Environmental & Geoanalysis Journal

Issue 2016 Volume 1 (1)

ISSN: 2544-9680

scipubl.eu

email: sciences.publisher@gmail.com

SCIENCE PUBLISHER

ISSN 2544-9680

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Heavy metals concentrations in the moss and lichens from Ruda Śląska – Wirek Zn-Pb slags.

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Key-words: heavy metals concentration, moss, lichens, Ruda Śląska, Zn-Pb slags

Abstract: Have been examined samples of plants and lichen from the heap in Ruda Śląska. This is a dumping ground for waste from reprocessing Zn-Pb ores of the nineteenth century, which was at the beginning of the twenty-first century, dug up and exposed. Studies have shown that the substrates are slags which are apparent associations including mineral sulfides, sulfates and carbonates contain heavy metals. Metals also sometimes in large concentrations has also been found in samples of plants. The highest concentrations are found in sward which grew directly on the waste in the zone of oxidation and precipitation.

1. Introduction:

Ruda Śląska is a city long associated with the mining and processing. In the district Wirek at Novara Street is located nineteenth century heap of waste metallurgical Zn-Pb [3, 13, 14]. Because of the type present in the slag it is a cumbersome danger to the surrounding environment (Fig 1, Tab. 1, [8, 9, 10, 12, 17, 20, 21]). These heaps can be found in various locations in the area of Ruda Śląska, which was carried out this type of operation.

Fig 1. Photographic documentation of the pile in 2013- 2016year. On the left side is visible dug up the spill, in the right -the different formations of slags with precipitates zone (white).

However, in this heap is an outcrop of the ongoing work of its re-use, which makes it at the moment heap is a much greater threat than other similar places, often already heavily overgrown [11]. In addition, in the area of Ruda Śląska is being carried out mining operations of coal, which makes the soil on the surface is unstable. Formed in the heap gap through which passes rainwater and flushes burdensome substances. This is evidenced by discovered by the author of numerous infiltrations made up of sulphates and carbonates containing metal ore. Conducted field research in the years 2014-2016 showed that the heap is automatically undergoes restoration. He enters in the surface vegetation that grows on the site with visible contaminated metals precipitates.

2 Methods:

Samples of the ground and the plants themselves were collected in 2016. The collected samples were desiccated plants. Comp plants and rocks were observed by binocular magnifying glass and the optical polarizing microscope in transmitted and reflected light. Then, their analysis was performed using a scanning electron microscope Hitachi SU6600 with an attachment EDS in variable vacuum sputtering without trials. Subsequently, these samples were tested by ICP-OES Varian heavy metal content. Microscopic analysis was conducted in the of Geology and Lithosphere Protection Department of Maria Curie – Skłodowska University (UMCS), chemical research in the of Soil Science and Soil Protection Department at the Earth Sciences and Spatial Management Faculty UMCS.

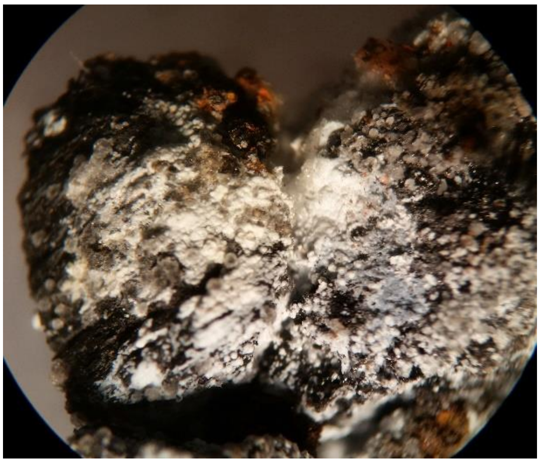
Tab 1. Samples localization in Ruda Śląska -Wirek.

No	Sample	Geographic position	
H01	Moss samples	50.26793N	18.87046E
H02	Moss samples	50.26743N	18.86996E
H03	Moss samples	50.26693N	18.86965E
H03a	Lichen samples	50.26693N	18.86965E
H04	Moss samples	50.26670N	18.86952E
H05	Moss samples	50.26691N	18.86935E
H06	Moss samples	50.26721N	18.86888E
H07	Moss samples	50.26742N	18.86892E
H08	Moss samples	50.26754N	18.86892E
H09	Moss samples	50.26740N	18.86865E
H10	Moss samples	50.26672N	18.86828E
H11	Moss samples	50.26628N	18.86740E
RS03	Katowicka St. moss samples	50.27109N	18.87172E
RS04	Nowarry St., Church plaster	50.26739N	18.86558E
Object 01		50.26709N	18.86960E
Object 01a	Geological samples of host slags	50.26707N	18.86984E
Object 02		50.26698N	18.86966E
Object 03		50.26814N	18.86757E
Object 04		50.26859N	18.86731E

3. Results:

Characteristics of background rocks. Visible in outcrops heaps of slag was formed as waste in the processing of Zn-Pb ores. It is mixed with the ceramic lining of furnaces and various waste management in a piecemeal manner. In some places on the surface of these creations has set up a small layer of soil was formed by processes of crushing the ingredients and to provide heaps of ingredients dusty. A microscopic material heap is a heterogeneous syndrome mingled waste containing vitrified variety of slag, residues of minerals genital and a new phase as a result of high-temperature processes in the blast, and the precipitates formed after the deposit of the heap as a result of infiltration of water (fig. 2).

sample 02p5



sample 03p1

Fig 2 A microphotographs of the selected slags: in left with glaze, in right with precipitations.

The study of these slags have shown that they have a variety, depending on where sampling. A total of 124 were examined in the micro sample of 7 observation points, leading the analysis of 1709 microregions. As a result of these studies it was found that it is most common carbonates and sulfates, sulfides and oxides and silicates. Silicates are generally glaze, relatively resistant to metal leaching processes. Sulphides such as pyrite, chalcopyrite, galena, sphalerite (or wurtzite) are probably the association of primary ore. Together with the sulfides are found in the slag also alloys of iron, tin, zinc and copper sometimes doped with arsenic, lead and cadmium. They are dangerous because they are easily oxidized and mobility [11], causing acidification migrant in the rocks and the formation of precipitates in the oxidation zone. Sulfates, in turn Most gypsum, barite less frequently accompanied dioxide to form encrusting’s and blooming migration in zones of water infiltrating the substrate. Chemical research carried out in samples of slag showed that they have a number of contamination by arsenic (up to 14ppm), cadmium (up to 1 ppm), chromium (up to 46ppm), copper to 176ppm), nickel (do7ppm), lead (up to 39ppm), and zinc to (73ppm, [15]).

Characteristics of soil. These heaps are derived from the nineteenth century, so the originally formed on the cap which sulfate-carbonate and certain soil. They were, however, re-skinned zones, discontinued operation. These soils are also peeled off in other places, exposed to flush and sliding of sediment often exacerbate also by people who practice extreme sports (eg.

Riding motocross). In other places created initialized soil created by mixing crushed fragments of the heap (slag) with a touch of blown dust and a small amount of humic substances formed from the remains of dead plants. Research carried out in soils showed that their composition in many places is the same as the Haldane. During the field test samples have been taken from 10 sites moss and lichen and higher plants (birch, grass) in one place. Table of these lichens is below and their location on the map (fig. 1).

Characteristics of plant samples. Directly on the heap samples of mosses (*Polytrichum commune*) and lichen (*Cladonia coniocraea*, sample 03P) and birch (*Betula betula*, sample 04). Samples were collected at different locations heap (Tab. 1, Fig 3) and from various plants, for comparing them with each other. (Figure 4). Both test microprobe and chemical analysis of samples stated in the plant dopant metals such as iron and minor amounts of titanium, zinc, lead, arsenic, copper, vanadium, bar.

Fig 3. A photographs of the moss (*Polytrichum commune*) and lichens (*Cladonia coniocraea*) based on the pure slags with precipitation areas rich with heavy metals.

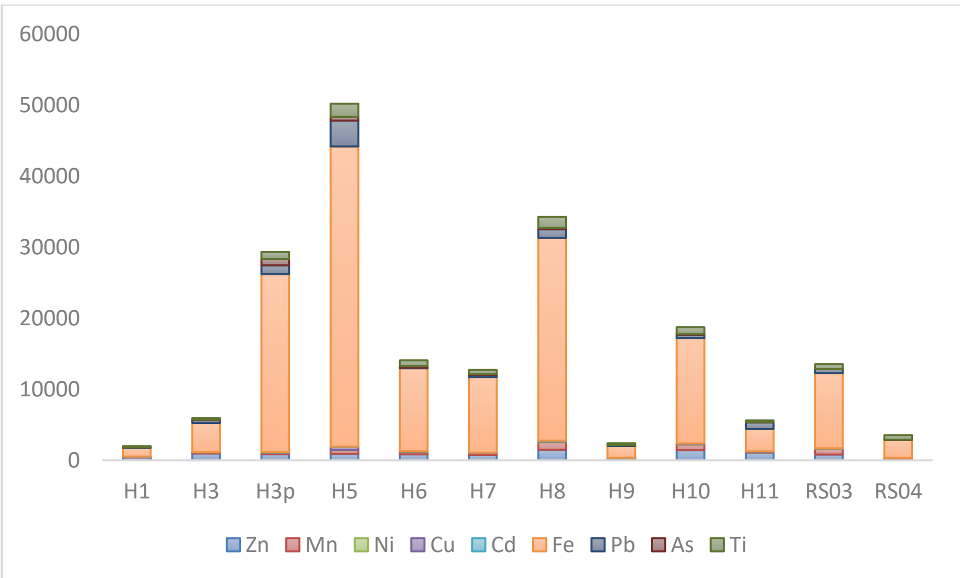


Fig 4. Summary diagram of the heavy metals contents in the moss and lichens samples using the ICP -OES method [mg/kg].

This analysis ICP-OES in the area of the heap were 9 samples of mosses (marked with H1-11) and one lichen (symbol H3p) and one reference sample, taken from the center of Ruda Śląska Street. Katowice, in the park, was designated RS03 (fig 4.). These studies clearly showed that all samples metal content is increased. The content of these metals is variable due to inhomogeneity's in the same heap. Geochemical background is also relatively high, as indicated by the study comparative sample. Research ICP-OES showed a significant increased element content. Relatively most metals had a sample of lichen that grew directly on the slag heap. Such a high content of these metals can be easily explained by the specificity of the substrate and the substrate material directly benefiting the lichen. In other samples, the content of mosses were also high.

4. Discussion

These studies clearly indicate that the area of the heap is a very dangerous place for a post-industrial, which at the moment is unprotected and exposed (dug up). Studies slag show that there are a plurality of polymetallic dopant including arsenic, cadmium, and many heavy metals such as lead, zinc, copper, nickel, titanium, iron, manganese. Their occurrence is related to many associations derived from the original ore, alloys obtained in the process of processing zones, and migration and oxidation of a solution which precipitates formed. These metals generally are present in all phases of slag and after the silicates are a high risk, can be leached, transported as well as the exhaust from the heap by the wind. The processes of uneven subsidence, causing it to open gaps and migration of water into the heap. The inconvenience of these metals to the environment is well known and widely described by many investigators [1, 5, 7, 8, 9, 16, 17, 18, 21, 22, 23]. Examined plant samples show a wide variation metal content, which is related to the heterogeneity of the heap. The highest metal concentrations were recorded in lichens and in samples of H5 and H6 mosses, located in the central part of it. The locations of the sampling plants grow practically directly on the heap or on small patches produced by the shattering of the material heaps of soil. This contributes to intensive migration of chemicals from the heap to the plants.

5. Conclusion

The above results indicate clearly that the heap in Ruda Śląska at the moment is a major threat to the environment. Workings are exposed, unprotected, washed away by rain and blown by the wind. In this form heap it is very dangerous for the environment. The substrate is enriched in a series of many heavy metals that even low levels may constitute a serious threat to the environment [1, 2, 4, 6, 10, 16, 19, 21, 24]. This heap is now overgrown with vegetation - "self-seeders', whose presence is due to their resistance to certain geochemical. Particularly interesting are the lichens that grow directly on the heap in the vicinity of polymetallic efflorescence. Such an arouse surprise and an example of adaptation to natural environment. Apart from these cases, a place that requires remediation especially as we are currently located in the city center, where there are residential buildings.

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Received: 14 Dec. 2016; **Revised submission:** 19 Dec. 2016; **Accepted:** 28 Dec. 2016

ISSN 2544-9680 Environmental & Geoanalysis Journal Research Article

Heavy metals concentrations in the selected moss from the central part of Karkonosze.

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Key-words: environmental characteristic, heavy metals concentrations, moss, Karkonosze

Abstract: It were subjected samples of selected species of moss growing directly on the substrate granitoide, greenstone, hornfels rocks and others. Examined a sample substrate to define the process of land reclamation after the pollutants that were emitted in the twentieth century. It has been shown that mosses are relatively clean, carrying only small concentrations of metals from the bedrock. This means that the area on which they grow has been restoration and cleaning compared to the previous years of the twentieth century.

1. Introduction:

Karkonosze is the culmination mountain range found in the south-western part of Poland, locating in the southern part of the Sudeten. These mountains in the twentieth century were heavily polluted acid rain resulting from the operation of decks and lignite in Poland, the Czech Republic and Germany. At the end of the twentieth century, this activity has been significantly reduced which resulted in air quality and reduction of pollution in the region Polish. They were subjected to analysis of mosses which are fruits of the forest (with the consent of the authorities of the Park), to determine the effect of the residual impurities that accumulate in the humus layer as a result of retention leaves of trees growing in the area. For this purpose, samples were taken from different regions of the moss Karkonoszy to determine the content of some heavy metals in the plants. The second objective was to determine bedrock to the metal content in these plants. Karkonosze is the area very interesting because within these mountains are exposed to many igneous and metamorphic [2, 3, 5, 6]. There are uneven-aged rock formations are often in contact with each other in a [1, 5] showing various processes magmatic, hydrothermal and secondary [9]. These mountains are built mostly of rock folded in Hercynian orogeny, rejuvenated block the movements of alpine [1,2,3]. Relevant to this discussion is the intrusion of granitoid rocks of the Karkonosze Mountains, breaking into a metamorphic gneiss and Jizera complex rock units Leszczyniec built with hornfelses, shale and amphibolites. With the subsequent processes he has contributed to the mineralization in these mountains [7,8].

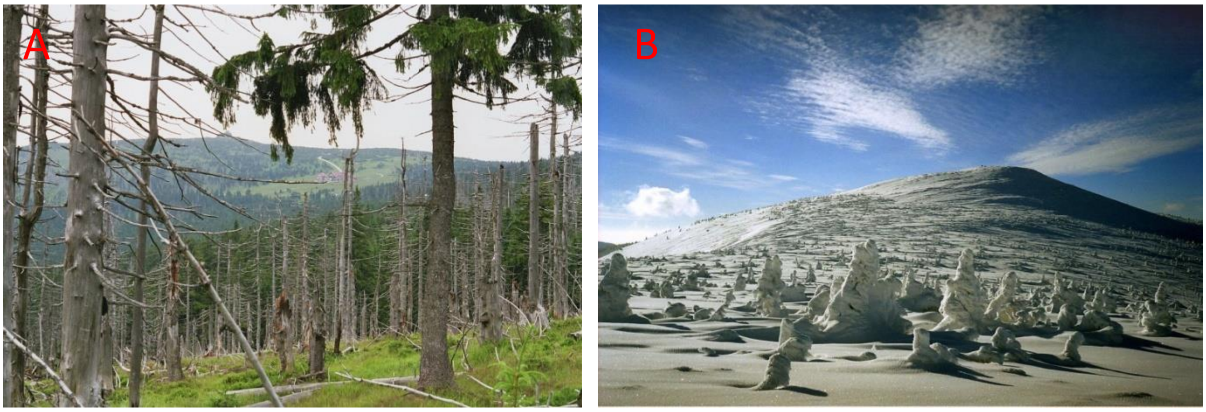

Fig 1. Examples of photographs of the Karkonosze: a: a forest destroyed by acid rain in the Giant [10], b: frost accumulated on trees around Little Shishak [10].

2 Methods:

Samples of moss and rocks were collected in the Karkonosze Mountains, in the vicinity of the Owl Valley, Table Rock, Śnieżka Valley Łomniczka, area Szklarska Poreba and Karpacz in 2015 with the knowledge and consent of the authorities of the KarkonoszeMountains National Park. Preparations were made of rocks and dry up mosses collected in the course of fieldwork. These samples were examined using a Leica DM2500P polarizing microscope in transmitted and reflected light and then the micro involving scanning electron microscope Hitachi SU6600. Rock samples were tested in addition to the participation of X-ray fluorescence spectrometer Epsilon 5 XRF PANalytical. Comp plant were reviewed by ICP-OES. Microscopic and spectroscopic studies were performed in the Department of Geology and Litosphere Protection in the Faculty of Earth Sciences and Spatial Management of the Maria Curie –Skłodowska University (UMCS). The samples investigated by ICP-OES examined in the Department of Soil Science and Soil Protection UMCS.

3. Results:

Karkonosze massif are the highest range of the Sudeten culminating Snieżka with a height of up to 1603m asl At an altitude of about 1400 m above the sea level It is paleosurface alignment, creates a much wider massif extent of 25 km, stretching from the west of the pass Okraj to Karkonoska Pass in the west and continue running in the direction of Szrenica. With the rejuvenation of the Karkonosze Mountains in the course of movements of alpine seen, numerous erosion with products of mountain glacier clear in the area in the form of bowls, ponds origin circus, or snow boilers, as well as periglacial formed into a boulder fields and tracks postglacial, the companion colluvium, pieces of physical weathering, as well as detrital material is transported via waterways. The impact of these factors differentiate the conditions for the formation of soil, where the silicate rocks (a composition similar to granite) did not have such a great impact on the soil-forming processes as a team of climatic factors connected with the statue of the mountains and the youngest episodes of erosion. This massif rainfall favors the retention of moisture-bearing clouds that whether from the north or from the south breaking through the mountains leave carries their water. This was the cause of contamination of the area in the twentieth century. At the moment, economic changes that have taken place in Poland, the Czech Republic and Germany contributed to much lower emissions which resulted in the reduction of harmful aerosols suspended in the atmosphere above

Karakonosze. It is seen well in the mountains where once observed regrowth of the damaged stand and in the same clarity and quality of the air.

Table 1. The list of samples of rocks and plants with finished studies.

Localization	Rocks samples	Moss samples
Sowia Valley	Quartz hematite veins, greenstone (sample KrK01)	*Brachythecilum Rutabulum* (sample 01), *Leucobravum Glaucum* (sample 04), *Hypnum Cupressifrorme* (sample 06)
Karpatka	Gneiss (sample KrK02)	*Dicranum Scoparium* (sample 02
Łomniczka Valley	gneiss	*Pseudoscleropodium Purum* (sample 03), *Hypnum Cupressifrorme* (sample 07)
Skalny Stół	Biotite schist (sample KrK03)	*Polytrichum Juniperinum* (sample 05)

If the air quality can be significantly improved so much faster accumulation of impurities in the fleece it can take much longer, due to the processes of accumulation and bind them in soil and plants. This causes a direct substrate in these mountains is greatly varied. In these mountains marked by a relatively well piętrowość plant. In the valleys there are coniferous and mixed woods, giving Pietru dwarf pine and alpine formations above. Fouling they are by different species of plants, which in spite of the northern exposure of the Polish part of the KarkonoszeMountains have a high species diversity.

Characteristic of the background rocks: In the area of the Karkonosze are exposed primarily Karkonosze granites associated with hercynian intrusion of these rocks (Table 1). Granites These coincide roughly with the peaks of the mountains, in the eastern part of the contact hornfelses that can be found on the slopes of Śnieżka and in the region Sowia Valley, where there are songs metamorphic units Leszczyniec. In this valley are exposed to numerous mica schists with magnetite, garnet, and amphibolites and lawns. In many places there are in addition a number of songs and hydrothermal strand of marginal importance for the vegetation. In the western part, in turn, appear gneisses Mountains located in the vicinity of the Karkonosze granite. Moreover, in the massif of the Karkonosze Mountains are found numerous rocks wire having, however, strictly local nature. Samples collected rocks and plants are presented in Table 1 (samples were collected in 2015, with the knowledge and consent of the Park Authority). In the area of the Massif Śnieżka and Owl Valley reveal the Karkonosze granites and mica schists with garnets and greens. In this region you are also seen hornfelses known contact zone (White) and numerous apophysis of interesting mineralization residual. **Hornfelses** there are rocks composed primarily of quartz, epidote, chlorites and biotite, accompanied by quartz and plagioclase (Figure 2a). These rocks often have a number of accessory minerals such as garnets, magnetite, hematite. Microprobe analysis of these rocks also showed the presence of minerals such as biotite, potassium feldspar and apatite-rich admixture of Ce and Nd.

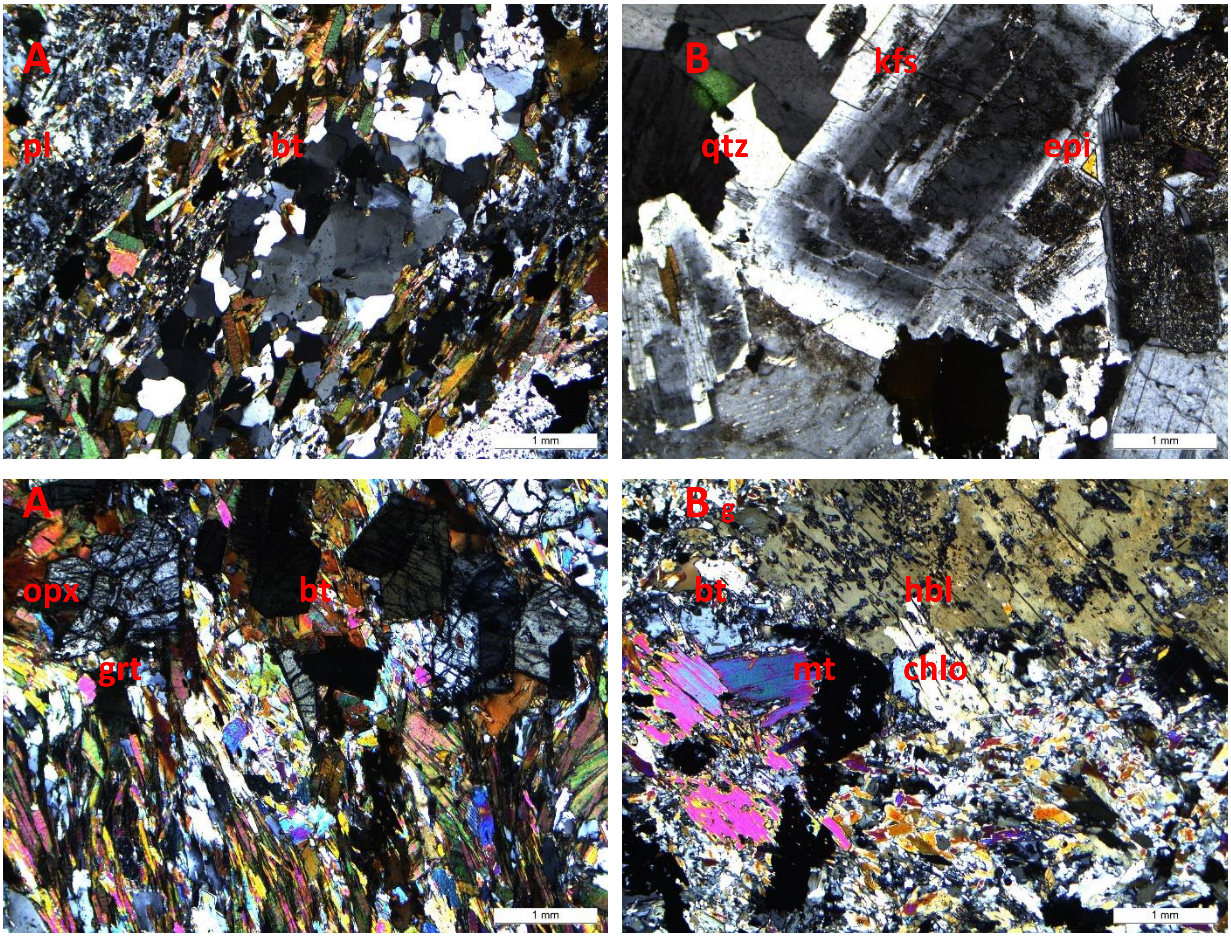

Fig 2. Microphotographs of the typical rocks samples from Karkonosze: a: hornfels from the Śniezka slopes, b: Karkonosze granite, c: quartz-mica-garnet schists, d: greenstone (kfs-alkali feldspar, pl-plagioklase, grt-garnet, qtz-quartz, opx-orthopyroxene, bt-biotite, epi-cpidote, chlo-chlorite, mt-magnetite).

Karkonosze Granite is built mainly of orthoclase -clearly visible to the whole rocks, and albite, accompanied by smoky quartz, biotite and Accessory minerals such as apatite, epidote, chlorite and ore minerals (fig 2b). Research in the micro also showed the presence of such minerals as quartz, potassium feldspar, biotite, quartz, apatite and phase enriched in Ce, La and Nd [4]. In addition, these rocks were also found Zirconia. **Mica-garnet schists** consists mainly of fengitu-biotite accompanied by grenades, quartz, and plagioclase and magnetite (fig 2c). In addition, research in the micro also found the presence of feldspar, hornblende and biotite ordinary, apatite in the apatite-rich cerium and quartz. Minerals including companion ilmenite and magnetite. **Greenstone** are rock the color of dark green built mainly of common hornblende, and epidote and chlorites, accompanied minerals such as plagioclase, quartz and subordinate magnetite, hematite (fig 2d). The owlish valley there are also numerous apophysis composed of minerals such as feldspar, quartz, fluorite, hematite, sometimes also containing polymetallic encrusting. In the area of Karpacz they are revealed in the micro studies have demonstrated the presence of mainly potassium feldspar, biotite, quartz, magnetite and additives Cerium-Neodymium apatite. **Gneiss**, which are composed primarily of quartz and orthoclase accompanied biotite and plagioclase and Accessory minerals such as titanite, ilmenite, which pass augite, epidote, chlorite. Research in the micro sample from Karpatka showed coexisting plagioclase albite acidic and basic labradore, accompanied by potassium feldspar, chlorite, biotite, augite, titanite and chlorite. In the sample of Dol. Łomniczki said next plagioclase quartz, epidote, chlorite, common hornblende, andradite, and ilmenite, and is doped barium feldspar and apatite enriched Ce, Ln, Nd [4]. **Mineral weins** are often negligible chemical composition contributes to the formation of numerous scattering aureole of elements associated such as iron, titanium, fluorine, and others.

Chemical composition of the background rocks. Zbadane próbki skał wykazują pewną zmienność w zakresie pierwiastków śladowych. We wszystkich próbkach występują niewielkie domieszki pierwiastków grupy ceru, ponadto w łupkach i gnejsach stwierdzono domieszki ołowiu oraz srebra i baru świadczące o hydrotermalnych procesach zaznaczających się w skałach (fig 3, tab 2). Z metali ciężkich stwierdzono występowanie Ti, Fe, Mn, Ni, Cu, Zn, Cr i As. Najwyższe zawartości tytanu, manganu, żelaza i niklu stwierdzono w próbce KrK01 (granite rocks). Najwięcej miedzi i arsenu i chromu zawierała próbka KrK03 (schsist). Najwyższe zawartości cynku stwierdzono w próbce KrK02 (gneiss).

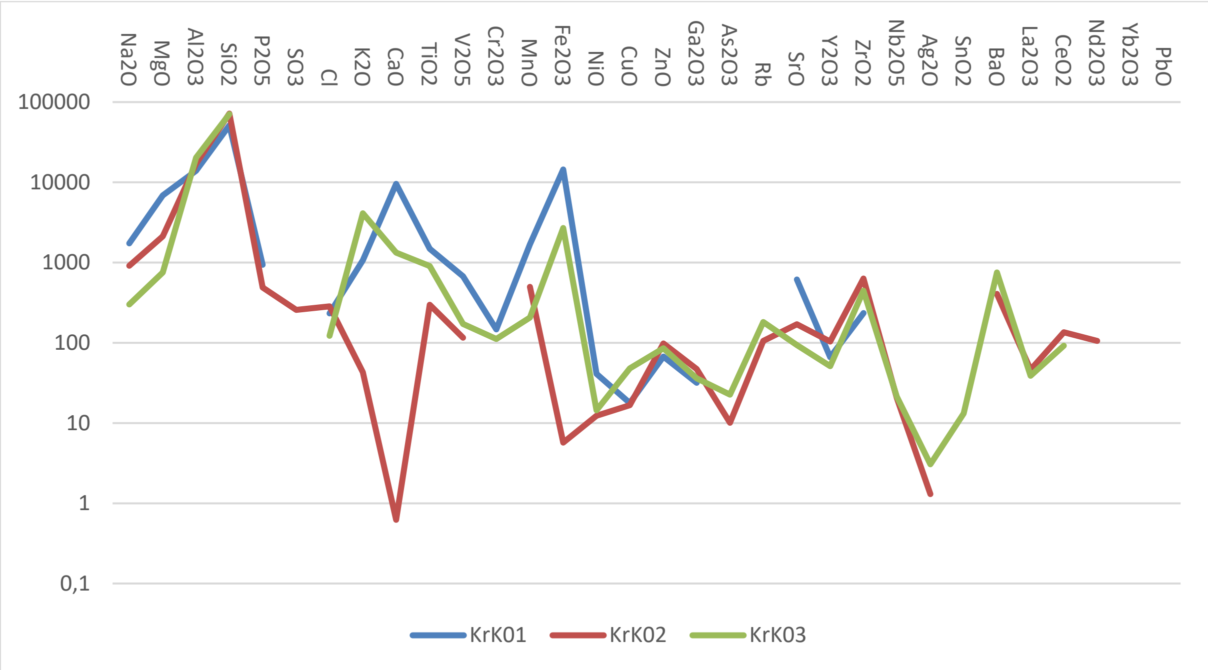

Fig 3. Chemical composition [mg/kg] of the rocks samples using XRF method.

Geochemical characteristics of mosses. Samples were collected from mosses Sowia Valley, Karpatka, Dol. Łomniczka, Skalnych tables. These samples are *Brachythecilum Rutabulum* (sample No. 1) Sowia Valley, Dicranum scoparium (sample No. 2) Karpatka, *Pseudoscleropodium purum* (sample No. 3) of Łomniczka Valley, *Leucobravum glaucum* (sample No. 4) of the Owl Valley, *Polytrichum juniperinum* (sample 5) the rock tables, *Hypnum Cupressifrorme* (sample No. 6) of the Owl valley and valley Łomniczki (sample No. 7, tab. 1). Samples examined in the micro mosses generally show a considerable purity. 176 Microanalysis carried out in all the samples showed that the moss sometimes include small quantities of calcium, sodium, magnesium, aluminum and silicon, chlorine, and bromine (Fig. 3, Tab. 2).

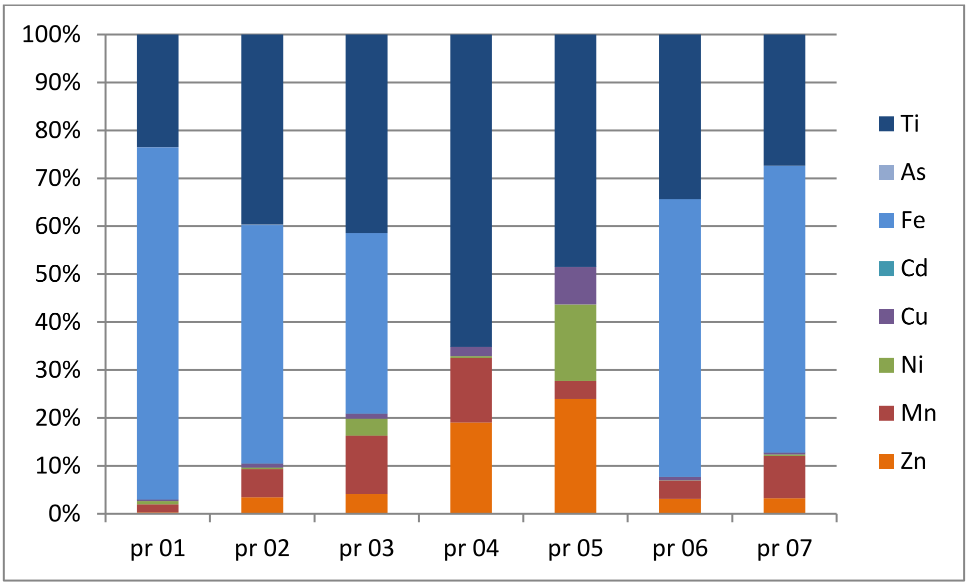

Fig 4. A diagram of the proportion of heavy element in studied moss samples.

Chemical studies of moss samples by ICP-OAS showed relatively small amounts of elements such as arsenic, lead, cadmium (often below the detection limit) and a relatively small content of Zn, Ni, Cu (Fig. 4). A content of the latter metals and iron and manganese due to the characteristics of bedrock and ore mineralization.

4. Discussion

Conducted field studies showed a significant improvement of the environment in comparison to the previous years of the twentieth century. It was noted far-reaching regeneration of the forest, much better weather conditions manifested among other things, increase the visibility of the air. Examined samples of bedrock have some variation characteristic of igneous and metamorphic rocks. Particularly interesting is the mineralization of metals, which is represented by a variety of ore minerals. They can penetrate into the soil and the plants further contributing to the accumulation. The investigated plants show relatively low metal content, in addition to small quantities of iron, titanium and manganese. It is also associated with a relatively contaminated area which are Sudety. Some of Zn, Ni, Cu may be associated with residual contamination of the area although it is conceivable that an impact on the content to a small amount of ore minerals associated with after-magma and hydrothermal processes.

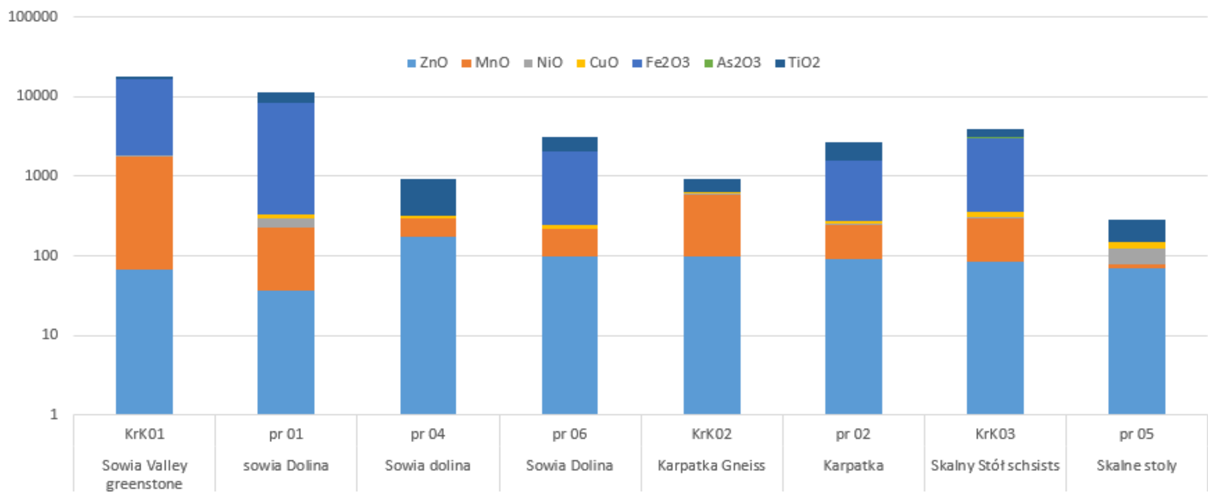

Fig 5. Comparasion of the moss and rocks chemical composition.

A comparison of samples of plants and rocks on the content of heavy metals showed some similarities and deviations (figure 05). Samples taken from the Sowia valley noted a small proportion of iron (only sample 01), manganese and zinc as compared to the parent rock. In Sample 01 had elevated copper and nickel as compared to the background rock. Samples 06 and 06 was a significantly more of titanium as compared to the parent rock. For Karpatka the amount of zinc is relatively constant manganese is less than the bedrock, and the oxides of iron, titanium, and the sample 05, nickel and copper is much more than in the rock ground. This may indicate a different source of contamination of the samples. It should also be noted that these metals are found in the sample *Brachythecilum Rutabulum* and *Polytrichum juniperinum*.

5. Conclusion

Karkonosze is an area with an interesting sculpture Alpine, with visible surfaces paleozrównania and culmination in the form of hills Snow White. Their orographic character favors the retention of aerosols carried through the clouds as well is visible especially in winter in the form of frosted slopes of the mountains. KarkonoszeMountains are also an area with very interesting geological structure resulting from a variety of geological processes taking place in these mountains in the past. Examined rock samples are relatively close to each other mineral and chemical composition, differing only accessory and ore minerals and additions. As a rule, the amount of impurities in the samples of mosses is significantly lower than in the rocks of the substrate, with the exception of samples 01 Sowia Walley and 05 from Skalny Stół. The protection area of the Karkonosze Mountains in the form of the Karkonosze National Park and the political changes in Poland and neighboring countries caused significant purification of the air in these mountains which also contributed to the relatively small dirt moss. This means that the current area has been to a large extent self-cleaning and regeneration.

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Tab 2. Chemical composition of the rocks samples measured using XRF method.

Elements	Sowia Valley greenstone KrK01	Karpatka gneiss KrK02	Skalny Stół schsists KrK03
Na2O	1735	914	300
MgO	6846	2129	750
Al2O3	13979	16994	20207
SiO2	51251	71891	70660
P2O5	940,99	488	
SO3		256	
Cl	231,44	283,52	122,62
K2O	1066,8	43	4096
CaO	9589	0,622	1330,5
TiO2	1483	299	903
V2O5	672,13	116	171,77
Cr2O3	147		111,76
MnO	1692,1	498,32	205,57
Fe2O3	14513	5,695	2697
NiO	41,041	12,363	14,41
CuO	17,753	16,705	48,033
ZnO	67,382	98,273	85,419
Ga2O3	31,77	47,001	36,118
As2O3		10,049	22,692
Rb		105,22	181,4
SrO	615,01	169,75	93,414
Y2O3	65,823	103,75	51,267
ZrO2	233,59	634,29	445
Nb2O5		20,528	21,428
Ag2O		1,3	3,06
SnO2			13,203
BaO	43,397	407,1	751,15
La2O3		46,057	38,702
CeO2		134,96	92,229
Nd2O3		105,55	
Yb2O3	171,33		
PbO		14,947	33,42

Received: 17 Dec. 2016; **Revised submission:** 21 Dec. 2016; **Accepted:** 28 Dec. 2016