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# Bioindication of environmental contamination of the MONDI Ružomberok surrounding area based on bryophytes

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**Abstract.** The present work provides the estimation of environmental load in the neighbourhoods of industrial complex MONDI SCP Ružomberok, northern Slovakia, based on bryophyte bioindication. The samples were collected within three protected areas: Low Tatra National park, Veľká Fatra Mts National park and National Nature Reserve Chočské vrchy Mts, while control sampling near Hrboltová settlement in Liptov Basin was performed. Imissions accumulated during winter in the snow after its melting did not affect significantly the concentrations of imissions in the tissues of bioindicator. A significant correlation was found with altitude in copper, molybdenum and lead. Contamination by Cu, Mn, Mo, Zn, Cr, Rb, and Ba caused by MONDI SCP the authors do not suppose. Emission sources were located NW, i. e. Krakow region, Silesia, Orava or Ostrava region, only in the case of sulphur is a local source probable.

K*ey words*: XRF spectrometry, bryophytes, bioindication, air contamination, pulp mill,

## Introduction

In 1980, throughout the Liptov and Spiš region, there was the production of a total 5 of 5733 tonnes of solid emissions and 72427 tonnes of gaseous emissions, while the largest producer of sulphur dioxide was Mondi SCP Ružomberok. As to solid emissions, compounds of Fe, Mn, Mo and Cr were produced by OPZ Istebné (Rak *et al.* 1982). The biggest emmissions producers were sites situated NW at a distance of 150-200 km, i. e. Ostrava region, Kraków region and Silesia region (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. Therefore the amount of arising AOH (Absorbable Organic Halogens) has been reduced by 58% and COD (Chemical Oxygen Demand) by 69%. Within the company, the project IMPULSE has been put into practice, to increase the quality of the output of pulp and paper, in connection with the environmental impact. Distinct improvements were seen in SOx emissions; they were reduced by 92% and in terms of TRS (Total Reduced Sulphur), emissions were reduced by 96% (Sotolová 2006). Such a condition has been achieved by the installation of a new recovery boiler (Sotolová 2006). The shift in the manufacturing process was also due to the introduction of the ANDRITZ automation (SPECTRUM No.21/1-2010 Magazine of pulp and paper).

Despite the measures referred above, according to the official measurements of the SHMÚ, the town Ružomberok is still highly polluted. This applies to the $PM_{10}$ pollution (particles with a diameter of 10 micrometres or less) or $PM_{2.5}$ (particles with a diameter of 2.5 micrometres or less). In 2011, the daily limit value for $PM_{10}$, at the station Ružomberok - Riadok was exceeded 131 times, this is the absolute maximum in SR. At the same time, this station also showed the highest average annual concentration of dust particles (50.6 $\mu g\ m^{-3}$).

The idea of bryophyte utilisation for bioindication arose in the seventies (Clymo 1963, Rühling and Tyler 1970). In terms of nutrition, bryophytes are completely independent from the substrate, bryophytes receive the majority of nutrients from precipitation or from dry deposition (Ratcliffe 1975, Burton 1990 and others). The high cation exchange capacity, lacking cuticle and simple thalli organisation make the bryophytes unable to avoid the heavy metal accumulation from deposition (Tyler 1990).

Bioindication based on bryophytes is a simple method, often used in Europe, as well as in the U.S.A., usually for the monitoring of ecosystems (Sumerling 1984; Zoltai 1988), or to identify the correlation between altitude and metal deposition (Zechmeister 1994).

In Slovakia, Šoltés (1992) assessed the results of chemical analysis of 267 bryophyte samples collected on the territory of the High Tatra. This author detected several trends, the most significant one was the correlation between the concentration of lead and the altitude. Šoltés (1996) analysed the relationship of the outbreak of bark beetle to heavy metal deposition. This author found out, that the centres of insect gradation correlate with the territories of maximum Cd and Cr deposition. The same author (Šoltés 1998), focused attention to the correlation of the accumulated elements with the altitude. A significant correlation was confirmed in the case of lead.

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Maňkovská (1997) founded in Slovakia 78 permanent plots with *Pleurozium schreberi, Hylocomium splendens* and *Dicranum scoparium* as bioindicators. The results have been compared with levels in 1991/1995. The contents of Cu, Fe and Ni has increased, while contents of Cd, Pb, and Zn have decreased. Maňkovská *et al.* (2003) analysed 831 samples of *Pleurozium schreberi, Scleropodium purum, Hypnum cupressiforme, Hylocomium splendens, Polytrichum formosum* and *Dicranum scoparium*. The method allowed the identification of the industrially mostly affected territories. Maňkovská *et al.* (2008) used the mosses *Pleurozium schreberi, Hylocomium splendens* and *Dicranum scoparium* to compare the level of contamination in Slovakia with that in Norway. In Slovakia a much higher contamination was showed, in particular by Hg, Cu, Pb and Cr.

Šoltés and Gregušková (2012) used the moss *Pleurozium schreberi* as a bioindicator. They identified the level of deposition in three different facing valleys, and found an influence of Silesian and Polish metallurgy. Šoltés and Gregušková (2013) studied the distribution of accumulated elements in the thallus of the moss *Polytrichum commune,* comparing the one-year segments with more - year segments. It turned out, that a number of elements are preferentially accumulated in the capsula - Zn, S, Cr, Mn, Mo, Ca, Cu. Lead favours gametophyte, while K and Sr prefer sporophyte. Fe is significantly accumulated in more year segments. The following goals have been addressed in this paper:

1. to estimate the environmental load on the territory,
2. to reveal the source of environmental contamination,
3. to create the base for the long-term ecosystem monitoring in the vicinity of MONDI Ružomberok,
4. to determine the correlations in the accumulation of various elements with altitude.

## Material and Methods

### *Sampling*

As bioindicators, we have used the moss species *Pleurozium schreberi* on acide bedrock and *Homalothecium philippeanum* on limestone. *Pleurozium schreberi* has been used as a bioindicator by other researchers (Šoltés 1992, Maňkovská 1997, Maňkovská *et al.* 2003, 2008, Šoltés and Gregušková 2012) also. The sampling area consists of regions close to the source of pollution (Mondi Ružomberok, up to 10 km) to the protected areas (National Park Nízke Tatry Mts, National Park Veľká Fatra Mts and National Nature Reserve Chočské vrchy Mts). The main sampling has been carried out on August - September, 2012 and 2013, with a supplementary (control) sampling on February, 2014.

The samples were collected within three protected areas (Fig. 1): Low Tatra National park (14 samples, altitude 653 - 1203 m a.s.l.), Veľká Fatra Mts. National park (11 samples, altitude 657 - 1333 m a.s.l.), National Nature Reserve Chočské vrchy Mts. (13 samples, altitude 714 - 1400 m a.s.l.), Mních Hill (20 samples, altitude 520 - 670 m a.s.l.) and two control samples collected in Liptov Basin, near Hrboltová settlement.

Bedrock consists mostly of granite, but samples no. 10 and 20 were collected on Mních, where the bedrock is formed by limestone. *Pleurozium schreberi* is an acidophilous species. If occuring on limestone, the geological substratum is isolated by a thick layer of acide raw humus. On limestone areas, we have used as bioindicátor *Homalothecium philippeanum.*

The samples were collected in fairly open stands with a distance of 5 m to the nearest tree. After the return to the laboratory, the plant samples were dried at 70˚ C for two days. After drying, the plant material was grinded by the mill into fine powder. The mill was made of hardened steel to minimize, if not eliminate the iron contamination. The samples placed in plastic sleeves are stored

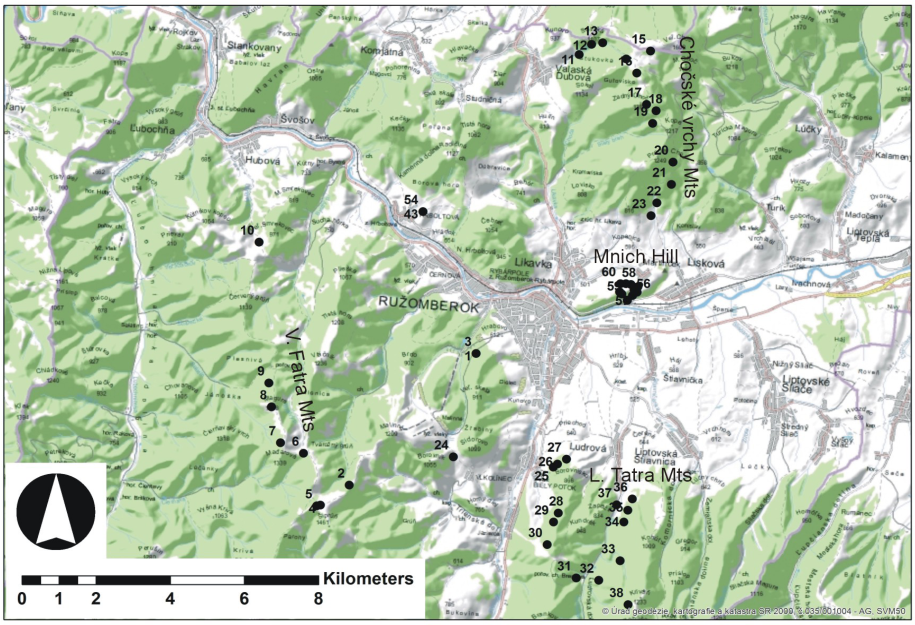

**Fig. 1.** Investigated area, sampling sites.

in the Institute of High Mountain Biology in Tatranská Javorina, Slovakia. The geographical coordinates were recorded in the system WGS 84, with the help of GPS Garmin Oregon 450 device.

*Instrumental analysis and statistics*

X-ray fluorescence spectrometry has been used (Stephens and Calder 2004) using the hand-held XRF spectrometer DELTA CLASSIC (USA). Non-metals (S, Cl) and metals (K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Rb, Sr, Zr, Mo, Ba, Pb) have been determined.

For statistical analysis, the CANOCO 4.5 for Windows package (Ter Braak and Šmilauer 2002) was used. To analyse the relation of environmental variables (element concentrations) and analysed samples, we had only single data set of variables. Since the length of the first gradient in the log report was < 0.6, we used the linear method of ordination (principal component analysis, PCA). For ordination analysis, we used ordinal element concentration data without transformation. Statistical graphics system STATISTICA (Release 7) have been used for the analysis of variance (ANOVA). Except for individual differentiation, the samples were sorted into groups according to location (Low Tatra Mts, High Fatra Mts, Chočské vrchy Mts Hills) and according to altitude. The differences between ecological groups were tested with one-way analysis of variance (ANOVA) of the component scores.

## Results

*Instrumental analysis results*

Concentrations of identified elements in sampling sites are reported in the Table 1.

The first axis explaines 75.4% of the variance, this axis highly positively correlates with sulphur and calcium, at a lesser extent with Pb, Fe, Ti, Sr. The second axis explains 20.4% of variance. This axis positively correlates with K, Mo, at a lesser extent with Cl, Cr, Ba, Mn, Rb, Zn and Cu. The indirect linear analysis (PCA) ordination diagram of 58 sites shows the major correlations in the direction of the first axis, Eigenvalue is 0.754 while in the direction of the second axis Eigenvalue is 0.204 (Fig. 2).

| **Sampling site** | **Elements, ppm** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **S** | **Cl** | **K** | **Ca** | **Ti** | **Cr** | **Mn** | **Fe** | **Cu** | **Zn** | **Rb** | **Sr** | **Mo** | **Ba** | **Pb** |
| 1 | 2205 | 1424 | 36788 | 26290 | 211 | 73 | 873 | 3682 | 242 | 164 | 39 | 10 | 14 | 129 | 28 |
| 2 | 824 | 0 | 16785 | 15976 | 158 | 57 | 961 | 2429 | 362 | 114 | 24 | 11 | 9 | 100 | 33 |
| 3 | 1629 | 0 | 32379 | 28608 | 254 | 195 | 2093 | 5684 | 142 | 126 | 21 | 10 | 18 | 230 | 30 |
| 4 | 1105 | 0 | 11951 | 13538 | 293 | 31 | 1611 | 5476 | 34 | 358 | 23 | 13 | 6 | 142 | 61 |
| 5 | 1122 | 0 | 22354 | 9792 | 660 | 77 | 1826 | 6351 | 191 | 151 | 43 | 4.1 | 10 | 103 | 33 |
| 6 | 1361 | 1521 | 22329 | 13070 | 202 | 54 | 1213 | 3556 | 0 | 211 | 29 | 13 | 11 | 65 | 39 |
| 7 | 2296 | 4072 | 51324 | 33263 | 306 | 73 | 491 | 4069 | 251 | 214 | 57 | 8 | 15 | 129 | 36 |
| 8 | 768 | 1423 | 15005 | 16181 | 142 | 31 | 282 | 3691 | 117 | 197 | 23 | 7.9 | 11 | 100 | 44 |
| 9 | 869 | 0 | 17826 | 11361 | 93 | 21 | 273 | 1741 | 37 | 133 | 4.1 | 6.1 | 4 | 55 | 23 |
| 10 | 1102 | 3791 | 15872 | 23029 | 154 | 32 | 340 | 1738 | 45 | 143 | 39 | 4.4 | 4.2 | 64 | 22 |
| 11 | 973 | 815 | 14326 | 13441 | 0 | 23 | 273 | 1340 | 78 | 188 | 21 | 22.4 | 6.4 | 48 | 26 |
| 12 | 845 | 0 | 11344 | 14373 | 141 | 29 | 344 | 3058 | 26 | 177 | 34 | 41 | 6 | 56 | 34 |
| 13 | 806 | 683 | 14276 | 22079 | 152 | 37 | 360 | 2961 | 93 | 185 | 26 | 22.4 | 9 | 64 | 29 |
| 14 | 1061 | 0 | 13879 | 24344 | 135 | 32 | 375 | 2906 | 57 | 178 | 25 | 21 | 10 | 70 | 34 |
| 15 | 502 | 834 | 8484 | 9770 | 81 | 17 | 201 | 1660 | 61 | 123 | 33 | 17.5 | 6.4 | 0 | 35 |
| 16 | 859 | 0 | 13795 | 8700 | 79 | 25 | 586 | 2254 | 31 | 171 | 28 | 7.7 | 7 | 67 | 33 |
| 17 | 836 | 553 | 12594 | 11412 | 70 | 20 | 1456 | 1654 | 1514 | 144 | 54 | 22.7 | 7.3 | 44 | 26 |
| 18 | 1160 | 771 | 18346 | 12777 | 183 | 26 | 318 | 3069 | 37 | 178 | 29 | 13.3 | 10 | 46 | 33 |
| 19 | 1452 | 1244 | 27399 | 22546 | 226 | 47 | 1152 | 4115 | 43 | 163 | 40 | 26 | 11 | 91 | 24 |
| 20 | 1526 | 0 | 8812 | 21456 | 160 | 23 | 505 | 3410 | 0 | 233 | 22 | 32 | 9 | 75 | 27 |
| 21 | 558 | 1735 | 17852 | 12519 | 81 | 22 | 886 | 1352 | 26 | 84 | 20 | 25 | 8 | 55 | 22 |
| 22 | 1761 | 0 | 23680 | 23644 | 193 | 44 | 349 | 3358 | 42 | 199 | 20 | 16 | 8 | 100 | 23 |
| 23 | 734 | 456 | 6648 | 12168 | 140 | 6 | 390 | 2088 | 15 | 131 | 15 | 13 | 6 | 35 | 25 |
| 24 | 739 | 968 | 18947 | 19289 | 100 | 17 | 296 | 1806 | 48 | 222 | 25 | 29 | 8.7 | 0 | 16 |
| 25 | 571 | 523 | 9842 | 15019 | 70 | 16 | 126 | 1506 | 0 | 77 | 21 | 5.8 | 6.9 | 0 | 25 |
| 26 | 639 | 1347 | 9051 | 17900 | 0 | 23 | 149 | 1677 | 0 | 91 | 20 | 10.3 | 8 | 55 | 22 |
| 27 | 1100 | 848 | 10397 | 23295 | 132 | 19 | 208 | 2733 | 91 | 155 | 25 | 19.5 | 9 | 50 | 24 |
| 28 | 789 | 1136 | 9509 | 11612 | 170 | 22 | 154 | 2539 | 55 | 130 | 37 | 3.7 | 5.9 | 36 | 26 |
| 29 | 984 | 1288 | 13786 | 13475 | 0 | 25 | 236 | 2392 | 404 | 106 | 43 | 27 | 9 | 67 | 23 |

*continued...*

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 30 | 1018 | 989 | 9522 | 16710 | 164 | 26 | 201 | 2735 | 35 | 193 | 38 | 34 | 8,3 | 53 | 24 | |
| 31 | 1153 | 0 | 13448 | 15621 | 126 | 35 | 284 | 2854 | 33 | 183 | 19 | 29 | 7 | 97 | 38 | |
| 32 | 0 | 3385 | 31590 | 34017 | 132 | 115 | 858 | 1789 | 57 | 183 | 30 | 38 | 15 | 302 | 32 | |
| 33 | 772 | 530 | 11796 | 10789 | 81 | 23 | 255 | 1731 | 0 | 105 | 18 | 34 | 9 | 42 | 21 | |
| 34 | 725 | 0 | 13824 | 11272 | 116 | 32 | 290 | 2119 | 50 | 118 | 32 | 11.1 | 9 | 54 | 24 | |
| 35 | 599 | 0 | 10029 | 11100 | 90 | 15 | 380 | 1194 | 24 | 88 | 23 | 8.5 | 6.8 | 32 | 17 | |
| 36 | 482 | 912 | 8538 | 7918 | 59 | 0 | 120 | 925 | 0 | 101 | 19 | 8.4 | 6.1 | 0 | 20 | |
| 37 | 499 | 477 | 8680 | 11177 | 62 | 16 | 111 | 1167 | 20 | 65 | 20 | 4.5 | 1.8 | 0 | 17 | |
| 38 | 838 | 1443 | 18238 | 9937 | 63 | 18 | 736 | 1685 | 0 | 144 | 54 | 16.1 | 12 | 53 | 28 | |
| 39 | 4499 | 0 | 8340 | 55529 | 341 | 42 | 465 | 13055 | 21 | 122 | 30 | 28 | 6.6 | 76 | 35 | |
| 40 | 4939 | 0 | 16715 | 28313 | 325 | 44 | 272 | 5708 | 23 | 120 | 34 | 15 | 5.3 | 112 | 28 | |
| 41 | 3162 | 0 | 11738 | 38259 | 595 | 24 | 308 | 6536 | 25 | 116 | 35 | 55 | 5.8 | 82 | 23 | |
| 42 | 3128 | 609 | 23873 | 23049 | 1284 | 27 | 246 | 5290 | 0 | 102 | 47 | 36 | 5.3 | 159 | 26 | |
| 43 | 2100 | 0 | 14981 | 34470 | 167 | 44 | 309 | 2978 | 0 | 60 | 27 | 17 | 8 | 79 | 25 | |
| 44 | 3019 | 0 | 7808 | 42312 | 1214 | 45 | 491 | 13563 | 33 | 179 | 32.9 | 57 | 0 | 130 | 53 | |
| 45 | 2716 | 0 | 7740 | 61481 | 692 | 16 | 250 | 7634 | 24 | 129 | 23.7 | 78 | 4.2 | 66 | 39 | |
| 46 | 2614 | 518 | 6736 | 32338 | 454 | 16 | 202 | 6144 | 13 | 225 | 22.8 | 29.1 | 4.2 | 30 | 27 | |
| 47 | 2238 | 0 | 6245 | 58298 | 566 | 18 | 230 | 7878 | 23 | 139 | 29 | 30 | 7.8 | 50 | 32 | |
| 48 | 2762 | 0 | 6386 | 90673 | 489 | 21 | 195 | 6772 | 20 | 102 | 21 | 43 | 4 | 56 | 21 | |
| 49 | 3229 | 0 | 5514 | 41404 | 165 | 16 | 164 | 2822 | 0 | 76 | 17.3 | 32 | 5.1 | 0 | 22 | |
| 50 | 4200 | 680 | 7511 | 52207 | 968 | 44 | 647 | 18162 | 47 | 222 | 32.2 | 72 | 4.4 | 127 | 57 | |
| 51 | 2272 | 0 | 5811 | 29362 | 695 | 50 | 337 | 11786 | 85 | 195 | 27.2 | 35 | 4.2 | 96 | 37 | |
| 52 | 2845 | 565 | 8049 | 43886 | 808 | 46 | 361 | 13293 | 95 | 190 | 24 | 35 | 7.5 | 95 | 38 | |
| 53 | 1618 | 555 | 6335 | 22260 | 653 | 38 | 260 | 9133 | 28 | 102 | 29.7 | 29.3 | 0 | 60 | 26 | |
| 54 | 4785 | 1098 | 15255 | 53116 | 1294 | 67 | 359 | 14038 | 57 | 175 | 36 | 23 | 8 | 112 | 31 | |
| 55 | 0 | 448 | 8286 | 31047 | 1406 | 49 | 323 | 13617 | 25 | 150 | 37 | 40 | 0 | 125 | 31 | |
| 56 | 2149 | 607 | 15643 | 19054 | 2648 | 82 | 650 | 19843 | 15 | 83 | 62 | 61 | 0 | 268 | 31 | |
| 57 | 1801 | 546 | 10093 | 16677 | 1044 | 46 | 285 | 10640 | 15 | 120 | 32 | 25.9 | 2.9 | 106 | 18 | |
| 58 | 3359 | 501 | 6943 | 30516 | 528 | 33 | 219 | 6042 | 15 | 129 | 20.2 | 14.7 | 3.6 | 52 | 43 | |
| 59 | 2894 | 947 | 5248 | 41736 | 624 | 48 | 285 | 7628 | 38 | 151 | 23 | 21.6 | 4.6 | 77 | 41 | |
| 60 | 3697 | 1262 | 7183 | 38036 | 349 | 23 | 275 | 5834 | 10 | 216 | 22 | 17.2 | 5.4 | 28 | 31 | |

**Table 1.** Results of chemical analysis, XRF spectrometry.

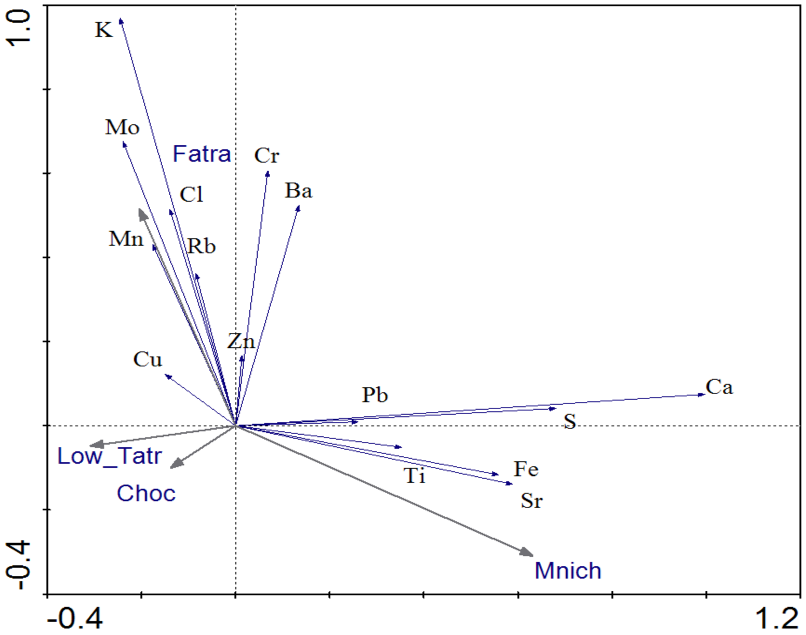

**Fig. 2.** PCA, ordination diagram.

### *The effect of winter inversions on the accumulation*

Five samples were taken during the winter period (February, 2014) to evaluate the impact of winter inversions on the accumulation of imission. The results of the analysis are shown in Table 2, Columns 1-5.

For the assessment of the impact of deposition in the winter period, we have used a canonical analysis. Matrix consisted of a group of variables (results of the analyses) acquired before the winter period in 2013 and from a group of variables (results of the analyses) acquired immediately after snow melting on late January or early February 2014 (Table 2). Samples for analysis were collected in approximately the same locations and about adequate altitude. Assumption for canonical analysis is a normally distribution of the input variables. Descriptive statistics have confirmed that not all variables met the condition for a normal distribution: there are ordinal differences in the concentrations of the elements. For this reason, the data were transformed logarithmically. The results of canonical analysis: Canonical R - 0,9991107 and Chi square - 231.2.

The value of the canonical R close to "1" shows that between the groups is a significant relationship. In other words, imissions accumulated during winter in the snow; after melting, the concentrations

| **Elements** | **Variables** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
| S | 1294 | 886 | 647 | 888 | 760 | 2205 | 824 | 734 | 739 | 806 |
| Cl | 1523 | 2119 | 1903 | 2018 | 1064 | 1424 | 0 | 456 | 968 | 683 |
| K | 17784 | 20211 | 11235 | 10813 | 15310 | 36788 | 16785 | 6648 | 18947 | 14276 |
| Ca | 26482 | 15311 | 10627 | 16538 | 12032 | 26290 | 15976 | 12168 | 19289 | 22079 |
| Ti | 0 | 159 | 115 | 214 | 93 | 211 | 158 | 140 | 100 | 152 |
| Cr | 46 | 26 | 20 | 27 | 16 | 73 | 57 | 6 | 17 | 37 |
| Mn | 276 | 265 | 186 | 718 | 201 | 873 | 961 | 390 | 296 | 360 |
| Fe | 2707 | 2445 | 2172 | 4403 | 1852 | 3682 | 2429 | 2088 | 1806 | 2961 |
| Cu | 42 | 0 | 39 | 24 | 24 | 242 | 362 | 15 | 48 | 93 |
| Zn | 170 | 127 | 155 | 155 | 140 | 164 | 114 | 131 | 222 | 185 |
| Rb | 48 | 22 | 26 | 34 | 21 | 39 | 24 | 15 | 25 | 26 |
| Sr | 6 | 10 | 12 | 15 | 17 | 10 | 11 | 13 | 29 | 22 |
| Mo | 9 | 5 | 9 | 6 | 8 | 14 | 9 | 6 | 8 | 9 |
| Ba | 62 | 66 | 0 | 93 | 0 | 129 | 100 | 35 | 0 | 64 |
| Pb | 15 | 31 | 25 | 33 | 19 | 28 | 33 | 25 | 16 | 29 |

**Table 2.** Matrix of variables for cannonical analysis. The first group of variables (1-5) is the sampling in spring time 2014 (January-February), the second group (6-10) is sampling in 2013.

| | **Root 1** | **Root 2** | **Root 3** | **Root 4** | **Root 5** |
|---|---|---|---|---|---|
| Sample 1 | -0.00110 | -0.09349 | 0.7526 | -1.17571 | -1.47092 |
| Sample 2 | 0.25339 | -0.23778 | 1.4495 | 2.85513 | -2.02272 |
| Sample 3 | 0.59752 | -0.33438 | 11.1529 | 1.63150 | 2.62288 |
| Sample 4 | -0.36811 | -2.06103 | -1.8000 | -1.95489 | 3.10529 |
| Sample 5 | -1.47659 | 2.53620 | -11.2999 | -1.31923 | -2.47835 |

**Table 3.** Cannonical factor load for the first group of variables (sampling in springtime 2014).

| | **Root 1** | **Root 2** | **Root 3** | **Root 4** | **Root 5** |
|---|---|---|---|---|---|
| Sample 6 | -0.150918 | -0.29429 | 1.86132 | -1.35742 | 5.33958 |
| Sample 7 | -0.001679 | 0.36225 | -1.41714 | -0.53988 | 0.39904 |
| Sample 8 | -0.205588 | -1.27506 | -1.68654 | 3.43509 | 2.77632 |
| Sample 9 | -0.813062 | 2.53457 | 0.08336 | 0.15248 | 0.86204 |
| Sample 10 | 0.151631 | -1.35837 | 0.77905 | -1.87899 | -9.11984 |

**Table 4.** Cannonical factor load for the second group of variables (sampling in 2013).

of these substances in the tissues of bioindicator were not affected significantly. The impact of winter inversion proved insignificant. Canonical factor loads for the first group of variables is shown in Table 3, and for the second group of variables in Table 4. Extreme factor load, at the root 1, in the first group of variables (Sample 3, Table 3) should be probably attributed to divergent sulphur and calcium concentrations.

*Correlation of elements with altitude*

To find out the relation of element concentrations with altitude, a correlation analysis was used. A positive correlation with altitude was found in Cl, K, Cr, Mn, Cu, Zn, Mo, Pb and others (Table 5). A significant correlation with altitude was found in copper ($p = 0.0070$), molybdenum ($p = 0.0003$) and lead ($p = 0.043$) (ANOVA). A negative correlation with altitude was reported for S, Ca, Ti, Fe, Sr.

*Contamination in the investigated area*

Contamination of the Veľká Fatra Mts is in accordance with the prevailing airflow (W, NW), but Mních Hill is highly contaminated as well (Fig. 2). For an explanation of the flux of contaminants throughout the investigated area, a key aspect is a comparison of levels of contamination in Northern and Southern slopes of Mních Hill (Table 6, 7).

The ordination diagram (Fig. 2) and box diagrams (Fig. 3, 4) suggest particularly a contamination of Veľká Fatra Mts. and Mních Hill. Veľká Fatra Mts. are contaminated in particular with Cu, Mn, Mo, Rb, Zn, Cu, Ba, K and Cl. Mních Hill is contaminated with Pb, Ca, Ti, Fe, Sr and S. The Low Tatra Mts. and Chočské vrchy Mts. (Fig. 3, 4) are the least contaminated.

| | **S** | **Cl** | **K** | **Ca** | **Ti** | **Cr** | **Mn** | **Fe** | **Cu** | **Zn** | **Rb** | **Sr** | **Mo** | **Ba** | **Pb** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **r** | -0.45 | 0.19 | 0.42 | -0.48 | -0.43 | 0.16 | 0.53 | -0.43 | *0.33 | 0.30 | 0.16 | -0.45 | *0.56 | 0.03 | *0.19 |

**Table 5.** Correlation between altitude and element concentrations, correlation coeficients. *Indicates significance.

| | **S** | **Cl** | **K** | **Ca** | **Ti** | **Cr** | **Mn** | **Fe** | **Cu** | **Zn** | **As** | **Rb** | **Sr** | **Zr** | **Mo** | **Ba** | **Pb** | **Slope** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2012** | | | | | | | | | | | | | | | | | | |
| 1 | 4499 | 0 | 8340 | 55529 | 341 | 42 | 465 | 13055 | 21 | 122 | 0 | 30 | 28 | 14.6 | 6.6 | 76 | 35 | S |
| 2 | 4939 | 0 | 16715 | 28313 | 325 | 44 | 272 | 5708 | 23 | 120 | 0 | 34 | 15 | 7.1 | 5.3 | 112 | 28 | S |
| 3 | 3162 | 0 | 11738 | 38259 | 595 | 24 | 308 | 6536 | 25 | 116 | 0 | 35 | 55 | 28.2 | 5.8 | 82 | 23 | S |
| 4 | 3128 | 609 | 23873 | 23049 | 1284 | 27 | 246 | 5290 | 0 | 102 | 11 | 47 | 36 | 52 | 5.3 | 159 | 26 | N |
| 5 | 2100 | 0 | 14981 | 34470 | 167 | 44 | 309 | 2978 | 0 | 60 | 0 | 27 | 17 | 3.6 | 8 | 79 | 25 | C |
| 6 | 3019 | 0 | 7808 | 42312 | 1214 | 45 | 491 | 13563 | 33 | 179 | 13 | 32.9 | 57 | 105 | 0 | 130 | 53 | S |
| 7 | 2716 | 0 | 7740 | 61481 | 692 | 16 | 250 | 7634 | 24 | 129 | 10 | 23.7 | 78 | 39 | 4.2 | 66 | 39 | S |
| 8 | 2614 | 518 | 6736 | 32338 | 454 | 16 | 202 | 6144 | 13 | 225 | 0 | 22.8 | 29.1 | 21.2 | 4.2 | 30 | 27 | N |
| 9 | 2238 | 0 | 6245 | 58298 | 566 | 18 | 230 | 7878 | 23 | 139 | 0 | 29 | 30 | 23 | 7.8 | 50 | 32 | N |
| 10 | 2762 | 0 | 6386 | 90673 | 489 | 21 | 195 | 6772 | 20 | 102 | 15 | 21 | 43 | 20 | 4 | 56 | 21 | N |
| 11 | 3229 | 0 | 5514 | 41404 | 165 | 16 | 164 | 2822 | 0 | 76 | 0 | 17.3 | 32 | 4.8 | 5.1 | 0 | 22 | N |
| **2013** | | | | | | | | | | | | | | | | | | |
| 1 | 4200 | 680 | 7511 | 52207 | 968 | 44 | 647 | 18162 | 47 | 222 | 27 | 32.2 | 72 | 48 | 4.4 | 127 | 57 | S |
| 2 | 2272 | 0 | 5811 | 29362 | 695 | 50 | 337 | 11786 | 85 | 195 | 11 | 27.2 | 35 | 50 | 4.2 | 96 | 37 | S |
| 3 | 2845 | 565 | 8049 | 43886 | 808 | 46 | 361 | 13293 | 95 | 190 | 23 | 24 | 35 | 19 | 7.5 | 95 | 38 | S |
| 4 | 1618 | 555 | 6335 | 22260 | 653 | 38 | 260 | 9133 | 28 | 102 | 7 | 29.7 | 29.3 | 33 | 0 | 60 | 26 | N |
| 5 | 4785 | 1098 | 15255 | 53116 | 1294 | 67 | 359 | 14038 | 57 | 175 | 0 | 36 | 23 | 32 | 8 | 112 | 31 | C |
| 6 | 0 | 448 | 8286 | 31047 | 1406 | 49 | 323 | 13617 | 25 | 150 | 9 | 37 | 40 | 92 | 0 | 125 | 31 | S |
| 7 | 2149 | 607 | 15643 | 19054 | 2648 | 82 | 650 | 19843 | 15 | 83 | 25 | 62 | 61 | 228 | 0 | 268 | 31 | S |
| 8 | 1801 | 546 | 10093 | 16677 | 1044 | 46 | 285 | 10640 | 15 | 120 | 6 | 32 | 25.9 | 65 | 2.9 | 106 | 18 | N |
| 9 | 3359 | 501 | 6943 | 30516 | 528 | 33 | 219 | 6042 | 15 | 129 | 0 | 20.2 | 14.7 | 15 | 3.6 | 52 | 43 | N |
| 10 | 2894 | 947 | 5248 | 41736 | 624 | 48 | 285 | 7628 | 38 | 151 | 8 | 23 | 21.6 | 22 | 4.6 | 77 | 41 | N |
| 11 | 3697 | 1262 | 7183 | 38036 | 349 | 23 | 275 | 5834 | 10 | 216 | 0 | 22 | 17.2 | 8 | 5.4 | 28 | 31 | N |

**Table 6.** Results of chemical analysis, Mních near Ružomberok, sampling in October 22, 2012 and October 28, 2013. S – South slope, N – North slope, C – control site.

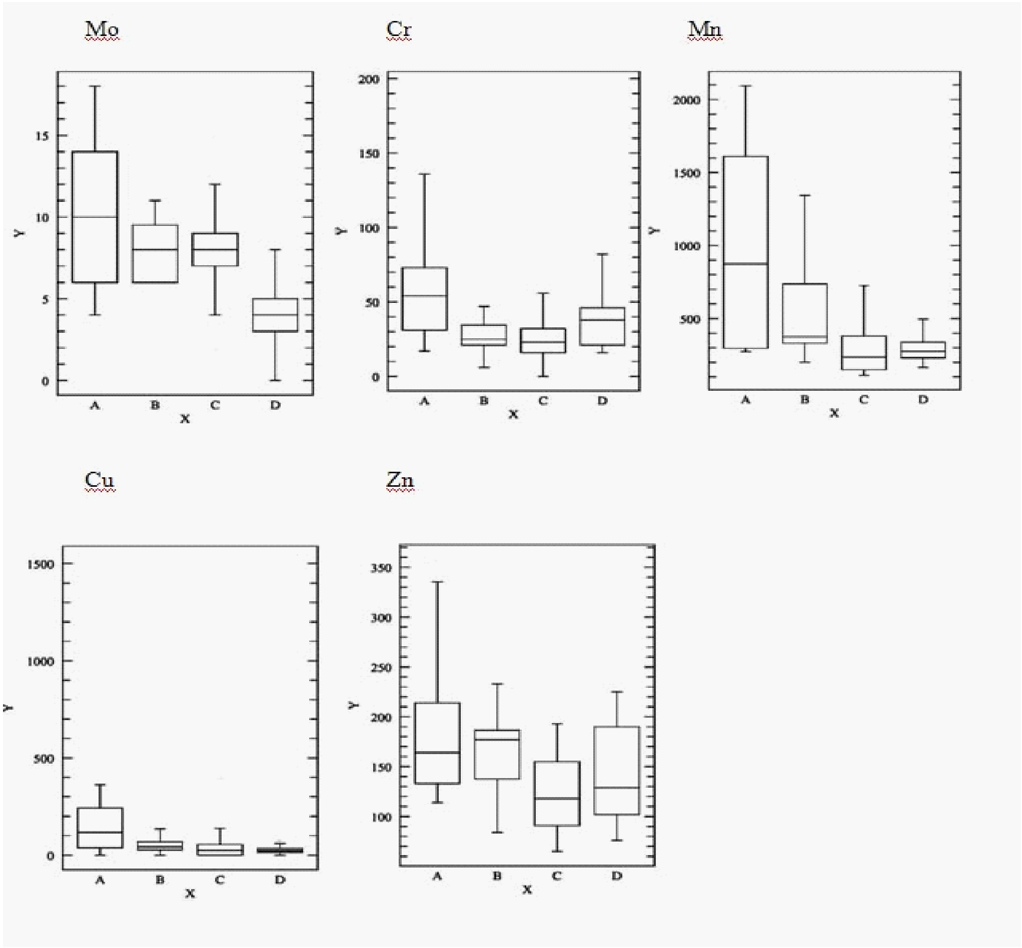

**Fig. 3.** Box diagrams. Elements contaminating predominantly V. Fatra Mts. A – V. Fatra Mts; B – Chočské vrchy Mts; C – Low Tatra Mts; D - Mních Hill.

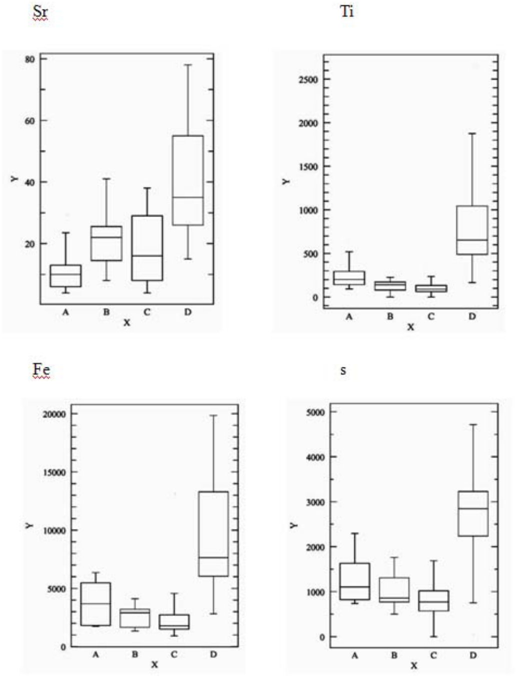

**Fig. 4.** Box diagrams. Elements contaminating predominantly Mních Hill. A – V. Fatra Mts; B – Chočské vrchy Mts; C – Low Tatra Mts; D - Mních Hill.

| Year | 2012 | 2013 |
|---|---|---|
| S | 0.104 | 0.645 |
| Cl | 0.143 | 0.153 |
| K | 0.860 | 0.343 |
| Ca | 0.773 | 0.501 |
| Ti | 0.869 | 0.114 |
| *Cr | 0.049 | 0.083 |
| *Mn | 0.021 | 0.032 |
| *Fe | 0.097 | 0.003 |
| *Cu | 0.029 | 0.090 |
| Zn | 0.881 | 0.457 |
| As | 0.893 | 0.007 |
| Rb | 0.529 | 0.158 |
| Sn | 0.305 | 0.010 |
| Zr | 0.466 | 0.164 |
| Mo | 0.522 | 0.964 |
| Ba | 0.278 | 0.056 |
| Pb | 0.107 | 0.325 |

**Table 7.** Mních, p values, N slope vs S slope, in 2012 and 2013. *Indicates significance.

## Discussion

The correlation of lead concentrations with altitude is commonly known, e. g. for a correlation of lead with altitude in the Alps, see Zechmeister (1994). In the Tatra Mts, this correlation has been recorded by Šoltés (1992, 1998) and by Šoltés and Gregušková (2012). Even if insignificant, this correlation has been confirmed in the Tian-Shan Mts (Ciriaková *et al.* 2011).

Comparison of contamination of Northern and Southern slopes of Mních Hill (Table 6) might indicate the direction of contamination. As can be seen from the results of analysis of samples collected in 2012 and 2013 (Table 6), nearly all the monitored elements have been approximately evenly distributed in the northern and southern slopes of the Mních Hill. Only Cu, Mn, Cr and Fe exhibits a significantly higher contamination of the southern slopes of the Mních Hill (Table 7). So, the direction of the imission spread is along the Liptov Basin, to the East, as the prevailing winds are West to the Northwest. The main imission sources were located NW, i. e. Krakow region, Katowice region, Silesia, Orava or Ostrava region (Rak *et al.*, 1982), in accordance with Veľká Fatra Mts contamination. Veľká Fatra are situated upwind, which explains its high contamination. An explanation is required for the contamination of Mních Hill. According to official measurements of Slovak hydrometeorological institute (SHMÚ), the town Ružomberok is highly polluted by dust particles. In 2011, the daily limit value for $PM_{10}$, at the station Ružomberok-Riadok, was exceeded by 131 times, this is the absolute maximum in SR. Solid emissions may apply as the carrier component compounds of heavy metals (Fargašová 2009). We assume that these sources would contaminate the Mních Hill. Despite a reduction in sulphur content by 96% (Sotolová 2006), a local source is probable in the case of sulphur.

The Northwest direction of air flow is prevailing, but East flow is essential also. East flow has about 20% of all the winds (http: //www.enviroportal.sk). In this direction, the main sources of pollutants were Chemosvit Svit (70 km) and Copper Smelter Krompachy (115 km). The plant Copper Smelter Krompachy is located in the Middle Scepusia region, which belong to the most affected territories within the Slovak Republik. Crucial is mercury content in soils, high concentrations were consequence of emission up to 4.6 tons of Hg per year (Fargašová 2009). In the investigated area, increased levels of mercury have not been recorded. During the last decades of the 20th century, Chemosvit Svit produced 3,415 tons of sulphur dioxide per year, 2,130 tons of carbon disulphide and 433 tons of hydrogen sulphide. Compounds of Fe, Mn, Mo and Cr were produced by Copper Smelter Krompachy (21,980 tons per year, Rak *et al.* 1982). Several authors have found that the emissions of metals in the ecosystem may persist in concentrations several thousand ppm (Hutchinson and Symington 1997), even long after the environmental contamination has stopped, according to Nriagu *et al.* (1998) well over 1,000 years. Effect of sulphur on ecosystems persists for a long time also. For example, the contamination with sulphur dioxide had devastated vegetation for miles around roasting bed near Sudbury (Ontario, Canada). The surface soils of the recovered forest were strongly acidic (pH 3.89–4.2) yet in the last decade of the last century (Hutchinson and Symington 1997).

The Copper Smelter Krompachy, in 2000, instigated a modernisation of production methods. Since then, the plant constantly upgrading the technologies to minimize the impact on the environment. Chemosvit Svit halted the production method based on viscose, which released a large volume of sulphur compounds, and it is now involved in the production of flexible films intended for packaging.

## Conclusions

1. The impact of the winter inversion proved insignificant. Imission accumulated during winter in the snow, after its melting, it did not affect significantly the concentrations of these substances in the tissues of the bioindicator.
2. Significant correlation with altitude was found in copper, molybdenum and lead. A negative correlation with altitude has been reported with S, Ca, Ti, Fe, Sr.
3. Resources located NW in 40 – 140 km (Krakow region, Katowice region, Silesia region, Orava or Ostrava regions) are probably imission sources. Only in the case of sulphur, a local source is probable.
4. V. Fatra Mts (Cu, Mn, Mo, Rb, Zn, Cu, Ba, K and Cl) and Mních Hill (Pb, Ca, Ti, Fe, Sr and S) are highly contaminated.

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