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# Bryomonitoring of element deposition in three walleys in the Tatra Mts (Slovakia) based on X-ray spectrometry

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**Abstract.** The moss species *Pleurozium schreberi* we have chosen for bioindication, this moss have often been used as imission bioindicator. Three different oriented valleys (transects) have been selected: South facing Velická dolina valley, North facing Bielovodská dolina (including Litvorová dolina valley) and East facing Žabia dolina valley.

It turned out that the effect of the Silesian and Polish metallurgy and domestic Ferrous-Alloy Mills Istebné is essential to the pollution in the investigated area. In all three transects lead correlates with altitude. Similar to the correlations are North-South transects (Transects A, B), where apart from Pb-altitude correlation, correlate also: Fe-altitude; Ti-Pb; Ti-Ba; Fe-Pb; Ba-Sr; Ti-Ba. Transekt (C) facing East is quite different.in correlations.

*Key words:* bioindication, elemental correlation, X-ray spectrometry, Tatra Mts.

## Introduction

The idea of bryophyte utilization for bioindication arose in seventies (Clymo 1963, Rühling and Tyler 1970). High cation exchange capacity, lacking cuticle and simple thalli organisation make the bryophytes unable to avoid heavy metal accumulation from deposition (Tyler 1990). From nutritional point of view, the bryophytes are indipendent of the soil (Ratcliffe 1975, Tyler 1990, Burton 1990 and others). The cation exchange capacity is related to the concentration of peptic substances in moss tissue.

Bioindication is a simple method, have widely been used all over Europe and the USA in the past, often for forest ecosystems monitoring or industrial areas monitoring (e. g. Sumerling 1984, Zoltai 1988) or for detection of correlation between altitude and deposition (e. g. Zechmeister 1994). The moss species *Pleurozium schreberi* have often been used as imission bioindicator. Spacious forest ecosystems monitoring in the territory of Slovakia based on moss species *Pleurozium schreberi*, *Hylocomium splendens* and *Dicranum scoparium* performed Maňkovská (1997). Maňkovská *et al.* (2003) collected 831 samples of *Pleurozium schreberi* and other bryophytes throughout Slovakia to identify the areas affected by industrial imissions. The moss species *Pleurozium schreberi* used Maňkovská *et al.* (2008) for bioindication of atmospheric deposition in the Carpathians.

Šoltés (1992) evaluated results of chemical analysis of 267 samples of 26 bryophyte species collected on the territory of the High Tatra Mts. Some important trends were revealed, disproportion between increasing Cr concentration and the other elements, increasing Pb concentration in relation to the altitude. In 1995 a large area of three north facing valleys of High Tatra Mts. was attacked by spruce bark beetle. Šoltés (1996) analysed relation of insect outbreak to heavy metal deposition. The peat moss *Sphagnum girgensohnii* used Šoltés (1998) for bioindication of imission load of Tatra Mts. with special focus to correlation between altitude and heavy metal deposition.

The following aims are addressed in this paper: (1) determination of heavy metal concentrations in collected samples in three altitudinal transects, (2) identification groups of elements based on correlations, (3) pollution sources identification.

## Material and Methods

*Sampling*

We have decided for *Pleurozium schreberi* as bioindicator, the species is growing abundantly in forest ecosystem and in alpine heaths as well. Other investigators used this species as bioindicator also, e.g. Maňkovská (1997), Maňkovská *et al.* (2003, 2008). The samples of *Pleurozium schreberi* were collected in three transects. South facing transect Velická dolina valley from 859 m asl to 2181 m asl, North facing transect Bielovodská dolina valley-Litvorová dolina valley from 950 m asl to 2154 m asl and a small, East facing transect Žabia dolina valley from 1259 m asl to 1656 m asl. The samples were collected in 2010, in clearings, at least 5 m from the immediate tree, in vertical interval approximately of 100 m.

*Instrumental analysis*

The samples were analyzed by X-ray fluorescence (Stephens and Calder 2004), using the hand-held XRF spectrometer DELTA CLASSIC (USA). The following elements were determined: S, Pb, Fe, Mn, Cu, K, Ca, Zn, Mo, Cr, Ba, Rb, Sr, Ti, Zr, Cl, As, Co, Cd, Sb, I. Since some examined elements need different thickness of pellets, e.g. S versus Pb (Richardson *et al.* 1995) we have decided to use method without pelletization (Stikans *et al.* 1988; Boman *et al.* 1993; Aslan *et al.* 2004). The plant material was crushed in mortar into fine powder. The epoxide frame of 2.0 x 2.4 cm was filled with 1-1.2 g of plant powder, up to 1 cm in thickness and analysed directly on protective prolen folium. The samples are stored in the Institute of High Mountain Biology in Tatranská Javorina.

*Statistics*

CANOCO 4.5 for Windows package was used for statistical analysis. The linear indirect methods – PCA (Ter Braak and Šmilauer 2002) has been used since the length of the first gradient in the log report was < 0.4. In order to relate the heavy metal concentrations and altitude, we used the correlation analysis. The correlation coefficients calculated by regression were tested for significance. Statistical graphics system STATGRAPHICS, Version 5.0 have been used for the correlation analysis.

## Results and Discussion

The results of chemical analysis of samples collected along transects are presented in Tables 1, 3, 5. Three different types of orientation patterns have been included: (A) South facing transect, (B) North facing transect, (C) East facing transect. S, Pb, Fe, Mn, Cu, K, Ca, Zn, Mo, Cr, Ba, Rb, Sr, Ti, have been identified in every sample. Below detection limit have been often recorded Zr, very rarely have been recorded Cl, As, Co, Cd, Sb, I., these elements were not included in the analysis.

In the past, influence of leaded petrol was distinct. According to Bednářová and Bednář (1978), the vegetation is highly influenced by lead in a belt of 150 m along the motorway. This fact has been confirmed by Šoltés (1998, p. 87), where extreme high concentrations of Pb has been recorded in samples of Sphagnum girgensohnii collected in 1986 – 1989 along motorway. Now, after change to unleaded petrol, we couldn't record higher Pb concentration in the samples collected close to motorway, despite the fact that *Pleurozium schreberi* is considered as a senzitive species for lead accumulation (Tyler 1990).

The southern slopes of the Tatra mountains are affected by the immisions from the following sources: Mondi SCP Ružomberok, Copper Smelter Krompachy, Chemosvit Svit, while North part of the Tatra Mts is stricken by Ferrous-Alloy Mill, Istebné. The most harmful substance in the Tatra Mts is sulphur dioxide.

The largest producer of $SO_2$ was MONDI CKP Ružomberok, the plant have several projects aimed at improvement of emissions. Distinct improvements

| No. | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m. asl. | 859 | 945 | 1048 | 1145 | 1258 | 1357 | 1449 | 1553 | 1670 | 1824 | 1954 | 2181 |
| S | 1875 | 3203 | 3042 | 4852 | 3350 | 1599 | 2579 | 2415 | 2389 | 3530 | 3341 | 3215 |
| Pb | 26 | 45 | 43 | 51 | 31 | 38 | 34 | 35 | 42 | 60 | 63 | 133 |
| Fe | 3912 | 2843 | 2663 | 2670 | 2369 | 1599 | 1730 | 2185 | 2306 | 3938 | 5298 | 11069 |
| Mn | 884 | 1005 | 981 | 763 | 974 | 393 | 1104 | 518 | 249 | 477 | 1362 | 175 |
| Cu | 15 | 14 | 17 | 24 | 18 | 19 | 16 | 16 | 18 | 16 | 26 | 18 |
| K | 15754 | 5301 | 8371 | 11390 | 14441 | 13922 | 8792 | 8979 | 5707 | 13838 | 11491 | 6692 |
| Ca | 7062 | 12634 | 10205 | 10395 | 10528 | 6216 | 10108 | 5957 | 3128 | 6170 | 15361 | 939 |
| Zn | 48 | 142 | 117 | 146 | 101 | 134 | 139 | 175 | 104 | 219 | 342 | 77 |
| Mo | 5.8 | 7.2 | 5.2 | 7.8 | 8.2 | 6.8 | 6.9 | 6.3 | 5.9 | 7.7 | 7.3 | 4.2 |
| Cr | 32 | 27 | 23 | 25 | 40 | 33 | 27 | 27 | 28 | 39 | 34 | 23 |
| Ba | 111 | 132 | 96 | 101 | 122 | 80 | 78 | 63 | 68 | 104 | 99 | 131 |
| Rb | 60 | 25.8 | 37 | 50 | 40 | 80 | 52 | 37 | 35.7 | 54 | 37 | 52 |
| Sr | 40 | 58 | 26.6 | 26.4 | 26.9 | 15.7 | 30.9 | 21.3 | 10.7 | 17.3 | 37 | 41.1 |
| Ti | 402 | 274 | 204 | 179 | 135 | 103 | 94 | 156 | 136 | 274 | 416 | 1034 |
| Zr | 12.6 | 4.9 | 4.6 | 14.8 | nd | nd | nd | nd | 4.6 | 24 | 7.0 | 34.6 |

**Table 1.** Heavy metal concentration (ppm) in the samples collected in Velická dolina valley, transect A
Sites locations:
1 Velická dolina valley, below Hubert holiday resort, 859 m asl, windthrow area, N49˚06,359; E20˚011,536
2 Velická dolina valley, below Tatranská Polianka settlement, 945 m asl, windthrow area, N49˚07,108; E20˚011,323
3 Velická dolina valley, 1048 m asl, windthrow area, N49˚07,636; E20˚10,901
4 Velická dolina valley, 1145 m asl, windthrow area, N49˚07,925; E20˚10,586
5 Velická dolina valley, 1258 m asl, clearing in forest ecosystem, N49˚08,251; E20˚10,510
6 Velická dolina valley, 1357 m asl, clearing in forest ecosystem, N49˚08,508; E20˚10,277
7 Velická dolina valley, 1449 m asl, clearing near timberline, N49˚08,811; E20˚10,053
8 Velická dolina valley, 1553 m asl, clearing in dwarf pine, N49˚09,069; E20˚09,773
9 Velická dolina valley, near Velické pleso lake, 1670 m asl, clearing in dwarf pine, N49˚09,457; E20˚09,403
10 Velická dolina valley, near Kvetnicové pleso lake, 1824 m asl, clearing in dwarf pine, N49˚09,731; E20˚09,134
11 Velická dolina valley, near Dlhé pleso lake, 1954 m asl, alpine heath, N49˚09,988; E20˚08,661
12 Poľský hrebeň ridge, slope to Velická dolina valley, 2182 m asl, granite rock covered by soil, N49˚10,394; E20˚08,450

| | alt | S | Pb | Fe | Mn | Cu | K | Ca | Zn | Mo | Cr | Ba | Rb | Sr | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **alt** | 1.00 | 0.09 | *0.71 | *0.62 | -0.39 | 0.33 | -0.20 | -0.38 | 0.43 | -0.21 | 0.08 | -0.11 | 0.03 | -0.24 | 0.52 |
| **S** | | 1.00 | 0.32 | 0.20 | 0.21 | 0.48 | -0.09 | 0.35 | 0.29 | 0.38 | -0.08 | 0.41 | -0.37 | 0.16 | 0.13 |
| **Pb** | | | 1.00 | *0.93 | -0.40 | 0.22 | -0.34 | -0.04 | 0.05 | -0.49 | -0.03 | 0.44 | 0.03 | 0.25 | *0.90 |
| **Fe** | | | | 1.00 | -0.28 | 0.15 | -0.19 | -0.37 | -0.02 | -0.55 | -0.21 | 0.55 | 0.03 | 0.39 | *0.99 |
| **Mn** | | | | | 1.00 | 0.36 | 0.18 | *0.94 | 0.40 | 0.43 | 0.15 | 0.19 | -0.35 | 0.47 | -0.27 |
| **Cu** | | | | | | 1.00 | 0.17 | 0.36 | 0.57 | 0.27 | 0.05 | -0.07 | 0.04 | -0.15 | 0.07 |
| **K** | | | | | | | 1.00 | 0.15 | 0.07 | 0.44 | *0.73 | 0.06 | *0.60 | -0.24 | -0.19 |
| **Ca** | | | | | | | | 1.00 | 0.54 | *0.61 | 0.19 | 0.17 | -0.37 | 0.40 | -0.38 |
| **Zn** | | | | | | | | | 1.00 | 0.45 | 0.31 | -0.18 | -0.22 | -0.47 | -0.11 |
| **Mo** | | | | | | | | | | 1.00 | *0.65 | 0.02 | -0.05 | -0.11 | -0.60 |
| **Cr** | | | | | | | | | | | 1.00 | 0.11 | 0.22 | -0.24 | -0.26 |
| **Ba** | | | | | | | | | | | | 1.00 | -0.14 | *0.73 | *0.58 |
| **Rb** | | | | | | | | | | | | | 1.00 | -0.33 | 0.04 |
| **Sr** | | | | | | | | | | | | | | 1.00 | 0.47 |
| **Ti** | | | | | | | | | | | | | | | 1.00 |

**Table 2.** Correlation coeficients between elements and altitude, Velická dolina valley, transect A
*Indicates significance

| No. | 1 | 2 | 3 | 4 | 5 | 6 | *7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m. asl. | 950 | 1038 | 1140 | 1366 | 1452 | 1540 | 1623 | 1718 | 1857 | 1960 | 2052 | 2154 |
| S | 3744 | 4585 | 3393 | 3256 | 3261 | 5390 | 3559 | 3175 | 2716 | 2715 | 3812 | 2737 |
| Pb | 33 | 50 | 44 | 52 | 60 | 63 | 198 | 56 | 72 | 68 | 82 | 85 |
| Fe | 1178 | 1756 | 1863 | 3827 | 2969 | 4574 | 5718 | 2767 | 4248 | 6053 | 5519 | 16765 |
| Mn | 182 | 742 | 557 | 1421 | 465 | 920 | 411 | 690 | 675 | 1480 | 587 | 288 |
| Cu | 27 | 21 | 13 | 21 | 29 | 33 | 26 | 25 | 25 | 19 | 21 | 13 |
| K | 17607 | 19546 | 9366 | 18235 | 11961 | 17991 | 9273 | 8265 | 8260 | 8096 | 13827 | 13018 |
| Ca | 15762 | 14221 | 8814 | 9304 | 9114 | 8576 | 4758 | 7026 | 7164 | 10189 | 7375 | 5039 |
| Zn | 160 | 197 | 166 | 140 | 169 | 406 | 213 | 165 | 147 | 424 | 274 | 77 |
| Mo | 6.6 | 7.0 | 4.1 | 6.0 | 7.4 | 6.7 | 4.4 | 6.1 | 6.3 | 6.2 | 6.4 | 3.3 |
| Cr | 28 | 29 | 28 | 37 | 32 | 54 | 32 | 40 | 35 | 38 | 43 | 36 |
| Ba | 69 | 143 | 70 | 135 | 107 | 185 | 109 | 126 | 100 | 143 | 141 | 335 |
| Rb | 26 | 31 | 44 | 72 | 45 | 56 | 43 | 35 | 34 | 34 | 39 | 72 |
| Sr | 29.5 | 21.7 | 17.0 | 30 | 23.1 | 21.0 | 22.0 | 8.5 | 7.9 | 24.5 | 22.3 | 146 |
| Ti | nd | 95 | 93 | 319 | 194 | 372 | 325 | 161 | 289 | 482 | 434 | 2031 |
| Zr | nd | nd | nd | 5.9 | nd | 9.7 | 8.0 | nd | 5.3 | 8.0 | 8.2 | 90 |

**Table 3.** Heavy metal concentration (ppm) in the samples collected in Bielovodská and Litvorová valley, transect B
*Rejected outlier

Sites locations:
1 Bielovodská dolina valley, 950 m asl, forest ecosystem, N49°14,919; E20°06,141
2 Bielovodská dolina valley, 1038 m asl, forest ecosystem, N49°13,727; E20°06,057
3 Bielovodská dolina valley, 1140 m asl, forest ecosystem, N49°12,729; E20°06,089
4 Bielovodská dolina valley, 1366 m asl, forest ecosystem, N49°11,497; E20°06,989
5 Bielovodská dolina valley, 1452 m asl, forest ecosystem, N49°11,056; E20°06,991
6 Bielovodská dolina valley, 1540 m asl, clearing in dwarf pine, N49°10,906; E20°07,052
7 The mouth of Kačia dolina valley, 1623 m asl, dwarf pine stand, N49°10,827; E20°07,140
8 Litvorová dolina valley, 1718 m asl, clearing in dwarf pine, N49°10,790; E20°07,450
9 Litvorová dolina valley, 1857 m asl, alpine heath, Juncetum trifidi, N49°10,743; E20°07,764.
10 Litvorová dolina valley, 1960 m asl, alpine heath, Juncetum trifidi, N49°10,677; E20°08,013
11 Litvorová dolina valley, Ľadové pleso lake, 2052 m asl, alpine heath, Juncetum trifidi, N49°10,606; E20°08,211
12 Poľský hrebeň ridge, slope to Litvorová dolina valley, 2154 m asl, granite rock covered by soil, N49°10,428; E20°08,342

| | alt | S | Pb | Fe | Mn | Cu | K | Ca | Zn | Mo | Cr | Ba | Rb | Sr | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **alt** | 1.00 | -0.44 | *0.94 | *0.72 | 0.14 | -0.20 | -0.51 | *-0.79 | 0.18 | -0.28 | 0.51 | 0.59 | 0.27 | 0.39 | *0.65 |
| **S** | | 1.00 | -0.26 | -0.35 | -0.03 | 0.50 | *0.71 | 0.38 | 0.42 | 0.41 | 0.41 | -0.05 | -0.06 | -0.27 | -0.32 |
| **Pb** | | | 1.00 | *0.75 | 0.06 | -0.19 | -0.31 | *-0.76 | 0.15 | -0.25 | 0.50 | *0.67 | 0.34 | 0.45 | *0.69 |
| **Fe** | | | | 1.00 | -0.12 | -0.46 | -0.12 | *-0.60 | -0.15 | *-0.65 | 0.23 | *0.93 | *0.61 | *0.91 | *0.99 |
| **Mn** | | | | | 1.00 | 0.00 | -0.02 | -0.03 | 0.55 | 0.21 | 0.36 | -0.05 | 0.20 | -0.32 | -0.17 |
| **Cu** | | | | | | | 0.27 | 0.24 | 0.33 | *0.80 | 0.43 | -0.31 | -0.25 | -0.49 | -0.48 |
| **K** | | | | | | | 1.00 | 0.53 | 0.00 | 0.29 | 0.08 | 0.13 | 0.24 | 0.10 | -0.07 |
| **Ca** | | | | | | | | 1.00 | 0.11 | 0.49 | -0.47 | -0.50 | -0.53 | -0.34 | -0.57 |
| **Zn** | | | | | | | | | 1.00 | 0.39 | *0.61 | -0.06 | -0.21 | -0.37 | -0.21 |
| **Mo** | | | | | | | | | | 1.00 | 0.15 | -0.52 | -0.50 | *-0.69 | *-0.69 |
| **Cr** | | | | | | | | | | | 1.00 | 0.37 | 0.32 | -0.04 | 0.18 |
| **Ba** | | | | | | | | | | | | 1.00 | *0.65 | *0.87 | *0.94 |
| **Rb** | | | | | | | | | | | | | 1.00 | *0.61 | *0.63 |
| **Sr** | | | | | | | | | | | | | | 1.00 | *0.95 |
| **Ti** | | | | | | | | | | | | | | | 1.00 |

**Table 4.** Correlation coeficients between heavy metals and altitude, Bielovodská and Litvorová dolina valley, transect B
*Indicates significance

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| | 1259 | 1340 | 1441 | 1554 | 1656 |
| S | 2123 | 3243 | 2336 | 2392 | 2183 |
| Pb | 39 | 44 | 46 | 48 | 50 |
| Fe | 1946 | 2735 | 1614 | 1815 | 2227 |
| Mn | 671 | 722 | 555 | 575 | 285 |
| Cu | 15 | 20 | 18 | 19 | 13 |
| K | 14650 | 13980 | 5119 | 11446 | 4684 |
| Ca | 7522 | 6994 | 4478 | 6113 | 3292 |
| Zn | 111 | 144 | 146 | 114 | 83 |
| Mo | 6.5 | 7.5 | 6.4 | 5.9 | 5.9 |
| Cr | 45 | 32 | 14 | 32 | 34 |
| Ba | 105 | 84 | 35 | 59 | 68 |
| Rb | 43 | 61 | 35.1 | 42 | 33.9 |
| Sr | 13.6 | 18.2 | 8.1 | 8.8 | 5.5 |
| Ti | 97 | 225 | 112 | 126 | 107 |
| Zr | nd | 4.1 | nd | nd | nd |

**Table 5.** Heavy metal concentration (ppm) in samples collected in Žabia Bielovodská dolina valley, transect C
Sites locations:
1 Žabia Bielovodská dolina valley, 1259 m asl., insect outbreak clearing, N49°12,677; E20°05,913
2 Žabia Bielovodská dolina valley, 1340 m asl., clearing in forest ecosystem, N49°12,616; E20°05,709
3 Žabia Bielovodská dolina valley, 1441 m asl., clearing in dwarf pine stand, N49°12,419; E20°05,600.
4 Žabia Bielovodská dolina valley, 1554 m asl., clearing in dwarf pine stand, N49°12,204; E20°05,680
5 Žabia Bielovodská dolina valley, 1656 m asl., clearing in dwarf pine stand, N49°12,032; E20°05,733

were seen in $SO_2$ emissions, they reduced sulphur by 96% (Sotolová 2006).

The Copper Smelter Krompachy produces more emissions, sulphur dioxide, carbon monoxide, oxides of nitrogen, lead, cadmium, nickel, arsenic, BaP (benzopyrene), $PM_{10}$ (suspended particulates less than 10 microns in diameter). The industrial plant is 45 km east of Tatra mountains, the prevailing airflow in Krompachy is the flow of Northern and Western directions. Thanks to air streams, these emissions do not constitute a more serious source for the Tatra Mts. In 2000, the Copper Smelter Krompachy instigated a modernisation of production methods, and the plant is constantly upgrading the technologies (Annonymus 2007).

Chemosvit stopped 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 (Annonymus 2012).

| | alt | S | Pb | Fe | Mn | Cu | K | Ca | Zn | Mo | Cr | Ba | Rb | Sr | Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **alt** | 1.00 | -0.29 | *0.96 | -0.14 | -0.87 | -0.31 | -0.73 | -0.83 | -0.56 | -0.71 | -0.27 | -0.56 | -0.56 | -0.81 | -0.27 |
| **S** | | 1.00 | -0.06 | 0.75 | 0.54 | 0.73 | 0.41 | 0.37 | 0.62 | 0.84 | -0.13 | 0.10 | *0.90 | 0.74 | *0.99 |
| **Pb** | | | 1.00 | -0.05 | -0.76 | -0.08 | -0.73 | -0.81 | -0.33 | -0.52 | -0.45 | -0.68 | -0.40 | -0.70 | -0.06 |
| **Fe** | | | | 1.00 | 0.17 | 0.13 | 0.37 | 0.23 | 0.02 | 0.68 | 0.36 | 0.51 | 0.77 | 0.62 | 0.80 |
| **Mn** | | | | | 1.00 | 0.70 | 0.82 | *0.91 | 0.73 | 0.72 | 0.13 | 0.38 | 0.74 | 0.86 | 0.51 |
| **Cu** | | | | | | 1.00 | 0.39 | 0.46 | 0.83 | 0.54 | -0.40 | -0.25 | 0.63 | 0.53 | 0.68 |
| **K** | | | | | | | 1.00 | *0.98 | 0.23 | 0.54 | 0.65 | 0.76 | 0.76 | 0.84 | 0.43 |
| **Ca** | | | | | | | | 1.00 | 0.38 | 0.56 | 0.52 | 0.67 | 0.71 | 0.84 | 0.43 |
| **Zn** | | | | | | | | | 1.00 | 0.69 | -0.57 | -0.27 | 0.50 | 0.55 | 0.55 |
| **Mo** | | | | | | | | | | 1.00 | 0.01 | 0.37 | *0.87 | *0.91 | 0.83 |
| **Cr** | | | | | | | | | | | 1.00 | *0.92 | 0.26 | 0.33 | -0.06 |
| **Ba** | | | | | | | | | | | | 1.00 | 0.49 | 0.62 | 0.16 |
| **Rb** | | | | | | | | | | | | | 1.00 | *0.93 | *0.91 |
| **Sr** | | | | | | | | | | | | | | 1.00 | 0.75 |
| **Ti** | | | | | | | | | | | | | | | 1.00 |

**Table 6.** Correlation coeficients between heavy metals and altitude, Žabia Bielovodská dolina valley, transect C
*Indicates significance

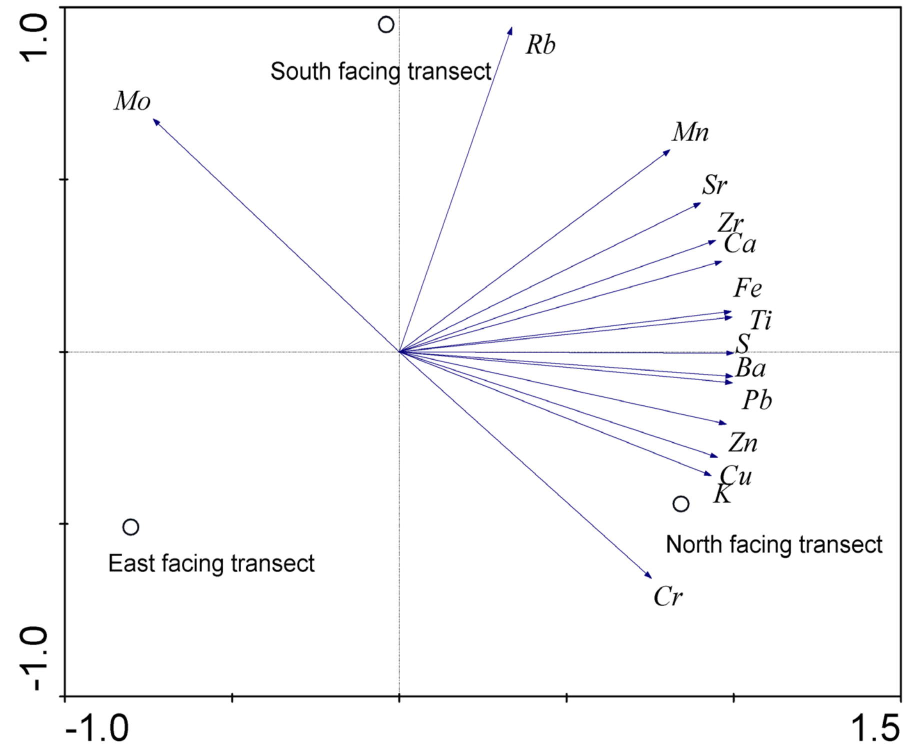


**Fig. 1.** Principal component analysis (PCA), biplot, relationship of heavy metal concentrations and analysed trasects

For the higher content of heavy metals in ecosystems of Orava region is responsible Ferrous-Alloy Mill, Istebné. The main industrial immissions in Istebné area are Cr and Mn. After the installation of separators in 1984-1985, the annual polymetallic deposition is 32,000 tonnes with an increased content of mobile forms of Cr and Mn (Fargašová 2009).

From location of emission sources and the measures taken to reduce emissions, arises that except for the effects of the Silesian and Polish metallurgy, an important source of polymetallic deposition is domestic Ferrous-Alloy Mills Istebné. The key components of the solid emissions from Ferrous-Alloy Mills Istebné are Mn and Cr compounds, in particular, soluble compounds of chromium easily enter into the plants. Other risk elements are Ti, Zr, Cu, Pb and others (Fig. 1; Fargašová 2009).

The sample Nr 7 (Table 3) at the altitude of 1623 m asl was collected at the place where Kačia dolina Valley runs into the Litvorová dolina valley. Air flow from the Kačia dolina valley has influenced the concentration of elements in the transect.

In all three transects lead significantly correlates with altitude (Table 2, 4, 6). In the North-South transects (Transects A, B) with the altitude significantly correlates also Fe. In addition to Fe-altitude correlation, North-South transects (Transects A, B) have more significant correlations: Ti-Pb; Ti-Ba; Fe-Pb; Ba-Sr; Ti-Ba (Table 2, 4).

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