

## BIOINDICATION OF CHEMICAL ELEMENTS DEPOSITION IN THE HIGH TATRA MTS (SLOVAKIA) BASED ON *CALLUNA VULGARIS* (L.) HULL; COMPARATIVE LEVELS AFTER THE IMPROVEMENT OF EMISSIONS

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**Abstract:** *Calluna vulgaris* was collected on the south slope of Lomnický štít peak in Skalnatá dolina valley (The High Tatra Mts) between 1987 – 1988 and repeat sampling took place in 2011, following reduction of emissions. Cu, Cd, Zn, Pb, Cr, Mn, Mo, Fe, S and F concentrations were determined in the samples. The results of ordination analysis and correlation analysis show a positive significant correlation of Pb, Fe and Cu ( $r=0.6320-0.9519$ ) with rising altitude and negative significant correlation of S ( $r=-0.7398$ ). Due to reduced emissions the sulphur correlation with rising altitude became positive not significant in 2011. In 1987-1988, Mo, Mn, Cr, Cd and Zn did not show any significant correlations with altitude. In 2011, Fe, Mo, Cr, Zn and Mn also showed no significant correlation with altitude. Pb and Cu retained a positive significant correlation with rising altitude. There was a significant change correlated to sulphur. In 1987-1988 the highest sulphur concentrations had been recorded up to 1300 m a.s.l. ( $>109.8 \text{ mg}\cdot 100\text{g}^{-1}$ ), whereas in 2011, the lowest sulphur concentrations were recorded at these altitudes ( $<87 \text{ mg}\cdot 100\text{g}^{-1}$ ) due to reduction of emissions. In 2011, data on fluorine has not been recorded. Despite the reduction of emissions, the accumulated heavy metals remain in the ecosystem for a long time and acceptable concentrations are mostly exceeded, approximately 2-4 times, in the case of chromium up to 10 times.

**Keywords:** Bioindication; deposition; *Calluna vulgaris*; Slovakia; The High Tatra Mts.

### 1. INTRODUCTION

The Tatra Mountains are located in the northern, highest section of the Carpathian mountain range (Central Europe), along the Polish-Slovakian border, and the highest peak is Gerlach, 2655 m a.s.l. In November 2004 forest stands in the TANAP were affected by windthrow and subsequently one year later fire broke out on a part of this affected area. The lee side of the Tatra Mts. has been continuously but irregularly affected by similar events. Since 1915 it was the 7<sup>th</sup> large-scale windfall of this nature affecting effectively the same territory (Fleischer & Koreň, 2007).

In terms of nutritional independence of the soil, mosses are widely used for monitoring of deposition of pollutants. Literature review on this topic has been compiled by Tyler, (1990). *Calluna vulgaris* has been similarly used in such work

(Pawer & Collins, 2010; Anderson & Hetherington, 1999; Gordon et al., 1999). Marris & Bannister (1978) found, that concentrations of 15 investigated elements in the tissues of *Calluna vulgaris* reflected the soil elemental concentrations. Murín & Mičieta (2010) also used *Calluna vulgaris* as a bioindicator and published results showing different sources of pollutants which included heavy metals.

*Calluna vulgaris* prefers moorlands (Anderson & Hetherington, 1999), but is a widespread and abundant species growing within a wide range of ecological conditions and soil types. *Calluna vulgaris* can grow in soils which have concentrations of elements normally considered toxic to other plants (Marris & Bannister, 1978). In the Tatra Mts., the species grows up to 2100 m a. s. l., rarely higher. Here, the species colonises acid and sandy soils, often secondary habitats. A study of the distribution of lead in the tissues of *Calluna vulgaris* showed that the

highest concentrations of lead were found in the woody parts of the plant (Marrs & Bannister, 1978).

At the time of the first sampling in 1987-1988, automobile traffic was the largest local emission producer, as leaded petrol was still in use. In the Tatra Mts region, major emission sources are located to the north-west at a distance of 150-200 km, i. e. Ostrava, Kraków and Silesia regions (Rak et al., 1982). In 1980, there were recorded in the districts of Dolný Kubín, Liptovský Mikuláš, Poprad, Spišská Nová Ves and Stará Ľubovňa of a total of 55,733 tons of solid emissions and 72,427 tons of gaseous emissions, whilst the largest sulphur dioxide producer is the paper mill Mondi SCP Ružomberok, previous CKP Ružomberok (10850 tons per year) and the Copper Smelter Krompachy (21980 tons per year). Chemosvit Svit produces 3,415 tons of sulphur dioxide per year, 2,130 tons of carbon disulphide and 433 tons of hydrogen sulphide. Furthermore, Mondi SCP Ružomberok produces dimethyltioether and thiomethanol. Compounds of Fe, Mn, Mo and Cr are produced by OPZ Itebné (the largest Slovak and Central European company producing casting alloys for the steel industry) and Copper Smelter Krompachy (Rak et al. 1982) and account for solid emissions.

In 2000, the Copper Smelter Krompachy, instigated a modernisation of production methods, and the plant is constantly upgrading the technologies it uses to minimize the impact on the environment. In 2006 it became a member of IPPC control system (Integrated Pollution Prevention & Control), falling under the administration of the Slovak Environment Inspection. The most harmful substance in the Tatra Mts is sulphur dioxide. Chemosvit halted the production method based on viscose which releases large volume of sulphur compounds and is now involved in the production of flexible films intended for packaging. The largest producer of SO<sub>2</sub> was former CKP Ružomberok (Mondi SCP), whose average annual concentrations in the 1980's was near 10µg.m<sup>-3</sup>, and occasionally the SO<sub>2</sub> concentration might reach above 100µg.m<sup>-3</sup> (Rak et al., 1982). Mondi SCP Ružomberok have several projects aimed at the improvement of emissions. Based on BAT (Best Available Techniques) the environmental impact was distinctly reduced by removal of conventional scouring and bleaching processes and its replacement by ozone bleaching, and therefore the amount of arising AOX (Adsorbable Organic Halogens) has been reduced by 58% and COD (Chemical Oxygen Demand) by 69%. Distinct improvements were seen in SO<sub>2</sub> emissions; they were reduced by 92% and in terms of TRS (Total Reduced Sulphur) emissions which,

reduced by 96% (Sotolová, Internet contact). Meanwhile, leaded petrol has been replaced by unleaded petrol.

The town of Tatranská Lomnica is situated 900 m SE from the first sampling points. This is one of the largest settlements in the area of the High Tatras. The number of permanent residents in the Tatranská Lomnica is 2000 and the settlement is frequently visited by motor vehicles. The average in 2004 was 902 vehicles per day (5-7 August 2004; Balaj & Štefány, 2005) while in 1981 it was 1233 vehicles per day (the average 6-8 August 1981; Strnka & Petro, 1983). After the partition of Czechoslovakia in 1993, the visitors to the Tatra National Park has rapidly declined. Presently, there is an upward movement in visitor numbers, but still, these numbers do not approach those of the beginning 1990's.

At the original sampling time (1987-1988), the emission production was at its height. As shown above, during the last two decades industrial plants have accepted measures to reduce emissions. Raw data from the late Anna Šoltésová shows emission data from 2 decades ago at the height of contamination and is therefore an important data set to analyse. In 2011, repeat sampling has been performed and the results were compared.

More recent textbooks related to „Bioindication and Biomonitoring“ have become available, e. g. Howe et al., (2004), Júdová et al., (2008), Fränzle et al., (2012). In South facing valleys, the prevailing wind direction is NW (Otruba & Wiszniewski, 1974). Similar wind conditions predominate the saddles. The average annual rainfall in the area of the High Tatras reaches about 1000 mm at a height of 1200 m a.s.l., while at the tops of the mountains about 2000 mm falls (Faško et al., 2008). The most acid precipitations are found in the eastern part of the High Tatras, in the area of Skalnaté pleso Lake (pH 4.3), whereas other parts of the Tatra Mts are less acid (pH 4.4-4.6) (Tužinský & Chudíková, 1991).

Heavy metal accumulation in mosses and their relation to altitude in the Tatra Mts has been studied Šoltés (1992, 1998). Pb, Cd and Zn show a relationship to altitudinal distribution and this group is associated with car emissions. A significant increase in heavy metal concentration with altitude is shown only in lead. The concentration of radionuclide <sup>137</sup>Cs in The Tatra Mts is mostly dependant on density of soil and altitude from which samples were collected. The level of <sup>137</sup>Cs and <sup>40</sup>K (and also some heavy metals) was measured in soil samples collected from polish part of Tatras.

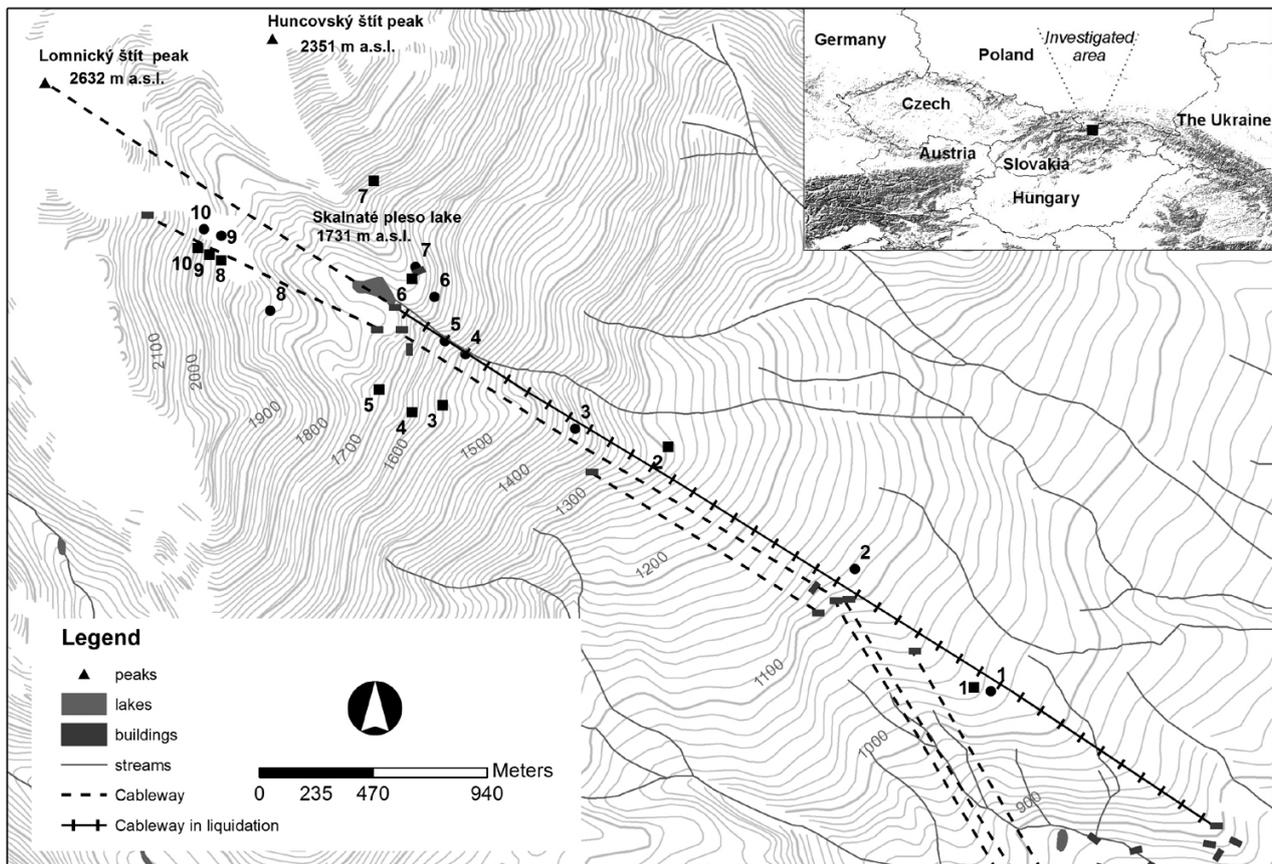


Figure 1. Map of area under investigation, full circles-sampling in 1987-1988, full squares-sampling in 2011 (Solár J., original).

Sampling site list, 1987-1988, full circles:

1. Between cableway station „Štart“ and Tatranská Lomnica, September 3, 1987, 49°10.490'; 20°16.075'.
2. Under cableway station „Štart“, September 15, 1987, 49°10.746'; 20°15.588'.
3. Above cableway station „Štart“, September 15, 1987, 49°11.024'; 20°14.610'.
4. Under Skalnáté pleso lake, September 3, 1987, 49°11.176'; 20°14.223'.
5. Under Skalnáté pleso lake, October 24, 1988, 49°11.203'; 20°14.150'.
6. Under public tourist path to Huncovský štít peak, September 14, 1988, 49°11.300'; 20°14.106'.
7. Skalnáté pleso lake, near Astronomical Institute of Slovak Academy of Sciences, October 18, 1988, 49°11.365'; 20°14.035'.
8. Skalnáté pleso, the slope of Lomnické sedlo saddle, September 3, 1987, 49°11.247'; 20°13.552'.
9. Lievikový kotol basin, September 15, 1988, 49°11.409'; 20°13.370'.
10. Skalnáté pleso, the slope of Lomnické sedlo saddle, September 15, 1988, 49°11.421'; 20°13.310'.

Sampling site list, 2011, full squares:

1. Between cableway station „Štart“, and Tatranská Lomnica, November 22, 2011, 49°10.497'; 20°16.016'.
2. Near cableway station „Štart“, November 22, 2011, 49°10.995'; 20°14.930'.
3. Ski resort „Čučoriedky“, November 22, 2011, 49°11.058'; 20°14.156'.
4. Above Ski resort „Čučoriedky“, November 22, 2011, 49°11.039'; 20°14.053'.
5. Above Ski resort „Čučoriedky“, above tourist path, November 22, 2011, 49°11.085'; 20°13.937'.
6. Skalnáté pleso, above Astronomical Institute of Slovak Academy of Sciences, September 7, 49°11.338'; 20°14.026'.
7. Skalnáté pleso lake, above tourist path to Veľká Svišťovka peak, September 7, 49°11.552'; 20°13.876'.
8. The SE slope of Lomnické sedlo saddle, December 2, 49°11.354'; 20°13.374'.
9. The SE slope of Lomnické sedlo saddle, December 2, 49°11.365'; 20°13.334'.
10. The SE slope of Lomnické sedlo saddle, December 2, 49°11.378'; 20°13.293'.

The following questions are addressed in this paper:

1. How are accepted measures aimed at emission

reduction reflected in environmental contamination?

2. How do the emissions correlate with altitude?

## 2. MATERIAL AND METHODS

### 2.1 *Calluna* sampling

The samples were collected in the autumn of 1987-1988 and repeat sampling performed in autumn of 2011. The sampling has been focused on a transect within the Skalnatá dolina valley (Fig. 1). Sampling points were established at approximately every 50-250 m (300 m) (in altitude), starting at a montane level (1,030 m a.s.l.), up to the alpine meadows, ending at 2,022 m a.s.l. At each site three samples of *Calluna vulgaris* stems were taken from different tussocks. Each sample contained a minimum of 10 randomly chosen stems from 3 to 5 *Calluna vulgaris* plants collected in fairly open stands. These were in a forest ecosystem with a distance of at least 5 m to the next tree. In the laboratory, plant samples were washed in distilled water and dried at 70°C for two days before sending for analysis. The geographical coordinates were recorded subsequently in 2011, using a WGS 84, Garmin eTrex Vista device.

### 2.2. Soil sampling

Samples of soil from the 1980's were obtained from old bryophyte specimens collected with enough soil and deposited in the Museum of the Tatra National Park in Tatranská Lomnica:

- Specimen of *Pogonatum aloides*, above Tatranská Lomnica, 1080 m a. s. l., spec. Nr. 1/03573, leg., det. Šoltés, May 4, 1983.
- Specimen of *Pogonatum urnigerum*, below Lomnické sedlo, 1975 m a. s. l., spec. Nr. 1/04930, leg., det. Šoltés, September 19, 1984.

### 2.3. Instrumental analysis

Chemical analyses (copper, cadmium, zinc, lead, chrome, manganese, molybdenum, iron, sulphur and fluorine) were carried out in the Geoecological Laboratory in Turčianske Teplice. The rough crushing was made on titanium steel equipment, and for the fine homogenisation an agitator was used. After ashing (450°C, 300 min.) the ash was digested in 20 ml 6 M HCl, and evaporated dry. The residue was dissolved in 40 ml 0.2 M HCl, filtered hot and the filtrates brought to a volume of 100 ml with 0.2 M HCl. The chemical analysis for copper, cadmium, zinc, lead, chrome, manganese and molybdenum was performed by atomic absorption spectrophotometry (Varian, Modell 1475, Australia). Iron was determined using the photometry method with sulphosalicylic acid

(SPECOL 11, Carl-Zeiss Jena, Germany). Sulphur and fluorine determination was made using a gravimetric method.

For sampling performed in 2011, X-ray fluorescence spectrometry has been used (Stephens & Calder, 2004) using the hand-held XRF spectrometer DELTA CLASSIC (USA). Pelletization at high pressure (10 tons) is recommended by some authors (Margui et al., 2009; Nečemer et al., 2008). Since some elements examined need a different thickness of pellets, e. g. S versus Pb (Richardson et al., 1995) we decided to use a method without pelletization (Stikans et al., 1988; Boman et al., 1993; Aslan et al., 2004). The plant material was crushed in a mortar into fine powder. The epoxide frame of 2x2.4 cm was filled with 1-1.5 g of plant powder, up to 1 cm in thickness and analysed directly on protective prolen folium. The samples are stored in plastic sleeves at the Institute of High Mountain Biology in Tatranská Javorina.

### 2.4 Statistics

CANOCO 4.5 for Windows package was used for statistical analysis. Since the length of the first gradient in the log report was < 0.2, we used the linear indirect methods – PCA (Ter Braak & Šmilauer, 2002). For ecological interpretation of the ordination axes, a geographical aspect of the sampling site was plotted onto a PCA ordination diagram as supplementary environmental variables (E, SE, S, SW). Regression analysis has been used in order to relate the heavy metal concentrations (including sulphur) with the independent variable – altitude. The correlation coefficients calculated by regression were tested for significance.

## 3. RESULTS AND DISCUSSION

The principal component analysis (PCA) ordination diagram of 10 sampling sites (sampling in 1987-1988) shows the major differences in the direction of the first axis owing to altitude (eigenvalue 0.991, species-environment correlation 0.580). Sampling sites at the alpine level, facing SE – SW, show higher concentrations of iron, lead, copper and molybdenum (Table 1, Fig. 2).

Using correlation analysis, positive correlations were obtained between altitude and concentration of lead ( $p < 0.001$ ), iron and copper ( $p < 0.02$ ), between lead and copper ( $p < 0.05$ ), but no significant association was found between altitude and concentrations of molybdenum, manganese, chrome, zinc and cadmium. Significant negative correlation was found between sulphur and altitude,

and significant positive correlation was found between altitude - copper and altitude - iron ( $p < 0.05$ ) (Table 4). In the direction of the second axis (eigenvalue 0.006, species-environment correlation 0.306), the major gradient in element distribution is associated with the East and the South aspect, and with this axis a correlation between chrome (negative correlation) and manganese (positive correlation).

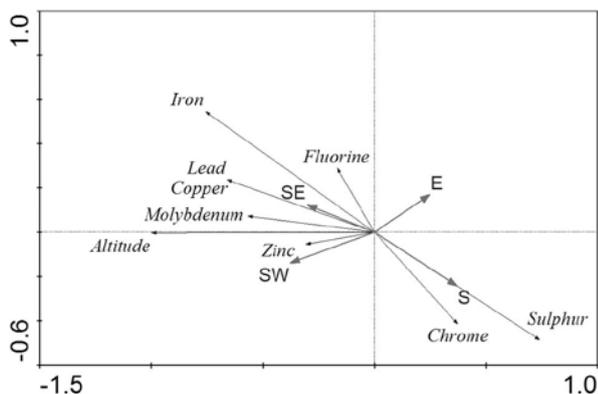


Figure 2. Principal component analysis (PCA), biplot, relationship between supplementary environmental variables and heavy metal concentrations including altitude (cadmium is not shown). SE south-east, SW south-west, E east, S south.

Due to ski resort construction, with accompanying field destruction, the sampling points between the two study periods are not exactly the same, but the soil conditions and ecological conditions of sampling points are the same. The minimal altitude, the maximal altitude and the vertical span is maintained (953 and 956 m).

The results of principal component analysis and correlation analysis of samples collected in 1987-1988 revealed relationships in the following groups of elements: (a) Pb, Fe, Cu, (b) S, (c) Mo, Mn, Cr, Cd, Zn.

a. This group shows a significant positive relation to altitude (Table 4). Pb is associated with traffic, in the form of aerosols which rise up into the higher sites. Fe and Cu could be attributed to long-distance transport from smelters located in western areas (Ostrava, Kraków and Silesia regions). These pollutants are transported by prevailing winds. In the alpine region, these pollutants are accumulated in plant tissues, which consequently enter the food chain.

b. Sulphur shows a significant negative correlation with altitude (Table 4). Sulphur producers are the southwards placed local plant Chemosvit (Fig. 2) or nearby Mondi SCP Ružomberok, and the sulphur emissions (sulphur dioxide, carbon disulphide) are to be found mainly in the lower air layer. c. This group of elements do not exhibit any significant correlation, neither altitudinally nor reciprocally (Table 4). Mo, Mn, Cr and Zn are industrial pollutants from local industrial plants (Istebné and the easterly localized Mn source at Krompachy, Fig. 2). Cd is omnipresent, the main source of cadmium is the super-phosphate fertilizer, where Cd content near areas treated with fertilizers is 38-48 ppm (Williams & David, 1973), traffic emissions is another cadmium source (Zechmeister, 1994) along with Zn. Despite reduction of emissions, we have recorded approximately the same elemental content in plant tissues in comparison with 1987-1988 (iron decreased in concentration and other elements slightly increased or remained stable, Table 3). A similar phenomenon was observed by Maňková (1997) in Slovakia.

The reason is explained by the ecosystem recovering after a few years since gaseous contamination (Boxman et al., 1998), but the metal contamination remained longer.

Table 1. Heavy metal concentrations (including sulphur and fluorine) in samples, 1987-1988 ( $\text{mg} \cdot 100\text{g}^{-1}$ ) nd- below the detection limit

	1	2	3	4	5	6	7	8	9	10	
Altitude m a.s.l.	1,026	1,117	1,426	1,595	1,642	1,711	1,762	1,841	1,917	1,979	mean
Cu	0.4	1	0.8	0.9	1	0.95	0.72	0.9	1	1.4	0.91
Cd	0.08	nd	nd	0.04	0.01	0.01	nd	nd	0.02	0.02	0.02
Zn	3.7	4.2	2.8	4.4	3.4	9.55	5.8	4.2	5.2	5.1	4.84
Pb	0.4	0.6	0.7	0.8	0.7	0.9	0.92	1.1	1	1.1	0.82
Cr	0.6	0.24	0.12	0.2	0.02	nd	0.64	0.04	nd	0.2	0.21
Mn	55	88	72	24.8	92	66.5	34	54	42	46	57.4
Mo	0.23	0.43	0.38	0.24	0	0.02	0.19	0.38	0.53	0.97	0.34
Fe	39.5	51.9	51.4	46.9	89.3	73.6	55.8	80.8	80	100	66.92
S	123.6	109.8	82.4	93.4	54.9	72.8	74.1	101.6	70	40	82.26
F	nd	nd	nd	nd	5	17	4	nd	nd	nd	2.60

Several authors have found that the emissions of metals in the ecosystem may persist in concentrations several thousand ppm (Hutchinson & Symington, 1997), even long after the environmental contamination has stopped, according to Nriagu et al. (1998) well over 1,000 years.

*Calluna vulgaris* is a member of the *Ericaceae*, which as a family exhibits a naturally high manganese content (Table 2). This has already been intensively investigated e. g. by Markert (1996) or Djingova et al., (2004). For this reason, manganese has not been included in the assessment of the biomonitoring.

**Table 3** Comparison of element content in samples collected in 1987-1988 and in 2011, mean values (mg.100g<sup>-1</sup>)

Element	Sampling in 1987-1988	Sampling in 2011	Difference, (mg.100g <sup>-1</sup> )
Cu	0.91	1.49	0.58
Zn	4.84	5.10	0.26
Pb	0.82	2.00	1.18
Cr	0.21	1.40	1.19
Mo	0.34	0.62	0.28
Fe	66.92	36.93	-29.99
S	82.26	122.2	39.94

The results of correlation analysis of samples collected in 2011 are similar to those collected in 1987-1988. The relationships in the following groups of elements have been noted: (a) Pb, Cu, (b) S, (c) Mo, Cr, Zn, Mn, Fe.

a. Pb and Cu show a significant positive relation to altitude (Table 5); the long-distance transport of emissions from smelters located in western areas (Ostrava, Kraków and Silesia regions) is still relevant.

b. A negative significant correlation with altitude changed to a positive insignificant correlation (Table 5), since the sulphur content in the lower air layer decreased substantially due to reduced sulphur emissions from local sources (Chemosvit, Mondi SCP), (Table 1, 2). The trend is supported by comparing current element concentrations in the soil with concentrations in the past (Table 6). Similarly, Hajdúk (1988) in the transect of Biela voda (3 km eastward) recorded in the soil at the altitude of 1,250 m a.s.l. (Šalvijový prameň spring) 120 mg.100g<sup>-1</sup> sulphur and at the altitude of 2,000 m a.s.l. (slope of Jahňací štít peak) 80 mg.100g<sup>-1</sup> sulphur.

c. Mo, Cr, Zn, and Fe did not show significant correlations; the high content of manganese - 203,6 mg.100g<sup>-1</sup> (Table 2, Site 1) must be attributed to the specific interaction of the plants with manganese.

Compared to sampling in the past, Fe content in the samples decreased mainly in the 1,800-2,000 m a.s.l. zone (Table 1, 2). At this altitude, Fe is deposited from sources located to the north-west, the decreased iron emission eliminated the positive significant correlation with altitude.

**Table 2** Heavy metal concentrations (including sulphur) in samples, 2011 (mg.100g<sup>-1</sup>)

	1	2	3	4	5	6	7	8	9	10	
Altitude m a.s.l.	1,031	1,297	1,598	1,649	1,708	1,766	1,881	1,933	1,948	1,987	mean
Cu	0.70	1.00	1.30	1.20	1.50	1.60	2.10	1.90	1.70	1.90	1.49
Zn	4.70	3.30	4.50	5.70	4.50	4.50	5.00	6.10	7.20	6.30	5.10
Pb	1.20	1.90	2.20	2.20	2.20	2.00	1.90	2.00	2.00	2.40	2.00
Cr	1.20	1.40	1.60	1.30	1.70	1.70	1.70	1.00	0.90	1.60	1.40
Mn	203.60	84.40	50.30	72.90	44.90	58.40	50.80	52.40	56.80	49.90	57.80
Mo	0.51	0.57	0.37	0.75	0.66	0.64	0.71	0.82	0.6	0.62	0.62
Fe	17.00	49.30	19.80	14.10	25.10	65.50	31.50	38.00	60.80	48.20	36.93
S	86	87	101	108	145	160	159	96	130	150	122.2

**Table 4** Correlation coefficients between heavy metals (including sulphur) and altitude, sampling in 1987-1988

	S	Fe	Mo	Cr	Pb	Zn	Cd	Cu	Altitude
Altitude	*-0.7398	*0.7565	0.3077	-0.4624	*0.9519	0.3716	-0.4546	*0.6320	1.000
Cu	*-0.7277	*0.7800	0.5826	-0.5894	*0.6459	0.1859	-0.4826	1.0000	
Cd	0.3967	-0.3832	-0.3860	0.4311	-0.5046	-0.1466	1.0000		
Zn	-0.2574	0.2152	-0.1949	-0.1375	0.3861	1.0000			
Pb	-0.5919	0.7065	0.4310	-0.4145	1.0000				
Cr	0.3754	-0.5878	-0.4820	1.0000					
Mo	-0.2779	0.3663	1.0000						
Fe	*-0.7821	1.0000							
S	1.0000								

\*Indicates significance. Note: Because a lot of F data measured are below the instrumental detection limit, F data have not been used for correlation analysis.

Table 5. Correlation coefficients between heavy metals (including sulphur) and altitude, sampling in 2011

	S	Fe	Mo	Cr	Pb	Zn	Cu	Altitude
Altitude	0.6253	0.4784	0.4900	0.0199	*0.7306	0.6417	*0.9266	1.0000
Cu	*0.7570	0.4017	0.5107	0.1522	0.5381	*0.6459	1.0000	
Zn	0.3498	0.2846	0.4200	-0.4534	0.4689	1.0000		
Pb	0.4428	0.1763	0.1847	0.3326	1.0000			
Cr	0.5319	-0.0792	-0.1947	1.0000				
Mo	0.3243	0.1038	1.0000					
Fe	0.4287	1.0000						
S	1.0000							

\* Indicates significance

Markert (1991) found positive correlation between Zn and Fe, but we could not confirm this trend; likewise Koniecznyński & Wesolowski (2007) recorded negative correlation between these metals.

Table 6. Sulphur concentration in soil samples, comparison 1983 and 2012 (mg.100g<sup>-1</sup>)

	1983	2012
Lomnické sedlo	278	nd
Tatranská Lomnica	326	nd

nd – below detection limit.

Similarly, Zechmeister (1994) divided emissions in the Alps into two groups, those released by steelworks (Fe, Ni, Cr, Co, V and As) and those derived from fossil fuel (Pb, Cd and S). Hajdúk (1988) pointed to a correlation between lead and altitude. The author investigated the element concentration (Pb, Cd, As, Fe, Cr, Zn, Cu, Ca, Mg and S) in the lakes deposition and in the soils in the Tatra Mts with respect to the influence of industrial emission. The author found the highest lead concentration in Litvorová dolina valley, at a distance of 15 km from the Litvorové pleso lake at the altitude of 1863 m a.s.l. (2.5 mg.100g<sup>-1</sup>). Hajdúk (1980) also noted the impact of this pollution from westerly located sources. The author found numerous examples of necrosis or dead leaves on more species in the West Tatra Mts, influenced from westerly located sources. Lead distribution along the road „cesta Slobody“ studied by Bednářová & Bednář (1978), they found increased Pb concentration up to 1,600 m a. s. l. Banášová & Hajdúk (1975) and Hajdúk & Hronec (1983a, 1983b) investigated emission influence to vegetation on a pan-Slovakian scale.

The quality of data was validated by calibrating the instrument, using it's own calibration system. Apart from sulphur, manganese and zinc, acceptable concentrations of emissions are exceeded. Concentrations of S at 180 mg.100g<sup>-1</sup> (Clement, 1985) and Mn 200 mg.100g<sup>-1</sup> (Vladovič, 1992) are in the permitted range. In the case of zinc, the optimal

concentration is exceeded (1.6-3.8 mg.100g<sup>-1</sup>; Bergman, 1986), quoted an acceptable concentration of 8 mg.100g<sup>-1</sup> (Vladovič, 1992) which was not exceeded. Acceptable levels of Cu (0.5 mg.100g<sup>-1</sup>; Jochheim, 1993), Pb (0.6 mg.100g<sup>-1</sup>; Hogan & Wotton, 1984), Cr (0.17 mg.100g<sup>-1</sup>; Jochheim, 1993) and Fe (30 mg.100g<sup>-1</sup>; Vladovič, 1992) are exceeded.

Based on *Calluna vulgaris* analysis, the highest fluorine concentrations have been found in the subalpine level at 1,660-1,780 m a.s.l. in the samples set collected in 1987-1988 (Table 1), where the thermolysis of fluoropolymers is the common environmental fluorine source (Ellis & Mabury, 2001). There are two incinerators of waste material situated directly in the investigated area (Poprad and Svit), the outlying incinerators are located in Liptovský Mikuláš (50 km West) and Levoča (30 km East). The XRF device does not measure fluorine.

The essential elements are Zn, Mn, Fe, and S, whereas non-essential elements are Cr, Pb, Cd. Non-essential elements tend to have a wider spread of values than essential elements (Timperly et al., 1970). In the case of *Calluna vulgaris*, non-essential elements occur in lower concentrations than the essential elements, the exception being molybdenum. Distribution of essential and non-essential elements in tissues of vascular plants varies. For example, accumulated Zn was located in leaf epidermises, while the majority of Cd and Pb was distributed within the mesophyll (Mikus et al., 2008).

#### 4. CONCLUSIONS

We have compared the data sets from 2 decades ago, at the height of contamination, with recent contamination levels. Despite the fact, that industrial plants have accepted measures to reduce emissions, in 2011 we have recorded approximately the same elemental contents in the plant tissues in comparison with 1987-1988. Following SO<sub>2</sub> contamination, the ecosystem has recovered after

only a few years, however the metal contamination was evident for a longer period. Acceptable concentrations of emissions are mostly exceeded.

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