plant organs were detected. This, in turn, allowed us to discuss the strategy of specific plant species in relation to these elements. Two main trends were observed. The highest content of most elements in the roots was observed in *E. cannabinum* and *Sl. canadensis*. The opposite behaviour was found for *Verbascum* sp. and *S. nigrum*. As such, the former species may be potential candidates for phytostabilization of many elements, whereas the latter ones may find use in phytoextraction. On the other hand, the high TF of boron calculated for *E. cannabinum* confirmed its potential as a hyperaccumulator as well.

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APPENDIX 1

Location of the plant sample collection spots and species identifications

Sample	Latitude	Longitude	City	Species	Habitat	Heap waste material	Local waste type
BST-VSc	50^{o} 22" 42'	18^{o} 53" 51'	Bytom	*Solidago canadensis*	heap top	mixed	coal
BST-VV1	50^{o} 22" 42	18^{o} 53" 51'		*Verbascum* sp.	heap top		coal
BST-VV2	50^{o} 22" 43'	18^{o} 53" 54'		*Verbascum* sp.	riverside		coal
BST-VRc	50^{o} 22" 43'	18^{o} 53" 54'		*Rumex crispus* L.	riverside		coal
BST-VAt	50^{o} 22" 43'	18^{o} 53" 54'		*Arctium tormentosum*	riverside		coal
BST-Bp	50^{o} 22" 43'	18^{o} 53" 53'		*Betula pendula*	heap slope, active fire zone		coal
BST-VP	50^{o} 22" 43'	18^{o} 53" 52'		*Populus* L..	as above		coal
BST-FSc	50^{o} 22" 43'	18^{o} 53" 52'		*Schizophyllum commune*	as above, on the bark of BST-VP		coal
BST-VTf	50^{o} 22" 40'	18^{o} 53" 55'		*Tussilago farfara*	internal heap escarpment		smelter
ZBB-VSn	50^{o} 19" 05'	18^{o} 49" 37'	Zabrze	*Solanum nigrum*	heap slope, active fire zone	coal	coal
RDT-VV	50^{o} 03" 43'	18^{o} 26" 30'	Rydułtowy	*Verbascum* sp.	heap top, plateau	coal	coal
SWA-VEc	50^{o} 19" 00'	18^{o} 54" 20'	Świętochłowice	*Eupatorium cannabinum*	pondside	smelter	smelter

BST – abbreviation of the study site name, V – plant vegetation, F – fungi, Sc – shortcut from the species name

APPENDIX 2

Results of the CHN elemental analysis (in wt.%) of the plant samples collected on the waste heaps of the Upper Silesian Coal Basin

Sample	BST-VSc				BST-VRc	BST-VAt	BST-VV1	BST-VV2		RDT-VV	NRS-VV	BST-FSc	Typical levels[3]
Plant part[1]	S	F	R	St	S	S	S	S	R	S	S		
Species[2]	*Solidago canadensis*				*Rumex crispus* L.	*Arctium tomentosum*	*Verbascum* sp.					*Schizophyllum commune*	
C	47.47	47.74	43.37	46.51	41.63	43.45	41.61	44.25	39.85	45.59		40.37	45.06
H	5.78	4.60	4.63	4.74	4.79	4.74	3.53	4.43	4.29	4.19		5.45	4.94
N	3.02	0.01	0.01	bdl[2]	6.25	5.35	0.01	0.01	bdl	0.01		3.61	0.59

Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	S	St	S	St	R	S	R	F	St
Species	*Populus* L.		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
C	49.81	51.83				25.06	45.63	43.03	37.04	39.14	43.58	43.28		44.62
H	4.99	4.72				2.46	5.76	2.46	4.44	3.90	4.59	4.93		4.76
N	bdl	bdl				bdl	2.55	6.49	3.24	0.02	0.01	bdl		bdl

[1] – V – plant vegetation, F in the sample name – fungi, W – wood, Bn – normal bark, Bb – burnt bark, S – shoots, St – stem, R – roots, F – flowers; detailed samples description is available in the Appendix 1; [2] – below the detection limit; [3] – geometric means calculated based on Kabata-Pendias and Pendias (1989), Jasinskas et al. (2000)), Ma et al. (2008), Shtangeeva (2008), Lutgen (2015), Tang et al. (2018), IPNI (2019); normal content with excess (potentially toxic) content in parentheses; the excess levels are approximate – see the main text for details

APPENDIX 3

Coefficient of variation (CV) of 38 elements measured in the plant tissues

Elements	CV [%]	Elements	CV [%]	Elements	CV [%]
Na	260	Zn	120	Co	88
Tl	251	Fe	115	Ti	86
Ba	245	La	112	Se	86
As	236	Mn	112	Ni	81
Al	229	Mo	110	Cu	75
Ga	195	Th	109	Sc	69
S	176	Au	107	Sr	66
Ag	164	Cd	104	Cr	56
N	151	Mg	102	V	54
U	150	B	100	H	17
Pb	142	Ca	96	C	15
Sb	136	K	96		
Hg	131	P	90		

APPENDIX 4

Results of the ICPMS analyses of additional elements in selected plant samples collected on the waste heaps of the Upper Silesian Coal Basin

Sample	BST-VV1-S	BST-Bp-W	BST-Bp-Bn	BST-Bp-Bb
		ppm		
Li	0.93	0.04	0.22	1.5
Be	<0.10	<0.10	<0.10	0.10
Ge	0.09	<0.01	0.04	0.19
Rb	14	1.6	5.8	2.4
Y	0.63	0.01	0.18	1.3
Zr	0.23	0.05	0.35	2.1
Nb	0.12	<0.01	0.07	0.25
Pd	0.05	<0.002	0.05	<0.002
In	<0.02	<0.02	<0.02	<0.02
Sn	0.77	0.63	0.52	0.63
Cs	0.29	0.10	0.17	0.52
Ce	1.9	<0.10	0.50	2.8
Hf	0.004	0.001	0.01	0.07
Ta	0.006	0.007	0.01	0.008
Re	0.002	<0.001	<0.001	<0.001
Pt	<0.001	<0.001	<0.001	<0.001

BST– Bytom heap, Bp – *Betula pendula*, W – wood, S – shoots, Bn – normal bark,
Bb – burnt bark

APPENDIX 5

Enrichment factors of the Upper Silesian samples with respect to Coal Clarkes, local coals and local shale concentrations

Sample	BST-VSc				BST-VRc	BST-VAt	BST-VV1	BST-VV2		RDT-VV	NRS-VV	BST-FSc
Plant part[1]	S	F	R	St	S	S	S	S	R	S	S	
Species	*Solidago canadensis*				*Rumex crispus* L.	*Arctium tomentosum*	*Verbascum* sp.					*Schizophyllum commune*
Trace elements [ppm]												
B	30[2]; 11; 27	11; 4; 10	7; 2; 6	8; 3; 7	4; 2; 4	4; 2; 4	4; –; 3	6; 2; 6	3; –; 3	5; 2; 5	3; –; 3	
Mn			–; 2			–; 2	–; 2	–; 3				
Ni										–; 2		
Cu							–; –; 2	–; 2; 3	–; 2; 3			
Zn	–; 5; 2	–; 4; 2	4; 7; 3	–; 6; 2	–; 3; –	5; 11; 4	4; 9; 3	9; 18; 7	6; 12; 4			3; 7; 3
As						3						
Se	46; 7	30; 4	27; 4	17; 2	9; –	7; –	13; 2	13; 2	11; 2	24; 3	9; –	10
Sr	–; –; 2		–; –; 3			–; –; 2	–; –; 2					
Mo	–; –; 2		–; –; 2		4; 16	2; –; 9	–; –; 2	–; –; 4	–; –; 3	–; –; 2		
Ag	2; –	2; –	2; –		2; –	3; 3	3; 2	4; 3	4; 3	12; 9; 3	3; 2	2; 2
Cd	26; 18; 4	29; 20; 4	49; 33; 7	28; 19; 4	5; 3	15; 10; 2	14; 10; 2	34; 23; 5	49; 33; 7			35; 24; 5
Sb			3; 3; 2			2; 2	3; 3; 2	5; 4; 3	4; 4; 3			3; 3; 2
Te							25				15	15
Ba						–; –; 8						
W						–; –; 2		–; –; 2	–; –; 2			–; –; 2
Au	–; 10; 20	–; 15; 30	–; 5; 10	–; 5; 10	–; 20; 40	–; 35; 70	–; 5; 10	–; 15; 30	–; 15; 30	–; 15; 30	–; 15; 30	–; 10; 20
Hg	–; 3	–; 2					–; 2					
Tl			–; 3	–; 2	2; 28; 6	–; 18; 4	–; 6	3; 40; 9	–; 18; 4		–; 3	–; 2
Pb			4; 2			8; 5; 3	5; 3; 2	12; 7; 4	9; 6; 3	29; 10		4; 2
Bi						2				3		
Main elements [wt.%]												
Na	–; –; 2	–; –; 2	–; –; 2	–; 2; 4	–; 38; 77	–; 6; 12	–; 3; 5	–; 3; 6	–; –; 3	–; 2; 5	–; 2; 4	–; –; 2
Mg	–; 2; 3	–; 2; 2	–; –; 2		–; 2; 3	–; –; 2	–; 2; 2	–; 2; 3	–; –; 2			
P	–; 6; 4	2; 9; 6	–; 3; 2	–; 4; 3	8; 43; 29	3; 17; 12	2; 12; 8	2; 12; 8	3; 15; 10	2; 8; 6	2; 12; 8	3; 16; 10
S	21; 5	17; 4	6; –	8; 2	14; 4	10; 3	15; 4	6; 2	4; –	5; –	6; –	10; 3
K	–; 16; 5	–; 27; 8	–; 13; 4	–; 28; 8	2; 99; 28	2; 80; 23	–; 22; 6	–; 39; 11	–; 24; 7	–; 47; 13	–; 20; 6	–; 6; 2
Ca	–; 3; 23	–; 2; 15	–; 3; 25	–; –; 10	–; –; 6	–; 3; 21	–; 2; 19	–; 3; 21	–; –; 6	–; –; 9	–; 2; 12	–; –; 9
Fe						–; 2						–; 2

Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	S	St	S	St	R	S	R	F	St
Species	*Populus* L.		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Trace elements [ppm]														
B		4; –; 4	2; –; 2	2; –; 2	5; 2; 5	6; 2; 5	6; 2; 5	5; 2; 4	5; 2; 4	3; –; 3	14; 5; 12	2; –; 2	8; 3; 7	2; –; 2
Mn					–; 2	–; 9; 3	–; 2	–; 8; 3	–; 4	–; 2	–; 3	–; 3	–; 2	
Zn	–; 2	5; 10; 4	3; 6; 2	6; 12; 5	13; 25; 10	38; 75; 29	12; 23; 9	3; 6; 2	3; 5; 2	3; 6; 2	21; 42; 16	32; 63; 24	15; 29; 11	4; 7; 3
As						9; 3; 3	2; –				31; 12; 9	54; 20; 16	22; 8; 7	4; –
Se	4; –	11; 2		7; –	54; 8	23; 3	19; 3	7; –	6; –	4; –	10; –	10; –	7; –	4; –
Sr		–; 2; 4			–; 2; 4	–; –; 3	–; –; 2	–; –; 2	–; –; 2		–; –; 2			
Mo					–; –; 4	–; –; 3		–; –; 5	–; –; 2	–; –; 3	–; –; 2	–; –; 2	–; –; 2	–; –; 3
Ag		3; –		4; 3		11; 8; 3	3; 3				29; 22; 7	44; 33; 11	13; 10; 3	3; 3
Cd	6; 4	37; 25; 5	5; 3	14; 10; 2	171; 116; 24	182; 124; 26	71; 48; 10	51; 35; 7	33; 22; 5	26; 18; 4	212; 144; 30	106; 72; 15	88; 60; 13	141; 96; 20
Sb	4; 3; 2	3; 3; 2		4; 4; 3	25; 24; 17		3; 3; 2		3; 3; 2	3; 3; 2	4; 4; 3	6; 6; 4	4; 4; 3	2; 2; 2
Te				20; –	60; 2		15; –							
W					–; 2									
Au	–; 4; 7	–; 20; 40	–; 5; 10	–; 3; 5	–; 4; 8	2; 50; 100	–; 10; 20	–; 10; 20	–; –; 2	–; –; 2	–; 5; 9	–; 3; 5	–; 2; 4	–; 2; 3
Hg				–; 2	2; 6									
Tl	–; 3	–; 2		–; 3	–; 8; 2	9; 137; 30	17; 267; 59	;– 6	–; 7; 2	–; 8; 2	–; 3	–; 7; 2	–; 3	
Pb		2		3; 2	7; 4; 2	29; 18; 10	13; 8; 4				31; 19; 11	59; 37; 20	27; 17; 9	5; 3; 2
Bi					5									
Main elements [wt.%]														
Na	–; –; 2					–; –; 2	–; 2; 3	–; 2; 4	–; 2; 3	–; 2; 3	–; –; 2			
Mg						–; 7; 10	–; 3; 5	–; –; 2						
Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	S	St	S	St	R	S	R	F	St
Species	*Populus* L.		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Al														–; 2
P	3; 16; 10	–; 3; 2	–; 2	–; 4; 2	–; 2	–; 6; 4	–; 5; 3	4; 21; 14	2; 13; 9	2; 10; 7	–; 6; 4	–; 5; 3	2; 9; 6	–; 2
S		5; –	4; –	5; –	33; 8	110; 27; 3	70; 17; 2	17; 4	10; 2	9; 2	62; 16	9; 2	10; 3	7; 2
K		–; 2		–; 3		2; 67; 19	3; 121; 35	2; 73; 21	2; 81; 23	2; 90; 26	–; 26; 8	–; 17; 5	–; 15; 4	–; 22; 6
Ca	–; –; 6	–; 6; 46	–; –; 5	–; 2; 13	2; 10; 77	2; 12; 92	–; 5; 36	–; 3; 21	–; 2; 14	–; –; 7	–; 7; 51	–; –; 10	–; 3; 20	–; 2; 13
Fe						–; 4					–; 2	–; 4	–; 2	

[1] – V – plant vegetation, F in the sample name – fungi, W – wood, Bn – normal bark, Bb – burnt bark, S – shoots, St – stem, R – roots, F – flowers; detailed sample descriptions are available in the Appendix 1; [2] – geometric means of multiplicity of Coal Clarke (first value), local coals (second value) and local shales (third value), calculated based on Parzentny (1994), Parzentny et al. (1999), Lewińska–Preis et al. (2008), Ketris and Yudovich (2009), Juda–Rezler and Kowalczyk (2013), Smoliński et al. (2014), Kokowska–Pawłowska (2015) and own data (including Kruszewski, 2018)

APPENDIX 6

Enrichment factors of the USCB heap samples considering mean (normal), moderately elevated (potentially toxic), and hyperaccumulator levels

Sample	BST-VSc				BST-VRc	BST-VAt	BST-VV1	BST-VV2		RDT-VV	NRS-VV	BST-FSc	
Plant part[1]	S	F	R	St	S	S	S	S	R	S	S		
Species	*Solidago canadensis*				*Rumex crispus* L.	*Arctium tomentosum*	*Verbascum* sp.					*Schizophyllum commune*	
Trace elements [ppm]													
B	4[2]; 5	–; 2											
Sc	5	5	8	4	3	5	3	3	3	4	3	14	
V	4	4	13	4	4	13	6	8	4	4	4	4	
Co	10	7	19	3		8	7	7	4	2	3	8	
Ni	3	2	6		4	9	3	4	6	17	2	5	
Cu	3	3	5	2	3	4	8	11	12	2	3	4	
Zn	5	4	7	5	3	10; 2; **2**	8; 2; **2**	17; 4; **3**	11; 2; **2**			7	
As						2							
Se	13	9	8	5	3	2	4	4	3	7	3	3	
Mo					9	5		2	2				
Ag						–; 2		–; 2	–; 2	2; 6			
Cd	40	45	75	44	7	23	22	52	75	2		55	
Sb	3	8	23	8	2	13	19	31	27	5		19	
Ba						5							
La			10			18	6	6	3	6	2	16	
Au						2							
Hg	120; –; **4**	80; –; **3**	30	10	15	30	90; –; **3**	50; –; **2**	30	40	20	40	
Tl	2	2	5	3	43; 4	28; 2	9	60; 5	28; 2	2	5	3	
Sample	BST-VSc				BST-VRc	BST-VA	BST-VV1	BST-VV2		RDT-VV	NRS-VV	BST-FSc	
Plant part	L	F	R	St	L	L	L	L	R	L	L		
Species	*Solidago canadensis*				*Rumex crispus* L.	*Arctium tomentosum*	*Verbascum* sp.					*Schizophyllum commune*	
Pb	9; 3	12; 4	29; 10	3	8; 3	68; 22	43; 14	99; 32	73; 24	238; 78; **2**		31; 10	
Bi			4			11	8			20	5	10	
Th			3			4		2		2		6	
U													

Main elements [wy.%]													
Al		3	17		3	27	9	11	6	9	4	24	
P		2			11	4	3	3	4	2	3	4	
S	4; 2	3; 2			3; 2	2	3; 2					2	
K		2		2	7; 2	5; 2		3	2	3			
Ti			4		2	7	2	3		2		5	
Fe	4	4	16		3	19	16	11	5	5	3	22	
Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc		
Plant part	W	B	W	Bn	Bb	L	St	L	St	R	L	R	F	St
Species	*Populus L.*		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Trace elements [ppm]													
B											2; 2			
Sc	3	3	3	3	8	10	3	4	3		4	4	4	
V	4	4	4	4	10	10	4	4	4	4	6	6	10	4
Mn						5		5	2		2	2		
Co		3		2	22	23	6	6	4	5	6	9	5	
Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	L	St	L	St	R	L	R	F	St
Species	*Populus L.*		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Ni	2	3		3	7	5	2	3	2	3	3	5	5	
Cu		2		3	3	4		4	2	3	3	4	3	
Zn	2	10; 2; **2**	5	12; 3; **2**	25; 5; **4**	73; 16; **13**	23; 5; **4**	5	5	5	41; 9; **7**	61;14; **11**	28; 6; **5**	7; 2
As						4					14	23; 2	10	2
Se		3		2	16	7	5	2	2		3	3	2	
Sr		3			3	2								
Mo					2	2		2	2		3			2
Ag				–; 2		2; 6	–; 2				5; 14	8; 22	2; 7	–; 2
Cd	10	57	7	22	264; 2	282; 3	109	79	51	40	327; 3	164; 2	136	218; 2
Sb			5	5	5									
Te					2									
La				2	9	9	2	3			4	4	3	
Au						3								
Hg	5	15	5	60	220	25	5	15	4	2	20	5	10	4
Tl	5	3	2	4; –; 2?	12; –; 7?	205; 18	400; 36	9	10	12	4	10	4	2

Pb		18; 6	2	24; 8	56; 18	238; 78; **2**	109; 36	4	4	4	259; 85; **2**	491; 161; **4**	221; 72; **2**	39; 13
Bi				5	34	7								
Th					2	6								
U					2?									
Sample	BST-VA		BST-Bp			BST-VTf		ZBB-VSn			SWA-VEc			
Plant part	W	B	W	Bn	Bb	L	St	L	St	R	L	R	F	St
Species	*Populus L.*		*Betula pendula*			*Tussilago farfara*		*Solanum nigrum*			*Eupatorium cannabinum*			
Main elements [wt.%]														
Mg						4	2							
Al	17			3	23	19	3	7			9	9	4	186
P	4							5	3	2			2	
S					6; 4	21; 13	13; 8	3; 2	2	2	12; 7	2	2	
K						4	8; 3	5; 2	5; 2	6; 2	2			
Ca		2			3	3					2			
Ti					3	3		2			3	3	2	
Fe		3		4	11	48	11	4	2		28	45	18	3

[1] – V – plant vegetation, F in the sample name – fungi, W – wood, Bn – normal bark, Bb – burnt bark, S – shoots, St – stem, R – roots, F – flowers; detailed sample descriptions are available in the Appendix 1; [2] – geometric means of multiplicity of enrichment as compared to normal (first value), moderately elevated (potentially toxic; second value), and elevated (including hyperaccumulator values) contents, calculated based on Martin (1937), Saric et al. (1995), Siwek (2008), McGrath et al. (2010), Ashraf et al. (2011), Chang et al. (2017), Gupta and Gupta (2017), Zhou et al. (2018), Aihemaiti et al. (2019), Nejad and Etassami (2020) and references listed below Table 1