Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Pol. J. Environ. Stud. Vol. 33, No. 5 (2024), 1-10
DOI: *10.15244/pjoes/177422* ONLINE PUBLICATION DATE:

Original Research

A Comparison of Co-Occurrence of Special Forms of Selected Metals in Soil, on the Example of Sycamore, Beech, and Spruce Forest Complexes in Urbanized and Non-Urbanized Regions of Tatra National Park

Łukasz Paprotny[1], Jerzy Kwapuliński[2], Dorota Wianowska[1], Maciej Gnatowski[1], Joanna Kasprzyk-Pochopień[3], Wojciech Piekoszewski[3, 4*]

[1]Research and Development Center ALAB Laboratories, Ceramiczna, 20-150 Lublin, Poland
[2]Department of Toxicology, Faculty of Pharmacy, Silesian University of Medicine, Jagiellońska, 41-200 Sosnowiec, Poland
[3]High Resolution Mass Spectrometry Laboratories, Faculty of Chemistry, Jagiellonian University, Gronostajowa, 30-387 Krakow, Poland
[4]Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University, Gronostajowa, 30-387 Krakow, Poland

Received: 8 August 2023
Accepted: 21 December 2023

Abstract

One of the most important issues considered in ecotoxicology is the elevated accumulation of different elements in soil as a consequence of anthropogenic activities. In this paper, determination of nine elements in soil obtained from three different forest complexes (sycamore, beech, and spruce) in urbanized and non-urbanized regions of Tatra National Park is presented. Additionally, a comprehensive presentation of detailed results of correlation analyses between individual elements in accordance to each valley, as well as to selected species of trees, is shown.

Speciation studies included chemical forms of the following elements: Fe, Mn, Zn, Cu, Pb, Cd, Ni, Cr, Co. Soil extracts were obtained in accordance with Rudd's methodology and all species were determined using atomic absorption spectrophotometry (AAS). The study compares the content of selected chemical forms (exchangeable and adsorbed, organic solutions and carbonates) of chosen metals in soil of four valleys of Tatra National Park: Chochołowska, Strążyska, Mała Łąka, and Kościeliska.

*e-mail: wpiekosz@tlen.pl

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

The first three (group A) are considered as non-urbanized areas, whereas the last four (group B), on the account of many home fireplaces located there, as urbanized areas.

Keywords: heavy metals, co-occurrence, National Park, trees, speciation analysis

Introduction

Nowadays, coexistence and accumulation of trace elements in soil are considered to be very important issues in ecotoxicology [1-5]. This is because of the fact that the specific participation of individual elements' compounds in the soil can influence the process of their cumulation in the so-called critical plant parts (usually underground organs or leaves, but also other morphological parts of the plant), and leads to their undesirable elevated levels [6-10]. As it is known, excess exposure to both essential and toxic elements either via the food chain or through direct exposure by dermal contact can be hazardous to human health [11-14].

In the process of accumulation of bioavailable compounds by the plant, a phenomenon of elements co-occurrence in the roots layer of soil occurs, and selected morphological parts of the plant will play a role [15-19]. However, the physiological properties of plants to discriminate between selected elements, as well as the availability in the so-called toxicological phase, will have a decisive role [20].

The nature of the co-occurrence is largely determined by the geochemical composition of soil [21-23], as well as its pH, and the mobility of elements depends on the content of organic matter and the presence of manganese and iron oxides, which have strong sorptive properties [24-27]. A previously published paper studied the influence of the type of tree habitat on the character of co-occurrence of selected metals in the soil of Tatra National Park. It was reported that, because of different metal quantitative composition and their form of occurrence in the soil of habitats of three different species of trees, metal co-occurrence varied, and the biggest changes were observed in the root area of spruce. The highest content of all the elements examined in the soil from all habitats was observed in the soil form of their organic compounds.

In this paper, the contents of specific forms of nine chosen elements in the soil of urbanized and non-urbanized regions of Tatra National Park and metal co-occurrence in all four valleys, in respect to three forest complexes, are presented [28, 29].

Fig. 1. Illustrative map of Tatra National Park with marked sampling locations.

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Table 1. Statistical characteristics of metals occurrence in selected forms in soil [μg/g] dry weight in non-urbanized and urbanized regions of Tatra National Park.

Metal	Non-urbanized regions					Urbanized region				
	Geometrical average	Range changes		Percentile		Geometrical average	Range changes		Percentile	
		min	max	10	95		min	max	10	95
Exchangeable form										
Fe	35.32	5.09	155.43	13.00	81.87	15.06	3.63	58.25	3.63	58.25
Mn	8.42	0.66	139.63	1.47	118.72	4.15	0.10	94.87	0.10	94.87
Zn	3.08	0.05	17.39	1.10	15.94	1.71	0.68	4.34	0.68	4.34
Cu	4.29	1.09	6.83	3.66	5.51	8.29	0.79	30.75	0.79	30.75
Pb	2.54	0.68	26.08	1.31	8.53	17.40	1.75	98.03	1.75	98.03
Cd	0.10	< 0.03	1.26	< 0.03	0.85	0.27	0.12	0.75	0.12	0.75
Ni	0.32	0.02	4.61	0.02	1.93	0.12	0.06	0.43	0.06	0.43
Cr	1.15	0.15	2.51	0.66	2.34	4.96	0.44	24.99	0.44	24.99
Co	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	0.05	< 0.01	0.05
Adsorbed form										
Fe	67.75	15.71	401.28	20.35	348.79	37.20	18.17	105.53	18.17	105.53
Mn	8.12	0.79	56.15	1.98	42.97	1.32	0.73	4.00	0.73	4.00
Zn	2.23	0.38	26.43	0.74	15.18	1.02	0.63	2.45	0.63	2.45
Cu	2.20	0.49	4.98	1.68	3.77	7.51	0.94	21.86	0.94	21.86
Pb	1.50	0.55	5.80	0.61	4.55	15.36	0.75	69.27	0.75	69.27
Cd	0.22	0.01	0.90	0.02	0.81	0.02	0.01	0.24	0.01	0.24
Ni	1.30	0.01	3.96	0.20	3.17	0.20	0.06	0.71	0.06	0.71
Cr	0.81	0.15	2.38	0.30	2.01	4.60	1.48	9.99	1.48	9.99
Co	0.02	< 0.01	0.40	< 0.01	0.19	0.23	0.05	0.83	0.05	0.83
Organic solutions										
Fe	1271.05	336.57	3637.21	478.43	3418.68	1370.17	402.77	2905.97	402.77	2905.97
Mn	112.91	10.16	531.35	44.75	274.63	109.30	39.96	272.40	39.96	272.40
Zn	34.77	7.76	206.40	15.43	125.96	37.20	4.48	526.95	4.48	526.95
Cu	2.65	1.53	5.81	1.98	4.83	16.56	8.10	55.82	8.10	55.82
Pb	17.27	4.00	54.60	9.23	32.37	54.78	41.24	82.44	41.24	82.44
Cd	1.91	1.04	4.12	1.17	3.17	1.28	0.25	6.38	0.25	6.38
Ni	1.38	0.00	4.92	0.00	3.56	1.66	0.06	14.27	0.06	14.27
Cr	3.96	1.04	6.74	2.83	6.46	8.11	4.00	11.65	4.00	11.65
Co	0.39	0.00	2.40	0.00	1.49	0.26	0.05	4.00	0.05	4.00
Carbonates										
Fe	1735.47	262.97	4900.20	818.51	3745.01	1796.76	919.61	3059.94	919.61	3059.94
Mn	162.92	8.99	1801.80	33.86	416.77	98.27	8.39	507.95	8.39	507.95
Zn	17.15	0.10	167.08	6.67	52.74	12.93	6.50	78.88	6.50	78.88
Cu	5.22	0.49	21.92	2.76	13.62	10.48	2.73	23.37	2.73	23.37
Pb	39.10	3.50	135.43	22.71	68.00	21.90	6.50	53.73	6.50	53.73
Cd	1.29	0.11	3.53	0.91	1.99	0.55	0.17	1.82	0.17	1.82
Ni	3.87	0.57	14.38	1.78	8.51	2.61	1.00	4.17	1.00	4.17
Cr	1.21	0.37	2.57	0.87	2.38	2.49	0.52	8.32	0.52	8.32
Co	2.37	0.17	8.67	0.53	8.00	2.00	0.80	4.99	0.80	4.99

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Material and Methods

6 samples (L/W/H 10 cm/10 cm/5 cm) taken from a surface layer in an open area without undergrowth were collected from each of four investigated sites located in the Tatra National Park's valleys: Chochołowska, Strążyska, Mała Łąka, and Kościeliska (Fig. 1).

After air-drying, milling, and sieving with 1 mm sieve, each sample was subjected to sequential extraction procedure according to Rudd's method (Rudd et al. 1988). In brief, 1 g of soil was exposed to the following solvents:

- for exchangeable form: 1,0 M KNO_3 ratio 1:40,
- for adsorbed form: 0,5 M KF (pH = 6,5) ratio 1:40,
- for organic solution: 0,1 M $Na_4P_2O_7$ ratio 1:40,
- for carbonates: 0,1 M EDTA (pH = 6,5) ratio 1:40,
- for sulfides: 6,0 M HNO_3 ratio 1:40.
- for residues: 5 ml HNO_3 (twice)

for 24 hours, centrifuged for 10 minutes (4000 rpm), rinsed with 25 cm³ of redistilled water, and centrifuged again for 5 mins (4000 rpm). Obtained extracts were acidified with 1% HNO_3 and subjected to measurements, and the residue treated with the next solvent. Three blank tests were prepared parallelly. All the reagents used in this study were spectrally pure and delivered by Merck.

An AAS spectrometer SP9 (Pye Unicam) was used to measure analytes concentrations in extracts – each result was calculated as an average of 6 samples after subtraction of the blank. Accuracy of the measurements amounted to 0,01 µg/g, and the recovery between 97-102%. Precision was controlled by using pattern solutions produced by WZORMAT, containing Pb, Cd, and Ni within the range of concentration in soil. Used methods were validated in collaboration with the Department of Inorganic Chemistry, The Silesian University of Technology, and varied in the range from 3.8% for Zn to 5.3% for Cr.

Results and Discussion

The remarks mentioned in the introduction regarding the bioavailability of selected metals in the soil should be considered as actual resources for the flora in selected types of forest complexes in Tatra National Park. In the four examined valleys, areas dominated by different tree species were identified in the following order: fir, beech, and spruce.

The original geochemical composition of the substrate, along with the involvement of wet atmospheric precipitation and metal compounds over a long period of time, has shaped the appropriate amounts of mobile compounds of individual metals in soils in uncontaminated areas (A), compared to soils in areas directly affected by industrial emissions (B) (Table 1) [30-35].

This has resulted in the occurrence of specific coexistence patterns. The presented relationships regarding exchangeable forms, adsorbed forms, organic compounds, and carbonates were statistically significant at $p \leq 0.05$ for values of $r = 0.30 – 0.45$ and $r = 0.5 – 0.80$ at $p \leq 0.01$, as well as $r > 0.90$ at $p \leq 0.008$, suggesting the presence of different relationships between the amounts of ions of individual elements in the soil, not only due to the nature of the given area (polluted, unpolluted), but also the chemical forms in which they occur.

In these areas, there is a characteristic interdependence between the changes in the content of Cd compounds and the changes in the content of Cr compounds. In polluted areas, this interdependence is described by a significant correlation coefficient of 0.77, while no interdependence was observed between these elements in exchangeable form in unpolluted areas. In unpolluted soils, the importance of the geochemical composition is emphasized by exchangeable forms of Mn and Co, Pb and Cd. The changes in the occurrence of exchangeable forms of Pb and Cd in unpolluted areas are described by a correlation coefficient of $r = 0.84$, while in polluted areas, it is $r = 0.68$ [36]. Similarly, the ion-exchange forms of Mn and Cd in unpolluted areas are described by a correlation coefficient approximately twice as high, equal to 0.5, compared to industrially unpolluted soils. In this regard, the common industrial origin of Cr and Pb is indicated by a correlation coefficient of 0.53 for polluted soils, whereas no such relationship is observed in unpolluted soils. This tendency in polluted soils also applies to the relationship in the occurrence of ion-exchange forms of Zn and Cd (0.78), which is not observed in unpolluted soils (exchangeable and adsorbed forms) [37]. The correlation coefficients regarding exchangeable forms, adsorbed forms, organic compounds, and carbonates listed in Table 2, confirm the distinct nature of selected interdependencies, which may affect the degree of availability of the investigated elements in their speciation forms during the toxicological phase.

A comparison of correlation coefficients also reveals the occurrence of characteristic mutual changes in the content or characteristic elements in selected chemical forms of their occurrence. The changes in the content of Mn, Cu, and PB in the adsorbed form in polluted soils, compared to unpolluted soils, are a good illustration of this observation. Another example of the distinctiveness of soils from industrially polluted areas compared to unpolluted areas is exemplified by the changes in the content of organic and carbonate forms of Zn with other investigated elements [30].

Using the example of soils subject to permanent industrial emissions and soils located at a large distance from the industrial center (80 km), it has been demonstrated that distinct chemical changes in the content of individual elements occur in different chemical forms in soils in areas with negligible industrial emissions, where sporadic long-range dust emissions occur. Such exemplary areas include the habitats of beech, spruce, and fir trees. Here, the soil in Tatra National Park (TPN) is characterized by

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Table 2. Correlations between metals in the soil in selected forms in non-urbanized and urbanized regions of Tatra National Park ($p \leq 0.05$ for $r \geq 0.30$).

	Urbanized area									
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Non-urbanized area	Exchangeable form									
	Cd			0.77			0.29		0.68	0.78
	Co						0.23			
	Cr								0.53	0.47
	Cu									
	Fe								0.22	0.21
	Mn		0.50							0.60
	Ni			0.34	0.63					
	Pb	0.84				0.45				0.22
	Zn		0.52		0.22		0.83			
	Adsorbed form									
	Cd		0.24	0.36			0.20			
	Co	0.58		0.30	0.26	0.28	0.32			
	Cr	0.26	0.42		0.55	0.64	0.91	0.42	0.44	
	Cu					0.92	0.59	0.51	0.80	
	Fe	0.32					0.71	0.54	0.85	
	Mn					0.79				
	Ni				0.29	0.29	0.52			0.44
	Pb					0.35	0.64	0.53		
	Zn						0.41	0.35	0.41	
	Organic solutions									
	Cd		0.59			0.24		0.21	0.59	0.45
	Co	0.30				0.25	0.27	0.34	0.55	0.24
	Cr	0.56			0.43	0.24	0.20			0.42
	Cu	0.26		0.38						0.40
	Fe						0.60	0.20	0.69	0.67
	Mn					0.55				0.52
	Ni	0.25								
	Pb						0.37			0.72
	Zn					0.42	0.46	0.32	0.20	
	Carbonates									
	Cd			0.38	0.51	0.22	0.58		0.76	0.61
	Co				0.48		0.65		0.41	0.32
	Cr		0.25		0.42	0.36	0.54		0.39	0.45
	Cu	0.34	0.20	0.31		0.73	0.72		0.47	0.54
	Fe	0.62		0.29	0.61		0.45			0.24
	Mn									0.72
	Ni					0.27	0.51			
	Pb		0.26	0.23	0.46	0.48	0.28	0.22		0.63
	Zn		0.39		0.57	0.31		0.25	0.63	

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Table 3. Co-occurrence of metals in bioavailable form in the soil in habitat of selected species of trees in non-urbanized and urbanized regions of the Tatra Mountain National Park.

	Chochołowska V.			Kościeliska V.		
	Sycamore	Beech	Spruce	Sycamore	Beech	Spruce
	Fe					
Mn	0.56	0.20	0.49	0.38	0.86	0.98
Zn	0.82	0.49	0.86	1.00	0.89	0.87
Cu	0.51		0.46	-0.59	0.82	0.75
Pb	0.19	-0.75	0.94	0.95	0.86	-0.34
Cd	0.30	-0.38	-0.42		0.92	0.61
Ni		0.70		-0.43	0.30	0.56
Cr	0.74		0.65	-0.58	0.56	
	Mn					
Zn		0.27	0.74	0.37	0.72	0.86
Cu	-0.42	0.42	0.60	-0.92	0.97	0.80
Pb	-0.41	0.50	0.58	0.23	0.60	-0.51
Cd	0.92	0.37	-0.60		0.91	0.76
Ni	0.23		0.27	-0.51	0.49	0.57
Cr		0.28	0.49	-0.78	0.68	0.16
Co		0.53			0.93	-0.68
	Zn					
Mn		0.27	0.74	0.37	0.72	0.37
Cu	0.89	0.84	0.29	-0.58	0.78	-0.58
Pb	0.36	-0.43	0.97	0.95	0.98	0.95
Cd	-0.30	-0.80	-0.26		0.94	
Ni	-0.30	0.91		-0.43	0.60	-0.43
Cr	0.81	0.81	0.38	-0.58	0.78	-0.58
Co	-0.42	0.94			0.50	
	Cu					
Mn	-0.42	0.42	0.60	-0.92	0.97	0.80
Zn	0.89	0.84	0.29	-0.58	0.78	0.38
Pb	0.63		0.26	-0.37	0.66	-0.74
Cd	-0.64	-0.52	-1.00		0.94	0.83
Ni	-0.24	0.54	0.91	0.30	0.68	0.93
Cr	0.81	0.99	0.96	0.63	0.83	-0.27
Co	-0.51	0.93			0.82	-0.92
	Pb					
Mn	-0.41	0.50	0.58	0.23	0.60	-0.51
Zn	0.36	-0.43	0.97	0.95	0.98	-0.15
Cu	0.63		0.26	-0.37	0.66	-0.74
Cd	-0.31	0.76	-0.23		0.87	-0.94
Ni	0.56	-0.77		-0.58	0.49	-0.57

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Table 3. Table continued.

Cr	0.80		0.42	-0.62	0.69	-0.19
Co	-0.92				0.41	0.94
	Cd					
Mn	0.92	0.37	-0.60		0.91	0.76
Zn	-0.30	-0.80	-0.26		0.94	0.46
Cu	-0.64	-0.52	-1.00		0.94	0.83
Pb	-0.31	0.76	-0.23		0.87	-0.94
Ni	0.53	-0.90	-0.92		0.64	0.60
Cr	-0.13	-0.57	-0.94		0.83	0.27
Co		-0.57			0.73	-0.95
	Ni					
Mn	0.23		0.27	-0.51	0.49	0.57
Zn	-0.30	0.91		-0.43	0.60	0.08
Cu	-0.24	0.54		0.30	0.68	0.93
Pb	0.56	-0.77	0.91	-0.58	0.49	-0.57
Cd	0.53	-0.90			0.64	0.60
Cr	0.30	0.53	-0.92	0.93	0.96	-0.60
Co	-0.71	0.72	0.84		0.15	-0.80
	Cr					
Mn		0.28	0.49	-0.78	-0.78	0.16
Zn	0.81	0.81	0.38	-0.58	-0.58	0.48
Cu	0.81	0.99	0.96	0.63	0.63	-0.27
Pb	0.80	0.07	0.42	-0.62	-0.62	-0.19
Cd		-0.57	-0.94			0.27
Ni	0.30	0.53	0.84	0.93	0.93	-0.60
Co	-0.87	0.88				

separate correlation coefficients, and clearly different total contents of individual metals in selected forms of occurrence, roles, and contributions of compounds of individual elements in shaping chemical equilibrium are observed. This diversity deepens the different nature of interdependencies in the tree-root-soil system between individual chemical forms of elements in the TPN area (Table 3).

In general, the largest amount of significant directly proportional changes in element content in the soil in the TPN area concerned carbonates. When comparing the respective correlation coefficients (Table 3), the greatest orderliness in occurrence changes was related to indirectly bioavailable forms of individual metal ions. For plants in the rhizosphere, changes in the content of exchangeable forms of metal ions Pb, Cd, and Mn with Zn compounds, are of significant importance. The role of these relationships regarding the adsorbed form of Pb is much weaker (r = 0.26 – 0.36).

The specified interdependencies of a certain magnitude (Tab. 4) determine the significant chemoeconomic differences between these forest complexes in the TPN [38-42].

Mineralogical studies generally indicate the significant role of the system of Fe and Mn oxides in soils in the TPN area in the process of accumulating other ions in relation to changes in soil mineral structure (Tab. 4). This is confirmed by the results of bivariate correlation analysis describing changes in the content of Fe and Mn compounds in the beech forest complex in the Chochołowska Valley, Kościeliska Valley, Strążyska Valley, Mała Łąka Valley, and beech habitats. However, this observation was not confirmed in the spruce forest complexes in the Strążyska Valley.

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Another characteristic set of elements participating in common content changes in the soil is Fe-Zn and Fe-Cu. The Fe-Zn relationship strongly occurred in soils in all valleys, regardless of the tree species composition, except for the spruce forest complex in the Strążyska Valley.

Uniform changes in Fe and Pb content (r = 0.64 – 0.95) occurred in soils in the beech forest complexes in the Strążyska Valley and Mała Łąka Valley, and in the case of beech forest complexes in the Kościeliska Valley and Strążyska Valley (r = 0.84), proportional changes in the content of Fe and Pb compounds were observed. Proportional changes in the content of Fe and Cr compounds were observed in beech and spruce habitats in the Chochołowska Valley (r = 0.74 and 0.53) and beech and spruce habitats in the Mała Łąka Valley (r = 0.65 and 0.87). In general, the greatest role of Fe compounds in relation to the compounds of individual elements in the soil was observed in the Kościeliska Valley, regardless of the type of forest complex. Significant correlation coefficients characterizing directly proportional changes ranged from 0.38 to 1.0.

Physiologically important relationships between Fe compounds and other metals, observed at the level of absorption by the underground organs of trees, were found in the beech forest complex in the Kościeliska and Strążyska Valleys [43-47]. Notably, a significant Fe and Cu antagonism in soil was observed in the habitat of beech trees in the Kościeliska Valley (-0.59). A similar antagonism between Fe and Cu ions was found in soils of the beech forest complex in the Strążyska Valley. Strong antagonistic relationships, described by values ranging from r = -0.67 to (-0.98), were observed between Fe and Ni in the spruce forest complexes in the Strążyska Valley and Mała Łąka Valley. Additionally, in the beech forest complexes in the Chochołowska Valley (-0.46) and the spruce forest complex in the Kościeliska Valley (-0.55), antagonistic relationships between Fe and Ni occurred in the soils [48]. The ions Zn, Cu, Cd, and Ni showed high affinity for Mn compounds in the beech forest complex in the Strążyska Valley. On the other hand, in the soils of the Mała Łąka Valley, Mn compounds changed directly proportionally to the variations in the content of Zn, Pb, Cd, Ni, and Cr. The simultaneous changes in the content of Mn and Zn compounds in the habitat of beech trees were only absent in the soils of the Chochołowska Valley. For comparison, a significant Mn-Zn relationship was confirmed in the beech and spruce forest complexes in all examined valleys. Furthermore, in the beech forest complex in the Kościeliska Valley, changes in the content of Mn compounds encompassed all the analyzed elements (r = 0.49), with Ni and Cu exhibiting a negative correlation coefficient (r = -0.97). The spruce and beech forest complexes in the Chochołowska and Kościeliska Valleys, as well as the spruce and beech forests in the Mała Łąka Valley, simultaneously displayed characteristic relationships between Mn and Cd ions. The changes in Co content were ambiguous in relation to Mn and Fe compounds.

In summary, it should be emphasized that each forest complex will have a specific characteristic regarding the total content of selected metal compounds. Regardless of the geochemical characteristics of the substrate, these large forest complexes can, over a long period of time, develop distinct patterns of co-occurrence of metals in the soil within the tree's rooting zone [49]. The specific interaction of soil solution, and indirectly the soil pH, can significantly influence the accumulation of selected metals in the soil, concerning the content of Fe and Mn compounds. Consequently, this can differentially affect their content in the soil and, as a result, shape the specific co-occurrence of the analyzed elements in the soil. This specific co-occurrence often determines the mobility and bioavailability of individual elements in competition for underground tree organs as receptors [50].

In the context of these remarks and the presented statistical calculations, a significant chemical-ecological distinctiveness of Tatra National Park is evident in comparison to polluted natural environments. This confirms that each natural area should primarily be characterized by the amount of bioavailable forms of individual metals and the nature of their co-occurrence in the rooting zone within one ecosystem [51-53]. Tatra National Park exhibits a significant variation in the individual forest complexes concerning their secondary interactions and species composition of trees.

Conclusions

The mineral composition of the soils of Tatra National Park varies in different valleys and the impact of human activities in the Kościeliska Valley can be clearly seen. Elevated levels of all speciation forms of Cu, Pb, and Cr, as well as of Cd and Co in their exchangeable forms were revealed in the urbanized part of the park. It was observed that with a change in the elemental soil composition, as well as in different trees' complexes, different relationships between chemical forms of various metals occurred.

Acknowledgment

The authors would like to thank Mrs. Jolanta Kowol and Renata Musielińska for their participation in the analytical work.

Conflict of Interest

The authors declare no conflict of interest.

References

1. KORZENIOWSKA J., KRĄŻ P. Heavy Metals Content in the Soils of the Tatra National Park Near Lake Morskie

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

Oko and Kasprowy Wierch - A Case Study (Tatra Mts, Central Europe). Minerals. **10** (12), 1120, **2020**.
2. ZENG X., JIN Q., WANG P., HUANG C. Distribution and Speciation of Heavy Metal(loid)s in Soils under Multiple Preservative-Treated Wooden Trestles., Toxics. **11** (3), 249, **2023**.
3. VAMERALI T., BANDIERA M., LUCCHINI P., DICKINSON N.M., MOSCA G. Long-term phytomanagement of metal-contaminated land with field crops: Integrated remediation and biofortification. European Journal of Agronomy. **53** 56, **2014**.
4. AROH K. Globalization, industralization and population growth the fundamental drivers of pollution in a given society (India). Available at SSRN: 10.2139/ssrn.3453740, **2018**.
5. MANIMARAN K., PRABU V.A. Effect of cadmium on growth, chlorophyll a and biomass production of Tetraselmis Sp. International Journal of Pharmaceutical, Biological and Chemical Sciences. **2** (4), 26, **2013**.
6. AISSA L., KÉLOUFI B. Determining the Heavy Metal Pollution in Mascara (Algeria) by Using Casuarina equisetifolia. Ecologia Balkanica. **4** (1), 1, **2012**.
7. STANISLAWSKA-GLUBIAK E., KORZENIOWSKA J., KOCON A. Effect of the reclamation of heavy metal-contaminated soil on growth of energy willow. Polish Journal of Environmental Studies. **21** (1), 187, **2012**.
8. SYSO A., SOKOLOV V., PETUKHOV V., LEBEDEVA M., CHEREVKO A. Ecological and biogeochemical evaluation of elements content in soils and fodder rasses of the agricultural lands of Siberia. Journal of Pharmaceutical Sciences and Research. **9** (4), 368, **2017**.
9. HUSSA ARA BEGUM M.H., ZAMAN K., SHINWARI Z.K., HUSSAIN A. Heavy metal analysis in frequently consumable medicinal plants of Khyber Paktunkhwa, Pakistan. Pakistan Journal of Botany. **49** (3), 1155, **2017**.
10. NAS F., ALI M. The effect of lead on plants in terms of growing and biochemical parameters: a review. MÓJ Ecology and Environmental Sciences. **3** (4), 265, **2018**.
11. TCHOUNWOU P.B., YEDJOU C.G., PATLOLLA A.K., SUTTON D.J. Heavy metal toxicity and the environment. Molecular, Clinical and Environmental Toxicology. **101** 133, **2012**.
12. ASLAM M., ASLAM A., SHERAZ M., ALI B., ULHASSAN Z., NAJEEB U., ZHOU W., GILL R.A. Lead toxicity in cereals: Mechanistic insight into toxicity, mode of action, and management. Frontiers in Plant Science. **11,** 1, **2021**.
13. ZHANG J., LJU K., HE X., LI W., ZHANG M., CAI Q. Evaluation of heavy metal contamination of soil and the health risks in four potato-producing areas. Sec. Toxicology, Pollution and the Environment. **11**, **2023**.
14. BARTKOWIAK A., PIĄTEK M. Analysis of heavy metal content in soil fertilised with fresh and granulated digestate. Mercury (Hg), **29,** 3517, **2020**.
15. MUNAWER M.E. Human health and environmental impacts of coal combustion and post-combustion wastes. Journal of Sustainable Mining. **17** (2), 87, **2018**.
16. HARMANPREET K., RAKESH S., PANKAJ S. Effect of Hoagland solution for growing tomato hydroponically in greenhouse. HortFlora research Spectrum. **5** (4), 310, **2016**.
17. TUNÇTÜRK M., ERYIĞIT T., KAYA A.R. Nutritional properties, minerals, and selected heavy metal contents in herby cheese plants of Lamiaceae. Applied Biological Chemistry. **60** (1), 41, **2017**.
18. ASHRAF U., KANU A.S., MO Z., HUSSAIN S., ANJUM S.A., KHAN I., ABBAS R.N., TANG X. Lead toxicity in rice: effects, mechanisms, and mitigation strategies – a mini review. Environmental Science and Pollution Research. **22** (23), 18318, **2015**.
19. ZHONG M.Y., ZHANG X.Q., YANG X.Y., HU Y.Y., JIANG X., LIE G. Recent advances in plant response to chromium stress. Pratacultural. Sci. **36**, 1962, **2019**.
20. KRZESŁOWSKA M. The cell wall in plant cell response to trace metals: polysaccharide remodeling and its role in defense strategy. Acta Physiologiae Plantarum. **33** (1), 35, **2011**.
21. PIRŠELOVÁ B., MISTRÍKOVÁ V., LIBANTOVÁ J., MORAVČÍKOVÁ J., MATUŠÍKOVÁ I. Study on metal-triggered callose deposition in roots of maize and soybean. Biologia. **67** (4), 698, **2012**.
22. GÜLER E.A. Determination effect of increased levels of cadmium and lead on plant growth and mineral contents of some maize and sunflower genotypes growing in nutrient culture. PhD Thesis /Atatürk Üniversitesi / Institute of natural and Applied Sciences, Department of Soil Science and Plant Nutrition. **2011**.
23. İĞDELIOĞLU S. Genotoxic and physiological effects of lead (Pb) element in Rye (*Secale cereale* L.) plant, Master Thesis, Marmara University/Institute of natural and Applied Sciences/Department of Biology. **2014**.
24. PARK W., HAN K.-H., AHN S.-J. Differences in root-to-shoot Cd and Zn translocation and by HMA3 and 4 could influence chlorophyll and anthocyanin content in Arabidopsis Ws and Col-0 ecotypes under excess metals. Soil Science and Plant Nutrition. **58** (3), 334, **2012**.
25. MAZUREK R., KOWALSKA J., GĄSIOREK M., ZADROŻNY P., JÓZEFOWSKA A., ZALESKI T., KĘPKA W., TYMCZUK M., ORŁOWSKA K. Assessment of heavy metals contamination in surface layers of Roztocze National Park forest soils (SE Poland) by indices of pollution Chemosphere, **168**, 839, **2017**.
26. LEE S.H., ASHAARI Z., LUM W.C., ABDUL HALIP J., ANG A.F., TAN L.P., CHIN K.L., TAHIR P. Thermal treatment of wood using vegetable oils: A review. Constr. Build. Mater. **181**, 408, **2018**.
27. XIU ZENG, QIAN JIN, PANPAN WANG, CHENGMIN HUANG. Distribution and Speciation of Heavy Metal(loid)s in Soils under Multiple Preservative-Treated Wooden Trestles.
28. GAO R., HUANG Y., GAN W., XIAO S., GAO Y., FANG B., ZHANG X,. LYU B., HUANG R., LI J. Superhydrophobic elastomer with leaf-spring microstructure made from natural wood without any modification chemicals. Chem. Eng. J., **442**, 136338, **2022**.
29. ERYIĞIT T. The Total Environment. 468, 8433, **2014**.
30. SAMECKA-CYMERMAN A., KOLON K., KEMPERS A.J., PIEKARSKA-STACHOWIAK A. Heavy metal contamination of the Tatra National Park in Poland: An effect of human activity and abiotic factors. Environmental Monitoring and Assessment. **190** (3), 149, **2018**.
31. ZIEMBIŃSKA K., SAMECKA-CYMERMAN A., KOLON K. Bioaccumulation of heavy metals by Vaccinium myrtillus L. in the Tatra National Park, Poland. Environmental Science and Pollution Research. **25** (2), 1370, **2018**.
32. KEMPERS A.J., GĄSIOREK M., SAMECKA-CYMERMAN A., KOLON K. Are endemic Tatra violets endangered by the heavy metal pollution? Environmental Science and Pollution Research. **26** (2), 1853, **2019**.

Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy • Author Copy

33. BINKOWSKI Ł. J., SŁOWIŃSKI M., MEISSNER W., BABCZYŃSKA-SENDEK, B., MICHALIK M. Heavy metal pollution in the High Tatras (the Tatra Mountains, Slovakia/Poland): Concentrations, distribution, and sources. Environmental Geochemistry and Health. **41** (4), 1585, **2019**.
34. FABIJAŃCZYK P., ZIÓŁKOWSKA M., BIZIUK M., MECHLINSKA A. Assessment of metal pollution in the High Tatra Mountains (Slovakia/Poland) using tree rings of Pinus mugo Turra. Environmental Monitoring and Assessment. **192** (4), 1, **2020**.
35. KOLON K., KEMPERS A.J., SAMECKA-CYMERMAN A., STANKIEWICZ A., GÓRALSKI G. Spatial distribution of heavy metal pollution in soil of the Tatra National Park (Poland). Environmental Monitoring and Assessment. **192** (1), 1, **2020**.
36. FAROOQ M.A., PRASAD M.N.V., LI Y. Cadmium uptake, toxicity, and detoxification in plants: Insights for improving food safety. International Journal of Environmental Research and Public Health. **15** (2), 209, **2018**.
37. CUI L., PAN G., LI L., YAN J., ZHANG A., BIAN R., ZHENG J. Effects of biochar on mobility and bioavailability of heavy metals (Cd, Cu, Pb, and Zn) in contaminated soil. Environmental Science and Pollution Research. **28** (8), 10313, **2021**.
38. MAŁECKA-ADAMOWICZ M., KICIŃSKA A., SMOLEŃ S. Heavy metal accumulation in different components of Norway spruce ecosystems in the Tatra Mountains. Environmental Science and Pollution Research. **25** (3), 2308, **2018**.
39. SAMECKA-CYMERMAN A., STANKIEWICZ A., KOLON K. Bioindication of trace metals with epiphytic lichens in Tatra National Park, Poland. Environmental Monitoring and Assessment. **190** (11), 666, **2018**.
40. KWIECIŃSKA-POPPE E., CISZEK D., BUJAKIEWICZ A., PAJĄK M. Comparison of the content of heavy metals in tree stands of various ages in the Gąsienicowa Valley in the Tatra National Park. Sustainability. **12** (15), 6122, **2020**.
41. ZIÓŁKOWSKA M., BIZIUK M., MECHLINSKA A. The content of heavy metals in tree rings as a potential indicator of environmental pollution in the Tatra National Park. Environmental Monitoring and Assessment. **192** (10), 646, **2020**.
42. FABIJAŃCZYK P., ZIÓŁKOWSKA M., BIZIUK M., MECHLINSKA A. Using tree rings of Pinus mugo Turra as an indicator of metal contamination in Tatra National Park. Environmental Monitoring and Assessment. **193** (4), 190, **2021**.
43. SAMECKA-CYMERMAN A., KOLON K., KEMPERS A.J., STANKIEWICZ A. The influence of soil properties on the bioaccumulation of heavy metals by *Vaccinium myrtillus* L. in the Tatra National Park, Poland. Environmental Science and Pollution Research. **24** (11), 10201, **2017**.
44. KEMPERS A.J., SAMECKA-CYMERMAN A., KOLON K., PIEKARSKA-STACHOWIAK, A. Variations in metal uptake by coniferous tree species growing in polluted areas. Environmental Science and Pollution Research. **25** (17), 17091, **2018**.
45. SZAJDAK L.W., CZEKAŁA W., ZALESKI T. The effect of liming and fertilization on the content of heavy metals in beech (*Fagus sylvatica* L.) and pine (*Pinus sylvestris* L.) stands. Journal of Elementology. **24** (2), 507, **2019**.
46. STANKIEWICZ A., KEMPERS A.J., SAMECKA-CYMERMAN A., KOLON K. Ecophysiological aspects of metal accumulation by Vaccinium myrtillus L. in the Tatra National Park, Poland. Environmental Science and Pollution Research. **27** (30), 37677, **2020**.
47. KEMPERS A.J., SAMECKA-CYMERMAN A., KOLON K., KEMPERS R.S. The role of underground organs of trees in metal accumulation in a forest ecosystem in the Tatra National Park, Poland. Environmental Science and Pollution Research. **28** (3), 3629, **2021**.
48. QIAN L., ZHANG W., YAN J., XU R., CHEN Y., ZHU Y., ZHANG X. Fractionation, speciation, and ecological risk assessment of heavy metals in the sediments of the Yangtze Estuary. Marine Pollution Bulletin. **142**, 320, **2019**.
49. GARMO Ø. A., DE WIT H. A., COLOMBO L., CURTIS C., FÖLSTER J., HOFFMANN A., WRIGHT R. F. Long-term monitoring of the water chemistry in acid-sensitive Norwegian lakes shows slow recovery, but high sensitivity to atmospheric deposition. Environmental Science and Technology. **53** (1), 194, **2019**.
50. TAN X., LIU Y., GU Y., ZENG G., WANG X., HU X., HE Y. Heavy metal pollution, ecological risk assessment, and spatial distribution of forest soils in the Pearl River Delta, South China. Ecological Indicators. **126**, 107641, **2021**.
51. SYSO A., SOKOLOV V., PETUKHOV V., LEBEDEVA M., CHEREVKO A. Ecological and biogeochemical evaluation of elements content in soils and fodder grasses of the agricultural lands of Siberia. Journal of Pharmaceutical Sciences and Research. **9** (4), 368, **2017**.
52. ASLAM M., ASLAM A., SHERAZ M., ALI B., ULHASSAN Z., NAJEEB U., ZHOU W., GILL R.A. Lead toxicity in cereals: Mechanistic insight into toxicity, mode of action, and management. Frontiers in Plant Science. **11** (1), **2021**.
53. ASHRAF U., KANU A.S., MO Z., HUSSAIN S., ANJUM S.A., KHAN I., ABBAS R.N., TANG X. Lead toxicity in rice: effects, mechanisms, and mitigation strategies – a mini review. Environmental Science and Pollution Research. **22** (23), 18318, **2015**.