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Heavy Metals Content in the Soils of the Tatra National Park Near Lake Morskie Oko and Kasprowy Wierch—A Case Study (Tatra Mts, Central Europe)

Joanna Korzeniowska *  and Paweł Kraż * 

Institute of Geography, Pedagogical University of Krakow, 30-084 Krakow, Poland

* Correspondence: joanna.korzeniowska@up.krakow.pl (J.K.); pawel.kraz@up.krakow.pl (P.K.);

Tel.: +48-12-662-62-61 (J.K. & P.K.)

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Abstract: This paper presents the content of selected heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in the soils of the Tatra National Park (TNP). In order to determine the anthropogenic impact on the environment, the following coefficients were calculated: enrichment factors (EF), geoaccumulation index (Igeo), contamination factor (Cf), degree of contamination (C_d), and modified degree of contamination (mC_d). It turned out that in the Kasprowy Wierch and Lake Morskie Oko test areas, the content of metals in the soil decreases with the increasing altitude above sea level. In both regions, the highest concentrations of cadmium and lead were found, for which the coefficients indicated significant environmental pollution. These metals, since they persist in the atmosphere for a long time and have a small particle diameter, can be moved over long distances. Long-range emission contributes to environmental contamination on a global scale. Under the influence of such emissions, even protected areas such as the Tatra National Park, considered to be of natural value, are exposed to the effects of human activities (industry in general, automotive industry in particular).

Keywords: heavy metals; soil; enrichment factor; geoaccumulation index; contamination factor

1. Introduction

Heavy metals pose a great threat to the natural environment [1,2]. The toxicity of metals results not only from the degree of environmental contamination, but above all from the biochemical role they play in metabolic processes. Heavy metals, such as: Cd, Cr, Cu, Ni, Pb, and Zn, pose a particularly high risk of chemical imbalance in ecosystems, if they are introduced in significant amounts [3].

Dust in the atmosphere, containing heavy metals, gets into the soil and falls on the above-ground parts of plants. As a result, the concentration of heavy metals in these elements of the environment increases. Natural contents of heavy metals in soils are closely related to the type of soil [3–5].

The sources of metals in the soil are bedrock material and atmospheric pollution caused by anthropogenic activities (emissions from the industrial and automotive sector). Heavy metals can travel long distances from emitters [6,7]. The spread of heavy metals over long distances is related to the long duration of dust pollution in the atmosphere. The length of time of particulate matter remaining in the atmosphere depends on the size of these particles, the terrain configuration, and the weather conditions. Low pressure, strong wind, considerable cloud cover and high precipitation contribute to the spread of pollutants over long distances [8]. The length of time of heavy metals remaining in the environment differs for individual metals. The metals that remain in the atmosphere for a long time and have a very small diameter of particles are lead and cadmium. Lead and cadmium are easily transported over long distances and, therefore, cause environmental contamination on a global scale [8,9].

Research on the content of heavy metals in the Tatra National Park (TNP) area was conducted by numerous teams. The Tatra National Park is a good place to conduct research aimed at assessing the scale of pollution introduced into this area, as for many years it has not been directly affected by human activity. The research area is diversified in terms of natural conditions determined by large differences in altitude. In Poland, the authors who investigated the relationship between height above sea level and the content of heavy metals in soils included Kubica et al. [10,11], Miechówka et al. [12,13]. Kubica et al. [10,11] investigated the concentrations of selected radionuclides and heavy metals (Zn, Pb, Cd, Ni, and Fe) in soil samples in the Kościeliska, Rybi Potok, and Chochołowska Valleys. The concentration of heavy metals in forestless soils was investigated by, e.g., Miechówka et al. [12]. The same team [13] analyzed the concentrations of heavy metals in rocky initial rendzinas (Lithic Leptosols). Wieczorek and Zadrożny [14] conducted an analysis of the content of Cd, Pb, and Zn only in podzolic soils in selected areas of the Tatra National Park. In the Slovak part of the Tatra National Park, related research was carried out by, among others, Barančoková et al. [15]. Similar studies have been conducted also in other protected areas in the Polish Carpathians, including in the Bieszczady National Park [16,17] and other parts of the main ridge of the Flysch Carpathians [18].

The aim of this study is to determine the effect of altitude on the content of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in soils in mountain areas.

2. Materials and Methods

2.1. Study Area

The Tatra National Park is one of 23 national parks in Poland, where high-mountain relief is provided, and valuable species of plants and animals (including endemics and relics) are protected. The research area is located in the Polish part of the Central Western Carpathians, in the northern part of the Tatra Range macroregion [19] and it is the highest part of the entire Carpathians. The specificity of this area is the complex geological structure [20–22], land relief heterogeneity (fluvial-denudation, karst, and glacial) [23–25], climatic conditions changing with the increase in altitude above sea level (air temperature, total precipitation, etc.). The specificity of the climate of the Tatra Range is determined by the incidence of different air masses. Arctic maritime air masses (PPm) have the largest share in the formation of weather, i.e., 65% of days a year, while continental polar air masses (PPk) approximately 20% of days a year [26,27]. The above elements determine the specificity of water circulation (spatially diversified possibility of water retention, the volume of runoff, water chemistry, etc.). The soil cover of the Tatra Mountains is strongly related to, among others, their geological substrate, morphogenetic processes, and climatic conditions, and its characteristic feature is openwork, as well as poorly developed soils (i.e., initial soils) [28]. All the physico-geographical zones, characteristic of high mountain areas, have developed in the Tatra Mountains. Two test areas (Figure 1) in the Tatra National Park in Poland, on the northern slope of the Tatra Mountains, were selected for the study. These areas were selected owing to the diversity of the natural environment, including the physico-geographical location, landscape zone, and geological structure. The test areas were given working names—Kasprowy Wierch (KW) and Morskie Oko (MO).

2.1.1. Kasprowy Wierch (KW) Tested Area

The area is located within two physico-geographical mesoregions—the Regłowe Tatras (collection points 1–4) and the Western Tatras (collection points 5–8) [29], and it ranges from the forest zone to the alpine zone. It is characterized by high lithological and tectonic diversity. This affects, among other matters, the lack of overlapping of the topographic watershed with the underground watershed. The area belongs to the Bystra catchment (with the Potok Jaworzynka sub-catchment) and the Sucha Woda Gąsienicowa catchment, which is part of the Dunajec basin. Depending on the altitude, the mean annual air temperature ranges from 0 to 6 °C [30], the annual total precipitation ranges from 800 to 1800 mm, and the length of the snow cover deposition ranges from 100 to 200 days a

year [31]. The soil cover is varied and dominated by the following soils: Fluvisols, Rendzic Leptosols, Folic Rendzic Leptosols, Cambic Rendzic Leptosols, Haplic Cambisols (Eutric), Haplic Podzols (Skeletal), Entic Podzols, Leptic Podzols, and Folic Leptosols [32]. The height difference within the sampling points is 750 m (1100–1850 m above sea level).

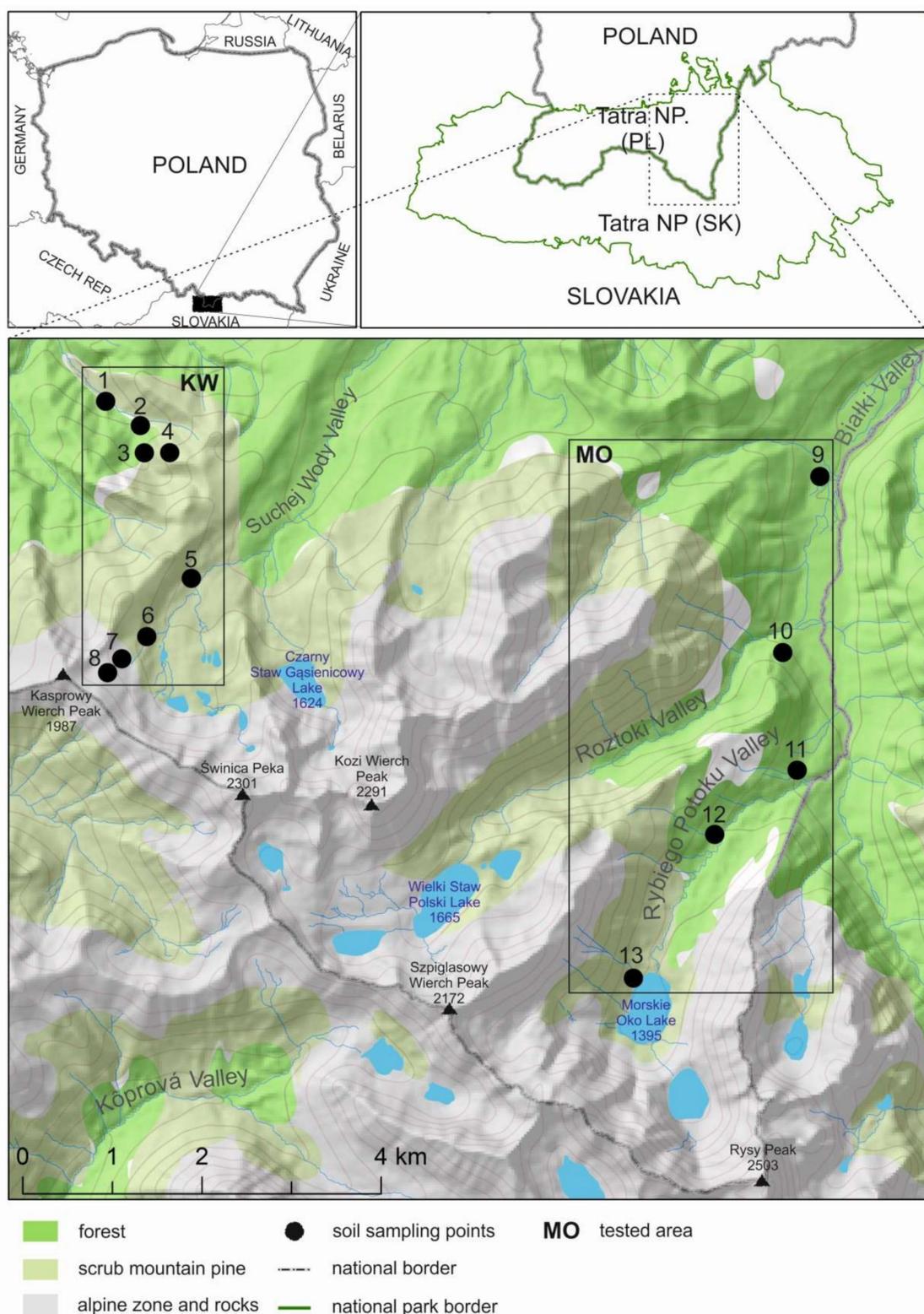


Figure 1. Location of the tested area on the background of the map of Poland and Tatra National Parks.

2.1.2. Morskie Oko (MO) Tested Area

The area is located within the High Tatras in the Białka catchment (the Dunajec river basin) drained by the Rybi Potok, Roztoka, and Białka. With regard to the zonality of the environment, it is entirely located within the forest zone. It is part of one of the largest U-shaped valleys in the Tatras. Depending on the altitude, the mean annual air temperature ranges from 2 to 4 °C [30], the annual total precipitation ranges from 1000 to 1400 mm, and the length of snow cover deposition ranges from 120 to 160 days a year [31]. The dominant soils in this part are, among others: Haplic Podzols (Skeletal), Haplic Cambisols (Dystric, Skeletal), Lithic Leptosols, and Regosols (Hyperskeletal) [32]. The height difference within the sampling points is 400 m (1000–1400 m above sea level).

2.2. Sampling and Analysis

2.2.1. Sampling

Top soil samples (0–10 cm) were taken from the Kasprowy Wierch and Morskie Oko tested areas in the Tatra National Park. The samples were taken every 100 m of altitude, starting from 1100 m above sea level for KW and from 1000 m above sea level for MO. During the field tests, a total of 130 soil samples were collected, 10 from each point (80 for KW, 50 for MO). The field tests were carried out on 4 September 2019 (KW), and 5 September 2019 (MO). The average temperature during the sampling was 10 °C and no precipitation was recorded. The characteristics of the sampling sites and the adopted designations are presented in Table 1.

Table 1. Selected characteristics of soil sampling points in the Kasprowy Wierch (KW) and Morskie Oko (MO) tested areas.

Test Area	Sample No.	Altitude (m asl)	Geographical Coordinates	Geological Structure [21,22]	Physico-Geographical Mesoregion [19]
KW	1	1100	49°15.572' N 19°59.322' E	Boulders, gravel, sand, and silts of stones and river terraces 0.5–3.0 m high, e.g., rivers (Holocene)	Reglowe Tatras
	2	1200	49°15.424' N 19°59.645' E	Dolomites, limestones, siltstones, and breccia (Lower Triassic)	Reglowe Tatras
	3	1300	49°15.254' N 19°59.681' E	Dolomites, limestones, siltstones, and breccia (Lower Triassic)	Reglowe Tatras
	4	1400	49°15.252' N 19°59.908' E	Dolomites and limestones, undivided (Middle Triassic)	Reglowe Tatras
	5	1550	49°14.497' N 20°00.097' E	Boulders, moraine rock debris, clayey (Pleistocene)	Western Tatras
	6	1650	49°14.133' N 19°59.671' E	Porphyry granites (Carbon)	Western Tatras
	7	1750	49°14.013' N 19°59.446' E	Boulders and rock debris of rubble cones (screes) (Quaternary)	Western Tatras
	8	1850	49°13.927' N 19°59.301' E	Boulders and rock debris of rubble cones (screes) (Quaternary)	Western Tatras
MO	9	1000	49°15.065' N 20°05.898' E	Boulders, gravel, sand, clayey sands and silts of cones, of fluvioglacial levels and terraces 12.0–15.0 m high, e.g., rivers (Pleistocene)	High Tatras
	10	1100	49°13.984' N 20°05.524' E	Granodiorites and tonalities, equal grained, grey (Carbon)	High Tatras
	11	1200	49°13.270' N 20°05.647' E	Boulders, moraine rock debris, clayey (Pleistocene)	High Tatras
	12	1300	49°12.893' N 20°04.867' E	Boulders, rock debris and silts of dump and alluvial cones (Pleistocene–Holocene)	High Tatras
	13	1400	49°12.021' N 20°04.115' E	Boulders, rock debris and silts of dump and alluvial cones (Pleistocene–Holocene)	High Tatras

2.2.2. Chemical Analysis

In order to determine the content of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in the sampled soil material (topsoil, up to 10 cm), the following laboratory work was carried out, in accordance with the methodology used for collecting and preparing samples for chemical analyses [33,34]:

- Cleaning the collected samples by removing foreign material (dry leaves, twigs, grass, etc.);
- Drying the samples at 70 °C;
- Grinding soil samples in a ceramic mortar and sieving through a sieve with a mesh diameter of 2 mm;
- Mineralization, which is performed to completely break down soil samples into simple, solid compounds—1 g of the dried sample material was treated with a mixture of acids and aqua regia in the proportion (1:1:1 HNO₃:HCl:H₂O). The resulting solution was filtered and stored in sealed polyethylene containers until sent for spectrometric analysis;
- Determination of the total content of heavy metals using the inductively coupled plasma mass spectrometry (ICP-MS) method in the Bureau Veritas laboratory. The use of the Bureau Veritas methodology made it possible to accurately determine the metal content in the soil material, with the following detection limits (µg/g dm) for Cd: 0.01, Cr: 0.5, Cu: 0.01, Ni: 0.1, Pb: 0.01 and Zn: 0.1.

2.2.3. Soil Pollution Indicators

There are many indices for determining the degree of soil contamination with heavy metals [35]. This work focused on the enrichment factor, geoaccumulation index, and contamination factor. As reference values (background) for the obtained results, the concentrations of metals in the soils of Europe given in the Geochemical Atlas of Europe [36,37] were adopted. On the other hand, to calculate the enrichment factor, the average Earth's crust values for granite rocks were used, given by Turekian and Wedepohl [38] and Wedepohl [39]. The average concentrations of metals in the soil (background) for the selected research area and Earth's crust for granitic rocks are presented in Table 2.

Table 2. Mean metal concentrations (background values) in soils according to Salminen et al. [37] and average Earth's crust according to Turekian and Wedepohl [38].

Element	Background Values (mg·kg ⁻¹)	Average Earth's Crust for Granitic Rocks (mg·kg ⁻¹)
Cd	0.14	0.13
Cr	21.5	13
Cu	15.8	14
Ni	21.9	15
Pb	22.8	17.5
Zn	54.6	50
Fe (%)	2.50	2.3

Enrichment Factor (EF)

The enrichment factor (EF) is used to determine the anthropogenic effect on soil contamination with heavy metals [40]. The recommended reference element—iron (Fe) [41], is used to calculate the index. Fe is recommended because it does not take an active part in biogeochemical cycles.

The enrichment factor is calculated according to the following equation:

$$EF = \frac{M_x \cdot Fe_b}{M_b \cdot Fe_x} \quad (1)$$

where M_x and Fe_x are the soil sample concentrations of the heavy metal and Fe (or another normalizing element), while M_b and Fe_b are their concentrations in a suitable background (average Earth's crust) [40].

The enrichment factor is classified as follows:

- EF < 2: deficient to minimal enrichment;
- $2 \leq \text{EF} < 5$: moderate enrichment;
- $5 \leq \text{EF} < 20$: significant enrichment;
- $20 \leq \text{EF} < 40$: very high enrichment;
- $\text{EF} \geq 40$: extremely high enrichment.

Geoaccumulation Index (Igeo)

In order to assess the degree of contamination of environmental components, Müller [42] suggested using the geoaccumulation index. He provided seven categories of contamination depending on the index value.

Geoaccumulation index is calculated as follows:

$$I_{\text{geo}} = \log_2\left(\frac{C_{\text{mSample}}}{1.5 \times C_{\text{mBackground}}}\right) \quad (2)$$

where C_{mSample} is the concentration of the element in the enriched samples, and $C_{\text{mBackground}}$ is the background value of the element (Table 2). The contamination categories given by Müller [42] are as follows:

- $I_{\text{geo}} > 5$: extremely contaminated;
- $4 < I_{\text{geo}} < 5$: strongly to extremely contaminated;
- $3 < I_{\text{geo}} < 4$: strongly contaminated;
- $2 < I_{\text{geo}} < 3$: moderately to strongly contaminated;
- $1 < I_{\text{geo}} < 2$: moderately contaminated;
- $0 < I_{\text{geo}} < 1$: uncontaminated to moderately contaminated;
- $I_{\text{geo}} = 0$: uncontaminated.

Contamination Factor (Cf)

The third factor determining soil contamination with heavy metals is the contamination factor (Cf). It is calculated according to the following formula:

$$C_f = \frac{C_{\text{mSample}}}{C_{\text{mBackground}}'} \quad (3)$$

where the contamination factor $C_f < 1$ refers to low contamination; $1 \leq C_f < 3$ means moderate contamination; $3 \leq C_f \leq 6$ indicates considerable contamination, and $C_f > 6$ indicates very high contamination.

Degree of Contamination (C_d)

Håkanson [43] proposed an overall indicator of contamination based on integrating data for a series of seven specific heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn) and the organic pollutant PCB. This method is based on the calculation for each pollutant of a contamination factor (Cf). The degree of contamination is calculated using the following formula:

$$C_d = \sum_{i=1}^{i=n} C_f^i \quad (4)$$

where n —number of analyzed elements, i — i^{th} element (or pollutant), and C_f —contamination factor.

To determine the level of soil contamination, the following ranges were adopted according to Håkanson [43]:

- $C_d < 8$: low degree of contamination;
 $8 \leq C_d < 16$: moderate degree of contamination;
 $16 \leq C_d < 32$: considerable degree of contamination;
 $C_d \geq 32$: very high degree of contamination indicating serious anthropogenic pollution.

Modified Degree of Ontamination (mC_d)

Abraham [44] extended Håkanson's formula [43] by introducing a modified degree of contamination and an appropriate scale of contamination. The modification of Håkanson's formula, carried out by Abraham [44], made it possible to determine the influence of all metals on soils, without quantitative restrictions. The modified degree of contamination is the sum of all contamination factors (C_f) for soil pollutants divided by the number of analyzed pollutants. The equation for calculating the degree of contamination is provided below:

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (5)$$

Due to the obtained values of the mC_d coefficient, the following scale of the degree of soil contamination was adopted:

- $mC_d < 1.5$: very low degree of contamination;
 $1.5 \leq mC_d < 2$: low degree of contamination;
 $2 \leq mC_d < 4$: moderate degree of contamination;
 $4 \leq mC_d < 8$: high degree of contamination;
 $8 \leq mC_d < 16$: very high degree of contamination;
 $16 \leq mC_d < 32$: extremely high degree of contamination;
 $mC_d \geq 32$: ultra-high degree of contamination.

3. Results

The average content of heavy metals in the soils of the test areas (KW and MO) and the pH value are presented in Table 3.

Table 3. Heavy metal content (average values) and soil reaction in the Kasprowy Wierch and Morskie Oko test areas.

Tested Area	Sample No.	Mean Metal Concentrations ($\text{mg}\cdot\text{kg}^{-1}$)							pH H_2O
		Cd	Cr	Cu	Ni	Pb	Zn	Fe (%)	
KW	1	1.3	49.2	12.9	15.6	117.8	122.5	4.2	7.5
	2	1.2	41.8	12.4	14.2	115.1	118.0	4.1	7.6
	3	1.1	40.5	10.9	12.5	113.7	96.8	3.7	7.7
	4	0.9	31.6	6.4	7.7	99.1	86.0	3.6	7.8
	5	0.7	31.9	5.6	6.2	85.4	79.8	2.9	5.2
	6	0.7	31.1	4.2	6.5	65.8	76.6	2.6	4.3
	7	0.5	26.0	4.0	5.5	54.2	74.1	2.3	4.9
	8	0.3	25.3	3.1	4.6	53.5	61.1	2.0	4.9
MO	9	1.3	32.6	14.8	5.8	161.1	125.4	4.9	4.0
	10	1.0	31.1	12.2	5.0	149.8	105.5	4.4	3.5
	11	0.9	31.3	11.6	5.1	129.3	84.1	3.9	3.6
	12	0.6	27.9	10.8	3.1	118.3	67.5	3.7	3.4
	13	0.5	27.5	9.2	2.7	114.6	52.2	3.3	3.8

On the basis of the conducted research, it was found that the highest average heavy metal content in soils for both test areas was recorded for Zn and Pb, and the lowest for Cd, Cu and Ni. Metal contents

in the soils for the KW and MO test areas decrease with the increase in the height in meters above sea level. By comparing the metal contents between the test areas at the same altitudes, higher lead contents for MO can be seen compared to the Pb content in KW. On the other hand, the content of Cr and Ni in the soil of the test areas is higher in the case of KW in relation to the content of these metals in the MO test area.

Soil reaction (pH) is the highest (from 7.5 to 7.8) for the soils sampled at an altitude of 1100–1400 m in the vicinity of KW. The lowest pH values were found for the soils of the MO test area (from 3.4 to 4.0) and for the soils of the KW area sampled at an altitude of 1550–1850 m above sea level. The reaction of the soils for the MO test area was similar to that of the soils sampled from the KW test area for altitudes higher or equal to 1550 m above sea level (for the highest absolute heights of the KW). Different values of soil reaction were observed for the KW test area, from very acidic to alkaline, which is related to the land cover.

Based on the data from Table 3 concerning the average content of metals in the soils in the study areas, as well as the background values and the average Earth's crust, the indices of soil contamination with metals were calculated. Table 4 and Figure 2 present the values of the given coefficients for soil samples. Sample numbers from 1 to 8 refer to the samples taken from KW, while numbers 9–13 refer to the samples taken from MO. On the basis of the conducted research, it can be concluded that in MO the concentrations of metals in the soil are higher than in KW. This relationship is illustrated by the coefficients presented below. Another regularity is the decrease in the content of metals in soil samples with the increase in altitude. This regularity occurs for all collected soil samples, both in KW and MO.

Table 4. Enrichment factors (EFs) for soil samples from the Kasprowy Wierch and Morskie Oko test areas.

Tested Area	Sample No.	Cd	Cr	Cu	Ni	Pb	Zn
KW	1	5.5	2.1	0.5	0.6	3.7	1.3
	2	5.4	1.8	0.5	0.5	3.7	1.3
	3	5.1	1.9	0.5	0.5	4.0	1.2
	4	4.3	1.6	0.3	0.3	3.6	1.1
	5	4.1	1.9	0.3	0.3	3.9	1.2
	6	5.0	2.1	0.3	0.4	3.3	1.4
	7	3.8	2.0	0.3	0.4	3.1	1.5
	8	2.7	2.2	0.3	0.4	3.5	1.4
MO	9	4.5	1.2	0.5	0.2	4.3	1.2
	10	4.0	1.3	0.5	0.2	4.5	1.1
	11	3.9	1.4	0.5	0.2	4.4	1.0
	12	2.7	1.3	0.5	0.1	4.2	0.8
	13	2.7	1.5	0.5	0.1	4.6	0.7
Average		4.1	1.7	0.4	0.3	3.9	1.2

In Table 4, the values for the enrichment factor (EF) are presented as the first factor. The highest EF values are for cadmium (about 5) and for lead (about 4) in KW and MO. EF values for other metals are much lower and do not exceed the value of 2.0, except for Cr, which means that they do not pose a threat to the environment. The EF for chromium for samples 1, 6, 7 and 8 was greater than or equal to 2.0 only for KW. Even for Cd and Pb, EF values fall within the range of up to 5, which classifies them as moderate enrichment. Only in the case of cadmium is there significant enrichment ($EF \geq 5$) for samples 1, 2, 3, and 6.

The other calculated index, presented in Table 5, is the geoaccumulation index (Igeo). As in the case of enrichment factors, this coefficient is highest for cadmium and lead. For cadmium for samples 1, 2, 3, 4, 9, 10, and 11, and for lead for samples 9 and 10, the Igeo values indicate moderate to strong contamination. For the other samples, in the case of cadmium and lead, the Igeo values are on the level

of moderate contamination. For the remaining measured metals, the Igeo index values are very low (<1), and thus do not indicate strong environmental pollution.

Table 5. Geoaccumulation index (Igeo) for soil samples from the Tatra National Park area (KW and MO).

Tested Area	Sample No.	Geoaccumulation Index (I _{geo})					
		Cd	Cr	Cu	Ni	Pb	Zn
KW	1	2.63	0.61	−0.88	−1.07	1.78	0.58
	2	2.58	0.37	−0.94	−1.22	1.75	0.53
	3	2.35	0.33	−1.13	−1.40	1.73	0.24
	4	2.07	−0.03	−1.88	−2.10	1.53	0.07
	5	1.68	−0.02	−2.08	−2.42	1.32	−0.04
	6	1.80	−0.05	−2.49	−2.35	0.94	−0.10
	7	1.25	−0.31	−2.58	−2.58	0.66	−0.15
	8	0.56	−0.35	−2.95	−2.84	0.64	−0.42
MO	9	2.58	0.02	−0.68	−2.51	2.24	0.61
	10	2.26	−0.05	−0.96	−2.71	2.13	0.36
	11	2.02	−0.05	−1.04	−2.70	1.92	0.04
	12	1.42	−0.21	−1.13	−3.42	1.79	−0.28
	13	1.25	−0.23	−1.37	−3.63	1.74	−0.65

The next calculated coefficients indicating the degree of environmental pollution with heavy metals are the contamination factors (C_f), the degree of contamination (C_d), and modified degree of contamination (m C_d). The values of these coefficients are presented in Table 6. The highest values of the C_f > 6 coefficient, indicating very high contamination, were obtained for cadmium (samples No. 1, 2, 3, 4, 9, 10, and 11) and for lead (samples No. 9 and 10). The values of the C_f coefficient in the range of 3–6 indicating considerable contamination were obtained for cadmium (samples No. 5, 6, 7, 12, and 13) and lead (4, 5, 11, 12 and 13). For chromium and zinc, in the case of all the samples, the values of C_f indicate moderate contamination, and for samples No. 1, 2, 3, 9, 10, and 11 the values of the factor are the highest. For copper and nickel, the contamination factor (C_f < 1) refers to low contamination.

Table 6. Degree of contamination (C_d) and contamination factors (C_f) for soil samples from KW and MO.

Tested Area	Sample No.	Contamination Factors (C _f)						C _d
		Cd	Cr	Cu	Ni	Pb	Zn	
KW	1	9.3	2.3	0.8	0.7	5.2	2.2	20.5
	2	8.9	1.9	0.8	0.6	5.0	2.2	19.5
	3	7.6	1.9	0.7	0.6	5.0	1.8	17.5
	4	6.3	1.5	0.4	0.4	4.3	1.6	14.4
	5	5.0	1.5	0.4	0.3	3.7	1.5	12.3
	6	5.0	1.4	0.3	0.3	2.9	1.4	11.3
	7	3.6	1.2	0.3	0.3	2.4	1.4	9.0
	8	2.2	1.2	0.2	0.2	2.3	1.1	7.3
MO	9	9.0	1.5	0.9	0.3	7.1	2.3	21.1
	10	7.2	1.4	0.8	0.2	6.6	1.9	18.1
	11	6.1	1.5	0.7	0.2	5.7	1.5	15.7
	12	4.0	1.3	0.7	0.1	5.2	1.2	12.6
	13	3.6	1.3	0.6	0.1	5.0	1.0	11.5
Average		6.0	1.5	0.6	0.3	4.6	1.6	14.7

The C_d coefficient is the highest in the case of soil samples No. 9, 1, 2, 10, and 3, which indicate a considerable degree of contamination. Cadmium for samples No. 4, 5, 6, 7, 11, 12, and 13 constitutes

a moderate degree of contamination. Only one sample (No. 8) with $C_d < 8$ indicates a low degree of contamination.

The values of the modified degree of contamination (mC_d) coefficient are presented in Figure 2. The figure shows that the mC_d values are the highest for samples No. 1, 2, 3, 4, and 9, 10 and 11. These samples are the soil material collected at altitudes of 1100, 1200, 1300, and 1400 m above sea level in the KW and at altitudes of 1000, 1100, and 1200 m above sea level in the MO. For the above-mentioned samples, the mC_d coefficient is in the range of 2–4, denoting a moderate degree of contamination. The remaining samples, i.e., samples No. 5–7 (1550, 1650, 1750 m asl), as well as 12 and 13 (1300 and 1400 m asl), for mC_d in the range of 1.5–2, indicate a low degree of contamination. Only sample No. 8 (1850 m asl), for $mC_d < 1.5$, indicates a very low degree of contamination.

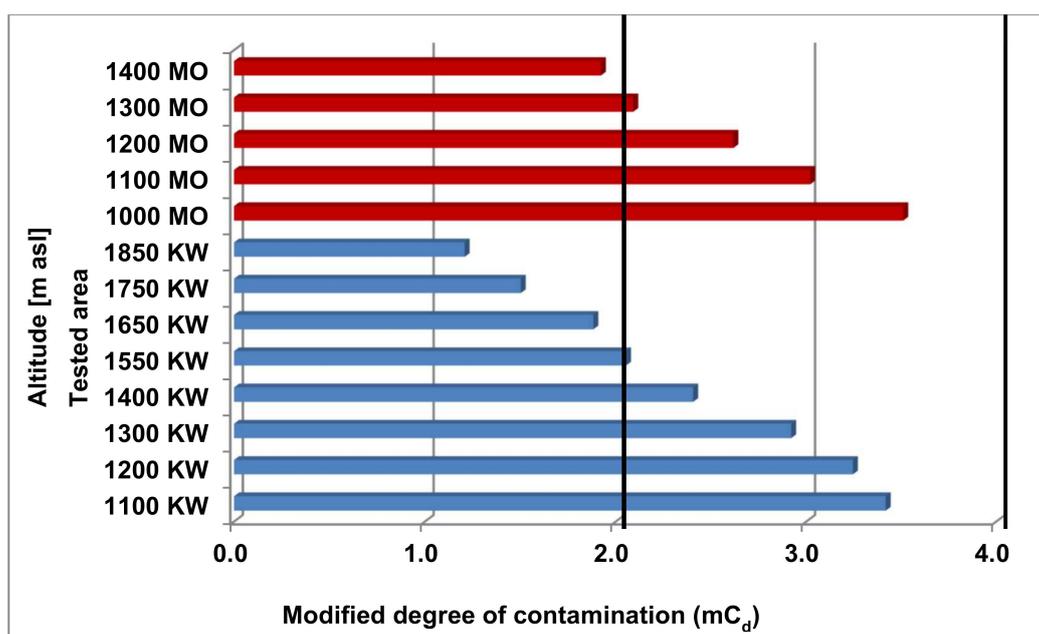


Figure 2. Histogram of the modified degree of contamination (mC_d) using Cd, Cr, Cu, Ni, Pb, and Zn in soil samples from the Tatra National Park. The two vertical lines represent the boundaries between low ($mC_d < 2$) and moderate ($2 \leq mC_d < 4$) degrees of contamination. Morskie Oko tested area is marked in red, Kasprowy Wierch tested area is marked in blue.

All the calculated coefficients in this study, except for EF, show that there is a trend for the content of metals in soils to decrease together with an increase in altitude.

4. Discussion

The conducted research concerning the determination of the content of selected heavy metals in the soils of the Tatra National Park (TNP) showed that, with the increase in the altitude of the terrain, the concentration of metals in soils decreases. This tendency was observed for all tested metals in the Kasprowy Wierch and Morskie Oko test areas. A decrease in the metal content in soils in mountainous regions with an increase in altitude was found by Kubica et al. [11]. The Pb content in the soil at an altitude of 1720 m asl was lower than the Pb content at altitudes of 1180 m asl and 1355 m asl. Similar relationships were found for Cr, the content of which in the soil at an altitude of 1720 m asl was lower than at altitudes of 1000 m asl and 1180 m asl. Miechówka et al. [13] found a decrease in the Cd content together with an increase in altitude above the upper forest limit. They observed lower Cd contents for the altitude range of 1850–2200 m asl than for the altitude range of 1100–1550 m asl. Similar to the authors, Stobiński et al. [45] found a decrease in Zn and Cr in the TNP soils together with an increase in altitude (the Zn content at an altitude of 1852 m asl was almost two times lower than at an altitude

of 1200 m asl; while the content of Cr at an altitude of 1850 m asl was lower than at an altitude of 1780 m asl). In the area of the Gongga Mountains (Eastern Tibetan Plateau), Bing et al. [46] found the lowest heavy metal content in soils for the altitude range of 3500–3700 m asl (above the upper limit of timberline forest). In the case of the conducted research, a similar relationship was observed for the KW area (in the Tatras, the upper forest limit runs at an average altitude of 1500 m asl).

The determined metal contents in the TNP soils (KW and MO test areas) are similar to those found by Stobiński et al. [45] for Cr and Zn in the soil samples collected in the High Tatras, and by Kubica et al. [10] for Cd, Pb, Zn in the soil samples collected in the Kościeliska and Rybi Potok Valleys. Niemyska-Łukaszuk et al. [47] obtained comparable Pb contents for the rankers of the non-forest areas of the TNP. In the Morskie Oko and Kasprowy Wierch test areas, the contents of Pb and Zn were found to be almost twice as high as those determined by Wiczorek and Zadrożny [14] in podsol soils (Podzols) in the TNP area, and by Kubica et al. [11] for Zn in the soils in the Chochołowska Valley. Similar lower concentrations of the metals Cu, Pb, and Zn were obtained by Skwaryło-Bednarz [48] in the forest soils of the Roztocze National Park.

The indices calculated in both test areas were not compared with each other due to the local differences in the geological structure affecting the soil pH. In the case of the MO, the bedrock consists of acidic crystalline rocks (e.g., granitoids and moraine formations) and the acid reaction of the soil was found (pH in the range of 3.4–4.0). On the other hand, in the KW area (predominant carbonate rocks, mainly limestones and dolomites) the acid reaction of soils was found (pH in the range of 4.3–5.2 for an altitude of 1550–1850 m above sea level) and a slightly alkaline reaction (pH in the range of 7.5–7.8 for an altitude of 1100–1400 m above sea level). The acid reaction of the soil is most likely the result of the falling of mountain pine needles and has favored the accumulation of metals. We observe high acidification of soils in the areas located higher, at an altitude of 1550 m above sea level, which may also result from the impact of long-range emissions on the condition of the natural environment (industrial and communication pollution, e.g., SO₂, CO₂, and NO_x). It is difficult to compare the results from the area of the Tatra Mountains with other high-mountain areas, because they are characterized by a different specificity determined by their geographical location, affecting the climatic and geological conditions, and also by an often unique type of plant communities (in the mountains that change zonally). The vicinity of high-mountain areas is also diversified in terms of land use, e.g., the range and intensity of impact of industrial, communication and highly urbanized areas. Therefore, the impact of the anthropogenic factor on mountain areas will be incomparable. Hence, the authors limited the comparison of their research results to the results of works from the same area.

The tests carried out in the MO and KW test areas showed that, among the six metals determined, the highest concentrations in the soil were found for cadmium and lead. This is owing to the small diameter of the particles of both elements and, consequently, the long duration of their lingering in the atmosphere. Such particles are easily transported, in the direction of prevailing winds, over long distances, up to 100–200 km (long-range emission). In the case of the studied areas (the Tatra National Park), taking into account the dominant south-western direction of winds, the content of metals in soils may be influenced by emissions from nearby countries, i.e., the Czech Republic and Slovakia, as well as from the Upper Silesian agglomeration. During their research in the Morskie Oko region, they found a high impact of long-range emissions on the content of heavy metals in soils and plants [49]. At the same time, they pointed out the slight influence of local pollution sources (including hotels, transport). The sampling sites were more exposed to the effects of long-range emissions as they are located on the northern slope of the Tatra Mountains. Long-range emission contributes to metal contamination of important natural areas and is currently a problem not only on a local (national), but also global (world) scale. Therefore, when examining environmental pollution with heavy metals, one should also take into account the emissions from neighboring areas, according to the prevailing wind directions.

5. Conclusions

The studied coefficients helped to determine the degree of anthropogenic impact on different natural environments of Poland, according to their altitude. The highest values of the calculated coefficients, i.e., the greatest impact of human activity on the environment, were found in the case of cadmium and lead. For the other elements (Cr, Cu, Ni, and Zn), the calculated coefficients were low, which proves that the environment was not contaminated with these metals at all, or only to a small degree. Long-range emissions influence the increased content of heavy metals in the TPN soils. The height above sea level, as well as the proximity of the main mountain ridge, affects the spread of pollution. Specific terrain conditions affect the increase in wind velocity, therefore, soils at higher altitudes and closer to the ridge contained fewer metals than those located lower and further from the ridge.

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