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ORIGINAL ARTICLE

Influence of the type of tree habitat on the character of co-occurrence of Fe, Mn, Zn, Cu, Pb, Ni, Cr and Co in the soil of the Tatra Mountain National Park

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Abstract

The objective of the research was to determine the effect of habitat type of selected species of trees on the nature of co-occurrence of Fe, Mn, Zn, Cu, Pb, Cd, Ni, Cr and Co. The presence of speciation forms of these metals was investigated, with reference to the species composition of tree stands in selected areas of the Tatra Mountain National Park (Chochołowska Valley, Strążyska Valley, Kościeliska Valley, as well as Mała Łąka Valley).

Contents of selected metals in samples were determined by the flame ASA method, with an accuracy of 0.1 µg/g. In habitats dominated by maples, the Pb content in the Chochołowska Valley, unlike Kościeliska Valley covered with beeches, the Pb content in the form directly bioavailable, was twice as high. This was clearly proved in the case of Strążyska Valley where the soil in beech tree habitats contained larger quantities of exchangeable forms of Pb, than that in the Chochołowska Valley. The soil of the valleys, including the Mała Łąka Valley, showed peculiar characteristic averaging of the contents of selected speciation forms of metals in the soil. Content corresponding to 10 percentile and geometrical average may be regarded as benchmarks in future studies of the Tatra Mountain National Park, or other protected areas.

Key words

Tatra Mountain National Park, soil, metals, co-occurrence, speciation

INTRODUCTION

While discussing the great problem of plant intoxication with specific elements, the character of their co-occurrence in a specific environment is of significant importance in the interpretation of their migration. The issue of the co-occurrence of selected metals has already been discussed as far as a particular element of the environment is concerned, in the morphological part of plants [1] and in combinations – dust-leaves [2, 3] and soil-subterranean parts of plants [3], as well as co-occurrence of a particular metal in different combinations of morphological plant parts – root-stem, stem-leaf, etc. Such an approach is applicable for areas under the influence of a high, differentiated emission of the metals in question. However, in the case of protected areas, located most frequently a long way from industrial sites, it is reasonable to ask how the characteristic, original species content in the chosen forest areas may decide about the different character of metal co-occurrence, despite similar soil characteristics.

It may also be expected that in the areas untouched by agricultural activities or forestry there may appear some specific characters of metal occurrence and co-occurrence in the soil solution of such historically original forest areas [4, 5] Undoubtly, the Tatra Mountain Park belongs to that group.

The problem of the content level of specific elements in soil, respectively to tree species characteristic for that soil, was analyzed by Kwapuliński and Paprotny. It turned out that in habitats of sycamores the content of Pb in the Chochołowska Valley was twice as high in the directly bioavailable form, in comparison to the Kościeliska Valley where beeches were predominant. This observation was also proved in the Strążyska Valley, where the soils in beech habitats contained much more interchangeable forms of Pb than that seen in the Chochołowska Valley. In the soil of the Chochołowska, Strążyska and Małej Łąki Valleys, speciation forms of the metals occurred with a characteristic specific average value.

In consequence of the above-presented facts, it was reasonable to conduct research to examine speciation forms of Fe, Mn, Zn, Cu, Pb, Cd, Ni, Cr and Co in relation to tree species content in specific areas of the Tatra Mountain National Park.

MATERIALS AND METHODS

In 2008, the content values of Fe, Mn, Zn, Cu, Pb, Cd, Ni, Cr and Co were measured in 60 samples, taken from 4 sites located in the Tatra Mountain National Park – the Chochołowska Valley, Kościeliska Valley and Małej Łąki Valley. The chemical form of the metals present in the soil was specified using Rudd's method (1988), which consisted in extraction using appropriate solvents at the ratio of 1:40 in 1g of soil, with the following solutions:

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- for interchangeable form: 1,0 M KNO_3 at ratio 1:40
- for adsorbed form: 0,5 M KF (pH=6,5) at ratio 1:40
- for organic compounds: 0,1 M $Na_4P_2O_7$ at ratio 1:40
- for carbonates: 0,1 M EDTA (pH=6,5) at ratio 1:40
- for sulphides: 6,0 M HNO_3 at ratio 1:40
- for residues: HNO_3 (twice)

Soil sample sizes measuring 10 cm × 10 cm and 5 cm deep was taken at the surface in an open area without undergrowth. The soil was air dried, ground up and sieved with a 1mm mesh sieve, exposed to the solvents for 24 hours, centrifuged for 10 minutes (4,000 rpm), rinsed with redistilled water and centrifuged again for 5 minutes. Extracts obtained were treated with 1% HNO_3. Reagents used for the analysis were spectrally clean (Merck).

Three blind tests were made for each series of measurements. Results from 6 samples were corrected with the results, taking into account values for the blind tests.

The content of heavy metals in the samples examined was specified by the ASA flame method, using a Philips spectrophotometer Pye Unicam SP-0 with an accuracy of 0.01µg/g. Chemical recovery for applied analytic procedures was between 97–102%: precision was controlled by using pattern solvents by WZORMAT, containing Pb, Cd and Ni in range of condensations tested in the soil.

The Toxicology Institute, where the laboratorial part of the studies were carried out, cooperated with the Faculty of Non-Organic Chemistry of the Silesian University of Technology in Gliwice and the Faculty of Environmental Monitoring of the Head Mining Institute in Katowice in the validating programme. Varieties in markings differed depending on the type of element, from 2.8% for Pb to 4.8% for Cd, 4.3% for Ni.

Statistical assessment of the results included calculation of the arithmetical mean, geometrical mean, range of changes, values corresponding to percentiles 10 and 95. Standard deviation determined the factors of metals correlation, and statistically the most probable range of changes.

RESULTS

In sycamore habitat, the tested elements complied with non-parametric distribution skewed to the right. From among them, the highest changeability of occurrence was assigned to Ni, Cd, Zn, Mn (100% – 290%), and the lowest to Cu (16%) and to Cr, Pb and Fe (39%-46%), which occurred in interchangeable form. Adsorbed forms of the elements tested also complied with the skewed to the right distribution, with the exception of Ni. Co and Cd, Fe and Zn were of the highest variability of occurrence (114% and 162%). The other elements in that form of occurrence were characterized by a much lower variability factor at 23% for Cu up to 80% for Mn. Forms bioavailable directly were characterized by low variability of occurrence: 17%-32% for Cd, Pb, Cu, Mn, Cr and 77%-103% for Fe, Ni, Co, Zn. In the case of carbonates, the highest variability also concerned Zn (124%), and content of the other elements in that form showed minor changes ranging from 17%-44%. Distribution of frequency of occurrence was non-parametrically skewed to the right, except for Ni in organic compounds and Pb in the form of carbonates.

The next habitat in which all forms of the elements occurred complied with the skewed to the right distribution, characterized by high variability of occurrence, was the habitat of beeches. Different from the habitat of sycamore, the variability of occurrence of the elements was lower and characterized by similar tendencies to variation with respective to the kind of element. Variability of occurrence of Mn, Cd and Ni in soil in beech habitat was similar to the variability of those elements in the habitat of sycamore and in the adsorbed form for Cd and Zn. There were significant differences in Co variability in occurrence in the adsorbed form (400% and 179%) A separate variability in the occurrence of metals in sycamore maple habitat, in comparison to the habitat of beeches, in interchangeable form was found in Zn and Pb compounds, and in interchangeable form compounds of Pb, Mn and Fe. A similar variability of the occurrence of metals observed in the habitats of the trees in question involved changes of Cu and Cr content changes in interchangeable and adsorbed forms. The type of habitat, on the example of beech soil, clearly differentiates the occurrence of the metals tested in potentially bioavailable forms in comparison to soils from the habitat of maple sycamore. Soils from beech habitats were characterized by not only lower variability of the occurrence of the elements, but also their high, comparable, same variability regardless the kind of element.

In comparison to the habitats presented above, the habitat of spruce is very different in the distribution of the occurrence frequency, and significantly higher variability of the occurrence of respective elements, regardless to their kind in interchangeable and adsorbed forms. This also concerns metals present in the soil in forms of organic compounds and carbonates marked with high variability of Mn and Cu occurrence, compared with the variability of occurrence of other elements. The difference in character of distribution of occurrence frequency concerns Cu and Cr in interchangeable form, and Cr in adsorbed form, namely for these elements which had their distribution of occurrence in their speciation forms was skewed to the left. Lack of a characteristic maximum of occurrence in soil was noted for Cr in interchangeable form, as well as for Cd, Ni and Cr in adsorbed form, with the exception of Mn, Zn, Cu and Cd occurring in the form of organic compounds (right skewed distribution). Frequency of occurrence of Cr, Ni and Fe in the form of organic compounds complied with the criteria of a normal distribution, similar to the carbonates of Fe, Cr and Co. The content of the remaining elements in the form of carbonates complied with the distribution skewed to the right. It was generally characteristic that the higher the skewedness, indicating the right skewed character, the higher the coefficient of variation describing the element. For example, the skewedness for organic compounds of Mn and Zn was 2.83 and 2.39 respectively; hence, their appropriate coefficients of variation were 103% and 70%, respectively. Similarly, Mn and Zn present in the soil in form of carbonates were characterized by the following skewedness and coefficient of variation: 3.43–156% and 2.64- 99%.

Table 1. Statistical characteristics of metals occurrence in interchangeable and adsorbed forms and organic compounds in soil [µg/g] dry weight in the Tatra Mountain National Park in relation to respective species of trees.

metal	Sycamore				Beech				Spruce			
	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]
						Exchangeable form						
Fe	17.01	81.87	38.51	47	25.13	113.79	40.10	51	6.55	155.43	28.54	91
Mn	1.47	128.07	7.90	159	3.89	139.63	12.65	158	0.70	77.86	5.98	148
Zn	1.10	15.94	2.88	100	1.25	16.88	3.77	90	0.53	17.39	2.70	100
Cu	3.71	6.83	4.63	16	3.75	5.43	4.51	12	1.24	6.73	3.79	34
Pb	1.31	4.17	2.08	40	0.74	26.08	2.66	143	1.43	20.55	2.97	113
Cd	0.00	1.26	0.17	222	0.00	1.21	0.08	400	0.00	0.85	0.10	249
Ni	0.00	1.76	0.16	290	0.00	2.57	0.47	164	0.00	4.61	0.80	151
Cr	0.92	2.51	1.41	38	0.90	2.04	1.14	36	0.16	1.87	0.95	47
						Adsorbed form						
Fe	19.00	348.79	53.49	115	21.54	302.23	76.46	77	32.70	401.28	76.04	108
Mn	4.52	42.97	9.73	80	3.91	56.15	9.56	103	1.00	51.46	5.76	121
Zn	0.79	26.43	2.29	163	0.38	16.68	2.15	116	0.82	15.18	2.26	107
Cu	1.86	3.94	2.45	23	1.74	3.38	2.21	19	0.64	4.98	1.96	49
Pb	0.56	2.40	1.07	37	1.13	4.55	1.67	63	0.75	5.80	1.88	66
Cd	0.00	0.81	0.29	118	0.00	0.78	0.34	104	0.00	0.90	0.35	102
Ni	1.48	3.96	2.00	39	0.00	3.26	0.97	121	0.00	3.17	1.16	103
Cr	0.30	2.23	0.76	61	0.30	2.38	0.86	57	0.31	1.68	0.83	47
						Organic solution						
Fe	502.41	3487.75	1190.24	63	835.66	3347.70	1451.43	49	350.73	3637.21	1188.66	77
Mn	92.58	274.63	147.42	34	44.75	283.70	119.75	47	29.36	531.35	81,54	104
Zn	17.17	206.40	34.25	103	16.60	125.96	37.04	65	11.21	134.02	33.13	71
Cu	2.19	5.81	2.94	33	1.88	4.83	2.60	30	1.69	5.71	2.44	41
Pb	10.31	28.07	14.06	36	10.26	54.60	19.76	50	8.35	32.56	18.53	41
Cd	1.36	3.17	1.92	25	1.17	3.63	2.02	36	1.05	4.12	1.79	39
Ni	0.00	3.61	1.86	78	0.00	2.89	1.28	95	0.00	4.92	1.80	68
Cr	3.33	5.65	4.05	18	3.28	6.46	4.28	26	1.63	6.74	3.57	44

Table 2. Statistical characteristics of metals occurrence in forms of carbonates, sulphides and the rests in soil [µg/g] dry weight in the Tatra Mountain National Park in relation to respective species of trees.

Metal	Sycamore				Beech				Spruce			
	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]
						Carbonates						
Fe	968.65	3310.07	1850.61	44	999.60	3735.77	1904.67	43	332.51	4900.20	1482.92	73
Mn	139.10	515.48	227.15	43	62.59	394.38	145.53	61	26.58	1801.80	130.81	156
Zn	13.68	167.08	22.33	124	6.15	52.74	17.57	59	3.74	96.10	12.86	100
Cu	3.87	14.53	6.23	49	2.10	12.26	5.31	48	2.41	21.92	4.29	87
Pb	31.20	56.14	41.27	19	22.71	97.83	39.72	46	16.59	135.43	36.45	65
Cd	1.05	1.73	1.32	17	1.01	2.96	1.36	35	0.87	3.53	1.20	50
Ni	2.35	8.69	4.71	41	1.96	8.51	3.71	49	0.86	14.38	3.32	78
Cr	0.87	2.51	1.25	40	0.88	2.38	1.28	36	0.51	2.57	1.10	44
						Sulphides						
Fe	1811.99	13636.03	4224.63	63	1740.02	6736.57	3397.88	41	714.95	7497.47	2589.42	70
Mn	26.86	198.87	79.91	54	23.22	148.15	51.43	56	6.70	148.63	41.60	81
Zn	14.53	86.49	31.39	56	13.00	49.64	25.03	41	3.23	420.34	23.87	189
Cu	2.50	9.92	4.05	52	2.21	5.97	3.30	35	1.38	6.96	2.69	54
Pb	4.16	9.97	5.85	33	2.64	10.50	5.39	43	0.58	32.50	5.23	99
Cd	0.89	1.14	1.00	8	0.92	1.24	1.04	9	0.33	1.18	0.88	28
Ni	1.22	36.60	6.64	104	0.00	26.61	6.06	106	0.00	19.68	4.52	114
Cr	1.17	12.38	2.44	88	0.00	5.46	0.02	98	0.00	4.73	1.90	81

Table 2 (Continuation). Statistical characteristics of metals occurrence in forms of carbonates, sulphides and the rests in soil [μg/g] dry weight in the Tatra Mountain National Park in relation to respective species of trees.

Metal	Sycamore				Beech				Spruce			
	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]	10 percentile	95 percentile	Geometrical average	Variation factor [%]
						Residues						
Fe	2172.88	6982.80	3533.86	45	1431.30	7147.34	3082.31	53	711.69	8654.03	2591.30	75
Mn	11.49	41.81	22.64	42	8.91	44.21	17.35	50	2.85	49.83	13.30	70
Zn	14.06	39.87	21.93	40	12.45	36.29	20.12	38	5.45	54.05	17.18	73
Cu	2.17	9.58	3.51	56	1.19	6.85	2.82	54	0.34	8.63	2.29	72
Pb	3.23	11.09	4.34	41	1.48	9.11	3.23	51	2.01	8.50	3.46	47
Cd	1.10	1.30	1.18	5	1.06	1.34	1.20	6	0.22	1.39	0.94	34
Ni	2.95	59.90	6.35	143	2.45	9.14	4.17	43	0.62	25.21	5.33	121
Cr	1.31	4.56	2.24	49	1.29	4.77	2.62	37	0.59	4.58	2.08	58

Table 3. Co-occurrence of metals in interchangeable and adsorbed form in soil in Tatra Mountain National Park in relation to respective species of trees.

Metal		Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co
Fe	**Sycamore**	0.41	0.46	0.13	0.31	0.31	-0.01	0.17	
	Beech	-0.14	-0.13	0.07	-0.08	-0.05	-0.14	-0.09	
	Spruce	0.43	**0.75**	0.39	**0.68**	-0.08	0.16	0.24	
Mn	**Sycamore**		**0.91**	-0.32	0.48	**0.96**	0.09	0.18	1.00
	Beech		**0.74**	0.12	0.00	**0.73**	0.00	0.03	1.00
	Spruce		0.34	0.09	-0.14	0.50	0.44	-0.06	1.00
Zn	**Sycamore**	0.34		0.05	0.41	**0.91**	0.10	0.41	0.91
	Beech	0.86		0.31	0.40	**0.66**	-0.14	0.29	0.74
	Spruce	0.94		-0.08	**0.81**	0.36	0.00	0.06	0.34
Cu	**Sycamore**	0.02	0.63		-0.04	-0.25	-0.12	**0.64**	-0.32
	Beech	0.44	0.35		-0.22	0.39	-0.03	**0.64**	0.12
	Spruce	0.73	0.69		-0.12	-0.48	0.39	0.21	0.09
Pb	**Sycamore**	0.26	0.84	0.27		0.40	0.03	0.32	0.48
	Beech	0.71	0.75	0.15		0.02	-0.29	-0.05	0.00
	Spruce	0.06	0.09	0.18		-0.02	-0.20	0.14	-0.14
Cd	**Sycamore**	0.50	-0.09	-0.32	0.06		0.08	0.22	0.96
	Beech	0.57	0.53	-0.07	0.66		0.16	0.04	0.73
	Spruce	0.52	0.57	0.51	0.27		0.10	-0.41	0.50
Ni	**Sycamore**	0.54	0.02	-0.28	0.21	0.41		-0.37	0.09
	Beech	0.43	0.55	0.42	0.44	0.25		-0.13	0.00
	Spruce	0.38	0.36	0.40	-0.31	0.29		-0.47	0.44
Cr	**Sycamore**	0.06	-0.16	-0.42	-0.10	0.16	0.19		0.18
	Beech	0.60	0.37	0.65	0.10	-0.03	-0.01		0.03
	Spruce	0.45	0.40	0.44	0.32	0.42	-0.01		-0.06

Table 4. Co-occurrence of metals in the form of organic compounds and carbonates in soil in Tatra Mountain National Park in relation to respective species of trees.

Metal		Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co
Fe	**Sycamore**	0.44	-0.05	-0.25	**0.71**	0.21	**0.50**	**0.68**	**0.59**
	Beech	-0.09	-0.17	0.22	-0.10	-0.21	0.35	0.22	**0.56**
	Spruce	0.43	**0.75**	0.39	**0.68**	-0.08	0.16	0.24	0.43
Mn	**Sycamore**		0.01	-0.24	**0.57**	0.37	**0.54**	0.09	**0.58**
	Beech		**0.55**	-0.06	0.45	**0.77**	0.15	0.12	0.44
	Spruce		0.34	0.09	-0.14	0.50	0.44	-0.06	1.00
Zn	**Sycamore**	0.04		-0.01	0.00	0.00	-0.32	0.05	-0.23
	Beech	0.21		0.02	**0.83**	**0.63**	0.10	-0.17	0.04
	Spruce	0.93		-0.08	**0.81**	0.36	0.00	0.06	0.34

Table 4 (Continuation). Co-occurrence of metals in the form of organic compounds and carbonates in soil in Tatra Mountain National Park in relation to respective species of trees.

Cu	**Sycamore**	-0.09	0.58		-0.45	-0.44	-0.16	0.03	0.06
	Beech	0.48	0.54		-0.39	-0.36	0.37	0.21	0.28
	Spruce	0.89	0.94		-0.12	-0.48	0.39	0.21	0.09
Pb	**Sycamore**	0.33	0.29	0.11		**0.53**	0.39	0.29	**0.50**
	Beech	0.57	0.80	0.68		**0.65**	0.05	-0.35	0.04
	Spruce	0.85	0.94	0.90		-0.02	-0.20	0.14	-0.14
Cd	**Sycamore**	-0.02	0.30	0.16	0.43		0.05	0.32	0.15
	Beech	0.34	0.88	0.61	0.84		-0.04	0.25	0.17
	Spruce	0.84	0.94	0.90	0.94		0.10	-0.41	0.50
Ni	**Sycamore**	0.21	0.23	0.48	0.17	0.18		0.33	**0.72**
	Beech	0.39	0.37	0.35	0.30	0.38		0.22	**0.52**
	Spruce	0.86	0.86	0.81	0.79	0.83		-0.47	0.44
Cr	**Sycamore**	0.25	0.59	0.61	0.21	0.25	0.22		0.40
	Beech	0.41	0.61	0.77	0.61	0.67	0.36		0.19
	Spruce	0.25	0.23	0.30	0.20	0.26	0,51		-0,06

Table 5. Co-occurrence of metals in the form of sulphides and residues in soil in Tatra Mountain National Park in relation to respective species of trees.

Metal		Mn	Zn	Cu	Pb	Cd	Ni	Cr	Co
Fe	**Sycamore**	**0.83**	**0.61**	**0.52**	**0.70**	0.04	**0.91**	**0.86**	**0.96**
	Beech	**0.62**	**0.70**	0.30	**0.56**	0.05	**0.77**	**0.56**	**0.75**
	Spruce	**0.76**	-0.10	0.10	0.14	0.26	**0.82**	0.35	**0.89**
Mn	**Sycamore**		**0.68**	0.34	**0.65**	0.07	**0.67**	**0.64**	**0.77**
	Beech		0.44	0.21	0.35	0.15	0.25	0.31	0.41
	Spruce		-0.16	0.41	0.20	0.24	**0.60**	0.23	**0.85**
Zn	**Sycamore**	0.75		**0.58**	**0.51**	-0.01	0.43	0.43	0.49
	Beech	0.61		**0.58**	**0.56**	0.17	**0.60**	**0.81**	**0.66**
	Spruce	0.82		-0.01	-0.10	-0.08	-0.17	**0.59**	-0.22
Cu	**Sycamore**	0.19	0.10		0.37	-0.29	**0.70**	**0.61**	0.48
	Beech	0.44	0.54		0.28	**0.56**	0.35	**0.59**	**0.66**
	Spruce	0.75	0.76		-0.06	0.36	0.23	0.50	0.13
Pb	**Sycamore**	0.32	0.49	-0.06		0.33	**0.57**	**0.67**	**0.66**
	Beech	0.16	0.24	0.13		0.14	0.37	0.41	0.40
	Spruce	0.54	0.70	0.68		**-0.79**	-0.10	-0.19	-0.05
Cd	**Sycamore**	0.00	0.38	-0.47	0.46		-0.16	-0.07	0.02
	Beech	-0.40	0.08	-0.11	0.20		0.27	0.13	0.43
	Spruce	0.32	0.10	0.18	-0.21		0.31	0.34	0.42

Table 5 (Continuation). Co-occurrence of metals in the form of sulphides and residues in soil in Tatra Mountain National Park in relation to respective species of trees.

Ni	**Sycamore**	0.32	0.22	0.28	0.06	-0.25		**0.92**	**0.90**
	Beech	0.50	0.40	0.55	0.11	-0.35		**0.56**	**0.69**
	Spruce	0.57	0.46	0.65	0.39	0.19		0.39	**0.76**
Cr	**Sycamore**	0.48	0.69	-0.05	0.01	0.28	0.38		**0.84**
	Beech	0.11	0.22	-0.01	-0.07	0.26	0.22		**0.59**
	Spruce	0.82	0.70	0.71	0.30	0.56	0.61		0.21

DISCUSSION

The problem of the metals in question in co-occurrence in the surface layer of soil has been discussed earlier [6]. Co-occurrence of metals in air and soil in recreational areas has been analyzed in the context of occurrence of respective forms of the metals in dusts settled on leaves of trees in Western Beskid (a set of mountain ranges spanning Poland, the Czech Republic and Slovakia) [7], and in dusts settled on paved surfaces [8]. This justified considering the level of an area emission, an important issue in ecotoxicology and chemoecology, in respect of the occurrence of metals in the air close to ground in a forest environment (ecotone) and in a surrounding belt 300m wide [9, 10, 11]. The issue of the location of habitats in mountain areas on the example of Western Beskid has been discussed with respect to the occurrence of Pb and Cd in macromycetes by Kwapuliński et al [12]. Therefore, the influence of the type of habitat on the character of co-occurrence of individual metals in the soil in respective habitats of trees had to be examined thoroughly. Undoubtly, the final accumulation of respective metals is determined by the type of interactions between these metals in soil solution and their specified chemical forms of occurrence [13, 14, 15, 16].

To compare the quantities of metals in specified speciation forms with other publications, Rudd's method was applied, which allowed differentiation of the following forms: interchangeable, adsorbed, organic compounds, carbonates and sulphides. These two facts explain the so-called 'phenomenon of availability in toxicological phase'. This consists in the fact that in the examined habitats of different trees the relationship between respective metals in soil solution may differ. This may be the result of a specific accumulation of metal compounds by subterranean parts of trees, but these subterranean organs may also selectively accumulate some ions of metals and result in different relations in co-occurrence of metals in respective chemical forms of occurrence [15, 16, 17]. In the presented study, it has been indicated that this difference may be characterized by different coefficients of variability of occurrence of the respective elements, both in an area scope in the Tatra Mountain National Park and the type of tree habitat (maple sycamore, beech, and spruce).

Interestingly, the occurrence variability of directly bioavailable forms was generally higher (Co, Fe, Zn). A specific variability of adsorbed forms was not noticed, depending also on the kind of metal and tree habitat; for example, differentiated variability of occurrence in beech habitat was not entirely proved in soil samples from the habitats of maple sycamore. Furthermore, the kind of habitat on the example of beech soil differentiates strongly the occurrence potentially bioavailable forms of respective elements in comparison to the habitats of maple sycamore.

Another parameter basic for the separation of soils of maple sycamore and beech habitats is the character of distribution. Variability of occurrence in indirectly bioavailable forms, e.g. Cu and Cr, is of a non-parametric right skewed character for soils in habitats of beeches; however, these two elements present in interchangeable forms or as an adsorbed one with right skewed distribution (Tab. 3, Tab. 4, Tab. 5). An especially convincing illustration is found in the observed co-occurrence of metals in habitats of three species of trees.

In the Tatra Mountain National Park the interchangeable forms are characterized by very important proportional changes of Fe with Zn and Pb, Zn with Pb, Cd with Co, Ni with Mn and Co, Mn with Cd, and inversely proportionally, Cu with Cd (-0.48), Cd with Cr (-0.41), Ni with Cr (-0.47), and in maple sycamore for the interchangeable form a strong correlation was noticed of Fe with Mn and Zn (0.41), Cd with Mn, Zn (0.91), Cr with Cu (0.64) and Zn (0.41). The non-existence of important correlations of Ni with other elements in an interchangeable form in soil was surprising. Similarly, as observed in the case of Fe in beech habitat, it was an interchangeable form that correlated in changes in the quantity of Zn and Cd (0.74), Zn with Mn and Cd (0.66 and 0.74). The interchangeable form of Cu is the most dependent on changes of content of Cr (0.64), and to a lesser degree is determined by changes of content of Zn (0.31) and Cd (0.39). Interchangeability of Pb was determined by the content change of Zn (0.4) and Cd with Mn (0.83), Zn (0.66) and Cu (0.39).

Similar to the case of sycamore habitat, in the habitat of beech no significant correlations were found between the interchangeable forms of metals. As in the sycamore habitat, in the beech habitat, proportional relations concerned the interchangeable form of Cr with Zn (0.29) and Cu (0.64) (Tab. 3). Table 4 shows the character of co-occurrence of respective metals in adsorbed form, and in the habitat of sycamore, the changes in Fe content corresponded in direct proportion with changes in the content values of Mn (0.6), Cd (0.4), Mn with Ni and Cd (0.5), Zn with Cu and Pb (0.63) and (0.84), Cu with Zn (0.63), Pb with Zn (0.84), Cd with Mn (0.5) and Ni with Mn (0.54) for the adsorbed form.

Generally, the highest number or proportional correlations was noticed in soil from beech habitat. A similar picture of co-occurrence was noticed for soil from spruce habitat (Tab. 4). Table 5 presents the relations in co-occurrence of metals in the form of organic compounds. Special attention should be paid to the proportional changes of Fe with Mn and Pb in the habitats of sycamore and spruce, and different ones of Fe with Zn in the habitat of spruce, and Fe with Ni, Cr and Co in sycamore habitat. In the latter, the correlations with the presence of Pb, Ni, Co and Mn were repeated. Content changes of Mn were mainly determined in beech habitat with Zn (0.65) with Pb (0.45), Cd (0.77), Co (0.44), and in the case of correlations Zn with other elements except Ni (-0.32). In soil from beech and spruce habitats, similar correlations were found between Zn with Mn, Pb and Cd in organic compounds. These organic compounds of Cu determine the occurrence of these forms for Pb, Cd in all the types of habitat. Relations of Cu with Ni and Cr in the soil of beech and spruce habitats have the character of constant proportional changes. Very differentiated relations were observed in organic compounds of Pb, namely, in sycamore and beech habitats proportional changes concerned Pb and Mn, Pb and Cd, and the inversely proportional concerned Pb and Cu. In addition, the content of Pb changes in a directly proportional way in the form of organic compounds with the content of Co in soil from sycamore habitat. In soil, a quite different character was presented in beech and spruce habitats by Zn in respect of Pb, compared to soil from sycamore habitat (0.81)

In all the habitats, directly proportional changes in the form of organic compounds concerned Cd and Mn (0.37) and (0.77) and Cd with Zn (0.36–0.63) in the habitats of beech and spruce, and Cd with Pb (0.53–0.66) in the habitats of sycamore and beech. Inversely proportional changes of organic compounds of Cd with compounds of Cu were characteristic. Strong correlations in changes of organic compounds of Ni and Co (0.44–0.82) in soil from all the habitats were also very significant. Attention should be paid to proportional changes of Ni with Mn content only in sycamore and spruce habitats, as well as in soil with Cu from habitats of beech and spruce.

Correlations concerning Cr and other elements had the character of inversely proportional changes in spruce habitat with Cd and Ni (-0.41 and -0.47). Similarly, in beech habitat, Cr with Pb (-0.35), and scarcely significantly proportional changes in Cr changed the content in sycamore habitat with Pb (0.29), Cd and Ni (0.32) and Co (0.44). In comparison to the forms of occurrence discussed earlier, metals present in form of carbonates in soil in respective habitats of trees showed a higher level of proportional changes (Tab. 6), for example, in soil from spruce habitat carbonates of Fe, Mn, Zn, Cu, Pb, Cd and Ni strongly correlated with other elements. Cr is an exception, the changes of which significantly determined only the content of Ni and Co (0.51). All other coefficients of correlations for changing elements in the soil of the habitat of spruce were at levels of 0.5 and 0.4. Similar conclusions concerned the soil from beech habitat where the relations were somewhat weaker; however, it was surprising that they involved changes in the content of Cr carbonates with a change of carbonates content of other elements. For soil from beech habitat, very weak relations were noticed between some forms of Zn and Mn. It should be mentioned that there were significant relations in soil in sycamore habitat which concerned Fe with all other elements, with the exception of Cu, Mn only with Co, and to a lesser extent with Pb, Zn, Cu and C (0.68), and inverse proportionally with Co (-0.32). Weak correlations in soil from sycamore habitat concerned Zn with Ni, Cd, Pb. Carbonates of Cu in a significant way changed with carbonates of Cr (0.48), Cd with Pb (0.47). It was characteristic that there were no significant correlations between the elements above in the form of the carbonates of Ni and Cr in soil from sycamore habitat. To provide complete information, the values of correlation coefficients have been given describing the occurrence of the metals examined in the forms of sulphides and rests in soil and in the habitats of respective tree species.

CONCLUSIONS

1. Habitats of respective species of trees differ with the level of metal content in soil in relation to their form of occurrence and the kind of correlation in their co-occurrence.
2. The biggest changes were observed in the root area of spruce.
3. Presence of bioavailable forms of respective metals in soil in habitats of respective species of trees in the Tatra Mountain National Park differs in area scope.
4. The highest content of all the elements examined in soil from all habitats was observed in the form of their organic compounds.

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