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Seasonal changes in the dust nuisance and contamination of mosses in the experimental study area Ružomberok

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Abstract. This study describes changes in dust composition during the growing season in the industrial zone of Ružomberok (northern Slovakia), analyzes how these changes are reflected in the composition of elements accumulated in the tissues of bryophytes and tries to identify which dust fractions are the carriers of chemical elements. For dust particle analysis, the environmental monitoring device GRIMM 1.109 (Germany) was used, and results were evaluated by multivariate analytical methods. Grain size fractions have been identified as those whose elements are fixed and not connected to any other fraction. This study deals with the differences between terrestrial and semi-terrestrial habitats in terms of accumulation of elements in bryophytes and with the kinetics of the uptake and discharge of heavy metals in the extra and intracellular compartments of bryophytes. While solving dust particle deposition at sites along river Váh near Lisková, three clusters were distinguished: I fraction 0.25 – 3.5 µm, II fraction 4.0 – 10.0 µm, and III fraction 12.5 - 20 µm. Sulphur binds to the finest fraction (0.25 - 3.5 micrometers), manganese, chromium, molybdenum, of non-metal chlorine bind to fraction II (4.0 to 10.0 micrometers). Only lead binds to fraction III (12.5 - 20 micrometers). Nearly 60% of dust deposition fell during the spring months (March to May). In flooded habitats, some elements are washed away by river water and discarded, while other elements are accumulated.

Key words: dust deposition, grain dust fractions, grain element carriers, element accumulation, bryophytes, Slovakia

Introduction

Bryophytes are an important component of biodiversity, and they have proven to be suitable bioindicators. Because of a lack of cuticle and simple thalli organisation, they are unable to avoid heavy metal accumulation from deposition (Tyler 1990). Bryophytes are independent of the soil (Ratcliffe 1975, Tyler 1990, Burton 1990 and others), and their rhizoids only serve to anchor to the substratum. Bryophytes receive nutrients from the environment through the entire surface of their cells and their high cation exchange capacity ensures a predisposition toward sensitive response to the concentration levels of metals in the environment. Thus, they respond more quickly to metal contamination than vascular plants. The idea of using bryophytes for bioindication arose in the nineteen seventies (Clymo 1963, Rühling and Tyler 1970). This method has been mainly used for analysis of the vertical distribution of elements in moutain ranges such as the Alps (Zechmeister 1994), the Tatra Mountains (Šoltés 1992, 1998); and the Tien–Shan (Ciriaková *et al.* 2011). To a lesser extent, the investigation focused on other objectives, such as how accumulated elements are distributed in moss tissues (Šoltés and Gregušková 2013). For grasslands monitoring, bryophytes are less commonly used. For example, Šoltés and Gregušková (2012) used bryophytes for detecting the distribution of heavy metals in the alpine vegetation zone of the Tatras, while meadow ecosystems in Slovakia were investigated to identify areas affected by industrial emissions (Maňkovská *et al.* 2003), and bioindication of atmospheric deposition was studied in the Carpathians (Maňkovská *et al.* 2008).

Airborne dust is defined as particles of varying size that are freely dispersed in the air. Its origin is in various technological processes. Dust particles are released by the burning of solid substances, and are present in exhaust gas of motor vehicles. They enter the air by disturbing the particles deposited on the ground (secondary dust). PM10 particles are classified as those where 50% of the particles have an aerodynamic parameter less than 10 micrometers. Particles of thoracic size may be emitted from natural sources (e.g. volcanic activity, dust storms), but are mainly from anthropogenic sources (power plants, industrial processes, transport, domestic heating, the incineration of municipal and industrial waste).

The only pathway by which PM can get into the human body is inhalation. The health significance of dust depends on the particle size. While larger particles (above 10 micrometers) only cause irritation of the upper respiratory tract with coughing, sneezing and conjunctivitis, smaller particles are delivered to the lower respiratory tract. and particles below 2.5 micrometers can penetrate into the lung's alveoli and either accumulate in the lungs, or even penetrate into the blood stream. Hence, we classify total dustiness (TSP) as the aggregate of particles less than 10 micrometers (PM10), and particles below 2.5 micrometers (PM2.5). Increased dust in the air is generally irritating to the respiratory system and is usually found together with other pollutants. such as sulfur dioxide or nitrogen oxides.

The region that is the subject of this study is situated in north-western Slovakia, and includes the industrial zone of Ružomberok in Liptov Basin. The environmental impact to the region is caused by the energy, chemical, machine, metallurgical and pulp and paper-industries. Elements emitted into the atmosphere are partially exported to more remote areas and contribute to the regional and territorial deposition rates. This region is also exposed to the long-range transfer of pollutants from the Ostrava and Katowice industrial zones.

As bioindicators we used the representatives of the genus *Brachythecium* (*Brachythecium salebrosum* and *Brachythecium rivulare*). The species of the genus *Brachythecium* are not commonly used as bioindicators, however, their use as a bioindicator is not unheard of, Vukojević *et al.* (2006) investigated the deposition of three heavy metals, cadmium (Cd), cobalt (Co) and chromium (Cr), in the county of Obrenovac (Serbia) using the bryophyte bioindicators, as well as representatives of the genus *Brachythecium*. The same authors (Vukojević *et al.* 2009) used the genus *Brachythecium* when examining the deposition of manganese (Mn), molybdenum (Mo) and nickel (Ni) in the county of Obrenovac (Serbia), while Sabovljević *et al.* (2007) examined copper (Cu), iron (Fe), mercury (Hg), aluminum (Al), arsenic (As), and boron (B) in the same area. Thompson and Proctor (1983) investigated plant distribution in soils rich in heavy metals. The list of studied plants also included the moss species *Brachythecium rutabulum*. Results obtained from the study of Tangahu *et al.* (2011) suggest that *B. populeum* can serve as a cost-effective indicator for the environmental quality of any area. Ötvös *et al.* (2003) investigated the heavy metal atmospheric deposition in Hungary using bryophytes, including the representatives of the genus *Brachythecium*.

Dust deposition has an adverse effect on vegetation. Dust may affect photosynthesis. respiration. transpiration and penetration of phytotoxic gaseous pollutants. Farmer (1993) identified effects of dust on crops, grasslands, heathlands, trees and woodlands, arctic bryophyte, and lichen communities. While site 1 and 2 are terrestrial habitats, site 3 and 4 have characteristics of semi-terrestrial habitats as they are approximately 25 cm above the water level and are periodically flooded with water. Such habitats are often the subject of investigation, e.g. Vincent *et al.* (2001) made the measurements of the contents of Al, Mn, Fe, Cu, Cd, zinc (Zn), and lead (Pb) in *Scapania undulata* in three streams in the English Lake District.

For the purpose of this work it is important to identify binding sites (intercellular, extracellular, and intracellular binding sites) and their dynamics, element uptake, and discharge. Intercellular metals are those dissolved in liquids surrounding cells. Extracellular metals are those temporarily bound in an exchangeable complex forming part of the cell wall or the outer surface of the plasma membrane. Intracellular metals are those contained within the cell itself. whether in soluble or insoluble form.

Tyler (1990) discusses uptake times for *Fontinalis antipyretica*. Intracellular uptake is a very short stage and is not influenced by temperature or light. The second stage is extracellular uptake, lasting around 90 minutes, and not significantly affected by temperature or light. The third stage is intercellular uptake, lasting several days and is strongly affected by temperature and light. Slightly different times are recorded for *Fontinalis antipyretica* by Fernández *et al.* (2006), who investigated the kinetics of the uptake and discharge of heavy metals in the extra and intracellular compartments. However, it appears that the release from extracellular compartments was faster than from intracellular compartments. In intracellular sites both uptake and discharge occurred more slowly. The results indicate different behaviour of the moss in strongly acidic environments in which the relative affinity of metals for extracellular binding sites is low.

Vázquez *et al.* (1999) used shoot tips of *Fontinalis antipyretica, Scapania undulata*, and *Fissidens polyphyllus* for the study of uptake of heavy metals by the extracellular and intracellular compartments. In most cases, more metal was taken up by the extracellular compartment than by the intracellular compartment. Brown and Beckett (1985) investigated intracellular and extracellular uptake of Cd in the moss *Rhytidiadelphus squarrosus*. This moss had a high affinity for intracellular Cd, but extracellular Cd binding capacity was also high. Carballeira *et al.* (2001) investigated the impact of sporadic acidification on the release of Cd from the aquatic bryophyte *Fontinalis antipyretica*. In these experiments, pH had a marked effect on the amount of Cd released, while Al concentration had no consistent effects.

Figueira and Ribeiro (2005) used transplants of the aquatic moss *Fontinalis antipyretica* to assess the contamination of a river located in south Portugal. The increase of Cu, and Zn was verified in the extracellular and intracellular moss fraction, especially for soluble Cu. Vázquez *et al.* (2000) investigated the effects of water acidity and metal concentration on the accumulation of heavy metals by the aquatic bryophyte *Fontinalis antipyretica*. The results showed that heavy metal uptake is clearly lower in acidic waters than in near-neutral waters. Vieira *et al.* (2009) evaluated the use of the aquatic moss *Fontinalis antipyretica* as a bioindicator of NH_4^+ aquatic pollution. The use of $NiCl_2$ as an efficient displacing agent confirmed extracellular and intracellular binding sites. Tipping *et al.* (2008) applied a modelling approach when calculating the chemical speciation and metal interactions with external binding sites on the plants. The speciation modelling approach shows smaller deviations between observed and predicted bryophyte contents of Cu, Zn, Cd and Pb. If these four metals and Ni are considered together, the model predictions are superior at the one per cent level.

The following questions are addressed in this study:

1. How does the structure of dust contamination change over the year?
2. Is there any relationship between the size of dust particles and transfered elements?

Material and Methods

This study is based on the principle that carpet-forming bryophytes absorb elements and particles from rain and dry deposition. The study utilizes measured concentrations of 16 elements (S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Zr. Mo, Ba, Pb) in carpets of the species of *Brachythecium salebrosum* and *B. rivulare* collected monthly throughout 2015 from four sampling sites within a contaminated area located east of Ružomberok as well as grain composition of measured dust fallout at Lisková station. The nomenclature follows Marhold and Hindák (1998), and those of bryophytes in Kučera *et al.* (2012). The geographical coordinates are recorded by a Garmin Dakota 20. WGS84 device. The samples are stored at the Institute of High Mountain Biology in Tatranská Javorina.

Sampling sites and sampling

The investigation is based on the principle that the sampling sites should have similar vegetation. Moss carpets must be large enough for sampling throughout the year. We chose riparian alder wood. dominated by *Alnus incana, Alnus glutinosa*, and *Salix caprea.*

Site 1 – Lisková (Fig. 1), by the bridge over river Váh, 49° 05.047´ ;19° 21.272, sampled species *Brachythecium salebrosum*, associated bryophytes *Syntrichia ruralis, Schistidium apocarpum.*

Site 2 – Lisková (Fig. 1), behind the bridge over river Váh towards to Mondi, 49° 04.939´ ; 19° 20.982, sampled species *Brachythecium salebrosum*, associated bryophytes *Brachythecium rutabulum*, *Schistidium apocarpum.*

Site 3 – Lisková (Fig. 1), behind the bridge, upstream river Váh, 49° 5.083´ ; 19° 21.397, sampled species *Brachythecium rivulare*, associated bryophytes *Brachythecium campestre*, *Bryum caespiticium.*

Site 4 – Lisková (Fig. 1), behind the bridge, upstream of the river Váh, 49° 05.097´ ; 19° 21.481. sampled species *Brachythecium rivulare*, associated bryophytes *Syntrichia ruralis*, *Amblystegium juratzkanum*, *Schistidium apocarpum.*

Sampling (Site 1 – 4) was conducted March 18, April 15, May 16, June 18, July 16, August 19, September 19 and October 15.

For sampling. two species of the genus *Brachythecium* were selected. Terrestric *Brachythecium salebrosum* and semiterrestric *Brachythecium rivulare.* The species are easy to recognise, *Brachythecium rivulare* has stem leaves that are broadly ovate, acute to obtuse, and angular cells are enlarged and hyaline, forming distinct decurrent auricles. *Brachythecium salebrosum* stem leaves are ovate - lanceolate, tapering to long acumen, and sparse angular cells are enlarged, forming small decurrent auricles (Fig. 2).

Instrumental analysis

X-ray fluorescence spectrometry has been used (Stephens and Calder 2004) using the hand-held

Fig. 1. Indicative outline of the treated area.

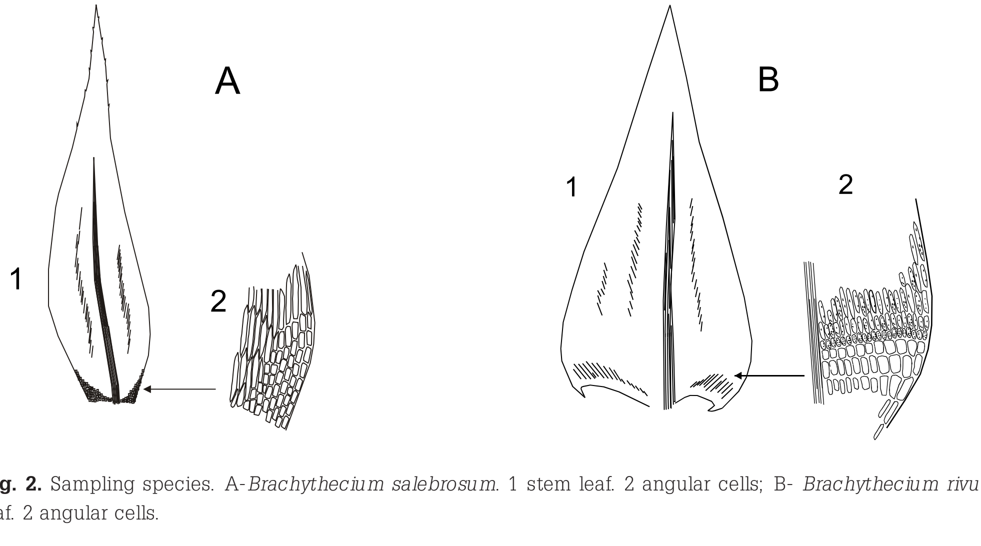

Fig. 2. Sampling species. A-*Brachythecium salebrosum*. 1 stem leaf. 2 angular cells; B- *Brachythecium rivulare*. 1 stem leaf. 2 angular cells.

XRF spectrometer DELTA CLASSIC (USA). Nonmetals (S, Cl) and metals (K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Zr, Mo, Ba, Pb) have been determined.

Statistics

CANOCO 4.5 for Windows package (Ter Braak and Šmilauer 2002) was used for all statistical analysis. Since the length of the first gradient in the log report was < 2, for relationship between dust fractions and elements accumulations we used the indirect linear method – RDA. DCA was used for ordination of the site data sets. The statistical significance of the explanatory (environmental) variables in canonical methods were determined by Monte Carlo permutation tests. Explanatory variables were tested separately (partial tests). For ordination analysis, we used ordinal data without transformation. For clustering objects (Sites) into groups, we used the Cluster analysis (STATISTICA) (Kubíková *et al.* 2014). Except for individual differentiation, the samples were sorted into groups according to the date of sampling. The differences between ecological groups were tested with one-way analysis of variance (ANOVA) of the component scores.

Dust particles analysis

For dust particles analysis. environmental monitoring device GRIMM 1.109 (Germany) was used.

Results

Along river Váh. near Lisková. four sites were sampled: Sites 1, by the bridge over river Váh, 49˚ 05.047´ ; 19˚ 21.272; site 2, downstream river Váh toward Mondi. 49˚ 04.939´ ; 19˚ 20.982; site 3, upstream river Váh, 49˚ 05.083´ ; 19˚ 21.397; site 4, upstream river Váh, 49˚ 05.097´ ; 19˚ 21.481 (Fig. 1). Sampling dates: March 18, April 15, May 16, June 18, July 16, Aug. 19, Sept. 19, Oct. 15. The results of XRF spectrometry for Sites 1-4 are presented in Tables 1-4.

Number of dust particles recorded by GRIMM device in laboratory in Lisková are presented in Table 5.

Additional calculations are required to transform a number of particles to a uniform. comparable unit of volume (μm^3). Calculations are based on the assumption that the particles are of spherical shape. The volume of particles for each particle size was calculated using the formula for calculating the volume of a sphere: $V=1/6\ \varpi \times d^3$. The summary volumes of deposition of particles of different grain sizes was calculated by multiplying the volume of particles and the number of particles. Results for monthly sampling are presented in Table 6.

Discussion

The categories PM1 and PM2.5 are zero (Table 5), all the mass is concentrated in the category of PM10. Solving the problem requires finding several clusters in the category PM10. The solution for achieving the desired results is seen in the cluster analysis of deposition (Fig. 3).

Three fractions are seen in Fig. 3: I. fraction 0.25 – 3.5 μm, II. fraction 4.0 – 10.0 μm, III. fraction 12.5 - 20 μm. The total volume of all fractions related to the monthly sampling are seen in Table 7.

Each I and II fraction forms approximately 40% of dust deposition. the remaining 20% accounts for III fraction. Fraction I. (the softest), is made up of particles 0.25 to 0.4 micrometers in diameter (Fig. 5). Fires and then road dust are the two most common factors in the production of PM 2.5. PM smaller than 2.5 micrometers, called fine particles or PM 2.5, are of major concern because they can pen-

	March	April	May	June	July	August	September	October
S	695.00	527.00	588.00	313.00	619.00	659.00	599.00	649.00
Cl	446.00	186.00	518.00	453.00	431.00	295.00	239.00	478.00
K	15.714.00	8.206.00	8.836.00	5.977.00	9.705.00	10.590.00	12.587.00	13.564.00
Ca	29.462.00	25.151.00	27.557.00	9.152.00	18.880.00	23.054.00	26.399.00	22.263.00
Ti	402.00	310.00	270.00	93.00	340.00	374.00	564.00	270.00
Cr	207.00	103.00	108.00	41.00	113.00	100.00	56.00	69.00
Mn	171.00	171.00	184.00	63.00	165.00	236.00	200.00	154.00
Fe	7.919.00	5.637.00	5.653.00	1.474.00	5.729.00	6.577.00	8.714.00	4.598.00
Cu	13.00	8.00	19.00	5.00	11.00	13.00	5.00	5.00
Zn	96.00	115.00	109.00	9.00	86.00	168.00	160.00	125.00
Rb	20.70	16.00	18.20	10.10	17.80	21.20	25.20	19.20
Sr	26.70	19.60	21.00	2.90	26.70	30.20	40.70	28.20
Zr	13.30	6.80	5.60	3.00	10.80	15.30	27.40	10.90
Mo	8.30	5.20	9.80	5.50	6.10	6.90	4.90	6.20
Ba	97.00	92.00	93.00	28.00	90.00	90.00	108.00	93.00
Pb	16.00	15.00	21.00	10.00	14.00	17.00	16.00	18.00

Table 1. Site 1. the results of XRF spectrometry (ppm).

	March	April	May	June	July	August	September	October
S	984.00	779.00	609.00	812.00	600.00	658.00	1.066.00	754.00
Cl	850.00	875.00	738.00	1.254.00	264.00	468.00	570.00	361.00
K	17.172.00	17.524.00	17.059.00	18.033.00	12.224.00	9.304.00	16.937.00	10.137.00
Ca	17.801.00	16.155.00	20.604.00	21.851.00	41.112.00	20.635.00	29.544.00	26.891.00
Ti	233.00	415.00	665.00	516.00	976.00	488.00	361.00	412.00
Cr	97.00	101.00	151.00	179.00	95.00	106.00	58.00	80.00
Mn	273.00	257.00	342.00	271.00	265.00	249.00	179.00	201.00
Fe	4.384.00	6.482.00	11.126.00	8.880.00	13.991.00	8.350.00	6.211.00	8.155.00
Cu	8.00	12.00	18.00	19.00	21.00	15.00	25.00	14.00
Zn	141.00	112.00	152.00	135.00	168.00	127.00	251.00	145.00
Rb	18.90	22.00	28.20	24.40	42.70	24.70	20.70	24.10
Sr	22.00	32.30	40.50	41.40	68.00	41.00	44.30	33.00
Zr	7.50	19.50	32.20	22.30	49.50	24.90	11.10	17.10
Mo	6.80	7.30	7.50	9.10	6.60	7.40	6.20	7.70
Ba	103.00	112.00	156.00	139.00	196.00	104.00	85.00	130.00
Pb	14.00	12.00	22.00	19.00	19.00	16.00	17.00	16.00

Table 2. Site 2. the results of XRF spectrometry (ppm).

	March	April	May	June	July	August	September	October
S	1,404.00	556.00	1,167.00	674.00	608.00	599.00	606.00	909.00
Cl	559.00	995.00	613.00	651.00	349.00	679.00	568.00	515.00
K	20,241.00	13,143.00	13,810.00	15,302.00	11,569.00	14,091.00	14,946.00	18,968.00
Ca	22,455.00	85,481.00	24,790.00	30,262.00	24,318.00	26,213.00	27,199.00	2,6814.00
Ti	253.00	284.00	337.00	1,789.00	1,548.00	1,770.00	1,592.00	1,312.00
Cr	89.00	82.00	66.00	87.00	173.00	71.00	68.00	164.00
Mn	213.00	204.00	208.00	1,241.00	1,061.00	1,295.00	677.00	641.00
Fe	5,703.00	4,597.00	6,393.00	16,677.00	15,728.00	15,911.00	16,729.00	18,007.00
Cu	26.00	5.00	16.00	14.00	14.00	16.00	23.00	15.00
Zn	162.00	79.00	203.00	89.00	78.00	88.00	85.00	90.00
Rb	29.20	23.20	29.30	59.20	53.50	60.10	54.30	45.80
Sr	29.90	46.40	43.60	99.00	84.10	87.00	81.00	56.00
Zr	5.00	10.70	11.50	141.00	104.00	136.00	95.00	45.00
Mo	6.50	6.40	6.30	3.60	7.70	4.10	5.90	8.50
Ba	106.00	71.00	104.00	245.00	234.00	272.00	245.00	227.00
Pb	17.00	14.00	17.00	18.00	20.00	22.00	23.00	24.00

Table 3. Site 3. the results of XRF spectrometry (ppm).

etrate deeper into the lungs and even be absorbed into the blood stream. Primary particles are formed from dusty roads, elemental carbon, and wood combustion released directly into the atmosphere. Secondary particles are the result of an oxidative reaction of primary gases, like sulfur and nitrogen oxides, emitted from power plants, industrial facilities, automobiles, and trucks. Huang *et al.* (2010) consider the fine dust particles to be hazardous, as particles of water-based paint dust (<1 μm) had high lead and zinc concentrations. The results of cluster analysis were submitted to RDA (Fig. 4).

The first axis explains 55.8 % of species-environment relation (Eigenvalue 0.55), this axis cor-

	March	April	May	June	July	August	September	October
S	1,404.00	556.00	1,167.00	674.00	608.00	599.00	606.00	909.00
Cl	559.00	995.00	613.00	651.00	349.00	679.00	568.00	515.00
K	20,241.00	13,143.00	13,810.00	15,302.00	11,569.00	14,091.00	14,946.00	18,968.00
Ca	22,455.00	85,481.00	24,790.00	30,262.00	24,318.00	26,213.00	27,199.00	26,814.00
Ti	253.00	284.00	337.00	1,789.00	1,548.00	1,770.00	1,592.00	1,312.00
Cr	89.00	82.00	66.00	87.00	173.00	71.00	68.00	164.00
Mn	213.00	204.00	208.00	1,241.00	1,061.00	1,295.00	677.00	641.00
Fe	5,703.00	4,597.00	6,393.00	16,677.00	15,728.00	15,911.00	16,729.00	18,007.00
Cu	26.00	5.00	16.00	14.00	14.00	16.00	23.00	15.00
Zn	162.00	79.00	203.00	89.00	78.00	88.00	85.00	90.00
Rb	29.20	23.20	29.30	59.20	53.50	60.10	54.30	45.80
Sr	29.90	46.40	43.60	99.00	84.10	87.00	81.00	56.00
Zr	5.00	10.70	11.50	141.00	104.00	136.00	95.00	45.00
Mo	6.50	6.40	6.30	3.60	7.70	4.10	5.90	8.50
Ba	106.00	71.00	104.00	245.00	234.00	272.00	245.00	227.00
Pb	17.00	14.00	17.00	18.00	20.00	22.00	23.00	24.00

Table 4. Site 4. the results of XRF spectrometry (ppm).

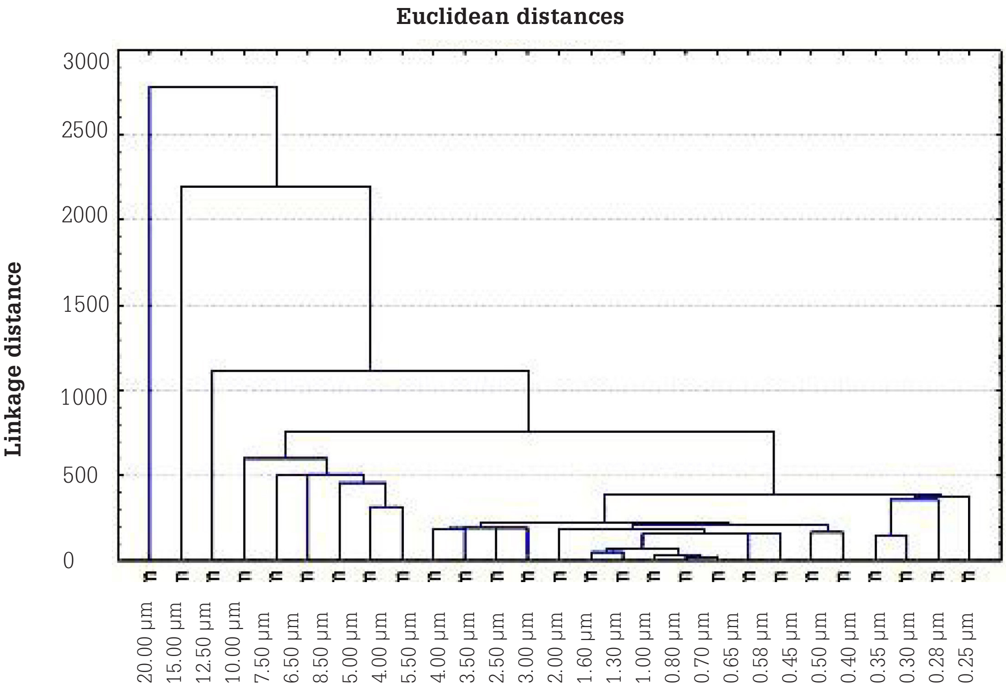

Fig. 3. Tree diagram for 27 variables (grain sizes).

relates with Cr (r=0.62, p=0.102), Pb (r=0.57), Mn (r=0.62). The second axis explains 16.2% of species-environment relation (Eigenvalue 0.16), this axis correlates with Sr (r=0.74), Cu (r=0.72), and to a lesser extent with Fe (r=0.68) (Fig. 4). Highly correlates concentrations of Ti-Rb (r=0.95), Ti-Sr (r=0.91), Ti-Zr (r=0.98).

S binds specifically to toraction I (0.25-3.5 micrometers) Mn, Cr, Mo and non-metal Cl bind to fraction II (4.0 to 10.0 micrometers). Only Pb binds to fraction III (12.5 to 20 micrometers) Zn, Ca, Cu, Fe, Ti, strontium (Sr), rubidium (Rb), zirconium (Zr), and barium (Ba) do not show preference to any grain size fraction (Fig. 4).

Between March and October 2015, during the investigation days, most dust deposition fell during the spring months (March to May), (up 56% (Table 8). Types of dust found in the environment include: mineral dust, metallic dust, other chemical dust, organic and vegetable dust, and biohazards, (Girts 2012). Deposition of atmospheric particles onto vegetation surfaces have three major routes:

	March 18	**April 15**	**May 16**	**June 18**	**July 16**	**August 19**	**September 9**	**October 15**
μm	**Number of grains**							
0.25	100,626	84,895	45,776	49,615	30,631	74,640	67,392	104,755
0.28	56,347	56,796	19,556	18,809	15,495	35,785	41,684	72,072
0.3	28,103	41,203	8,839	8,024	8,886	18,208	27,032	53,441
0.35	14,541	28,773	4,046	3,455	4,761	9,441	14,029	36,772
0.4	6,117	12,192	1,402	1,163	1,592	3,572	5,229	18,194
0.45	2,545	4,539	508	423	460	1,210	1,602	7,299
0.5	2,101	4,548	621	564	450	1,384	2,051	8,047
0.58	1,079	1,315	308	251	124	439	519	2,126
0.65	405	404	134	113	43	160	163	571
0.7	361	359	144	125	42	165	157	471
0.8	201	211	107	88	28	106	90	191
1	159	196	110	76	24	92	59	102
1.3	76	122	67	47	11	47	30	39
1.6	68	109	76	52	21	58	36	44
2	49	63	67	43	30	61	26	33
2.5	36	43	55	29	23	49	16	21
3	15	19	31	12	6	24	5	8
3.5	13	14	26	9	6	17	2	6
4	21	21	39	14	12	26	4	9
5	12	12	24	8	6	13	1	3
6.5	4	3	8	2	3	4	0	2
7.5	3	3	4	2	2	3	0	0
8.5	2	2	5	1	2	2	0	1
10	2	2	2	1	1	1	0	0
12.5	1	0	2	0	1	1	0	0
15	0	1	0	0	1	0	0	0
20	0	0	1	0	0	0	0	0
	μg/m^3							
PM 10	37.2	37	38.6	17.8	18	31.5	15.3	29.8
PM 2.5	0	0	0	0	0	0	0	0
PM 1	0	0	0	0	0	0	0	0

Table 5. The number of particles of different grain size.

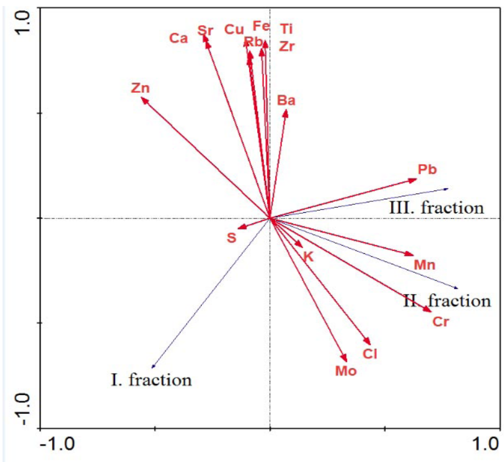

Fig. 4. RDA. relationship between dust fractions and elements accumulations *(Brachythecium salebrosum).*

(1) wet deposition, (2) dry deposition and (3) occult deposition i.e. fog and mist interception. The third fraction (12.5-20 μm) is often lacking, particularly in the autumn months. It seems that this fraction, consisting of the thickest diameter (12.5-20 micrometers) is easily eluted by precipitation (Table 7), as precipitation events clean the air (Prajapati 2012). Sites 1 and 2 are terrestrial. and are exposed only to air emissions. They are in close proximity to heavy traffic enroute to the MONDI factory, and close to traffic travelling to the spa resort Lúčky. At these locations, the moss species *Brachythecium salebrosum* was selcted as a bioindicator. These locations may be increasingly contaminated by metals from transport. Anonymous (2015) cites that common metals in road runoff include Pb, Zn, Fe, Cu, Cd, Cr, Ni and Al. The origin of lead is leaded gasoline, tire wear. lubricating oil and grease, and bearing wear. The source of Zn

μm	Particles volume μm3	March 18	April 15	May 16	June 18	July 16	Aug. 19	Sept. 19	Oct. 15
The volume of array of particles (μm3)									
0.25	0.0081	815.07	687.65	370.79	401.88	248.11	604.58	545.88	848.52
0.28	0.011	619.82	624.76	215.12	206.90	170.45	393.64	458.52	792.79
0.3	0.014	393.44	576.84	123.75	112.34	124.40	254.91	378.45	748.17
0.35	0.022	319.90	633.01	89.01	76.01	104.74	207.70	308.64	808.98
0.4	0.034	207.98	414.53	47.67	39.54	54.13	121.45	177.79	618.60
0.45	0.048	122.16	217.87	24.38	20.30	22.08	58.08	76.90	350.35
0.5	0.065	136.57	295.62	40.37	36.66	29.25	89.96	133.32	523.06
0.58	0.102	110.06	134.13	31.42	25.60	12.65	44.78	52.94	216.85
0.65	0.144	58.32	58.18	19.30	16.27	6.19	23.04	23.47	82.22
0.7	0.180	64.98	64.62	25.92	22.50	7.56	29.70	28.26	84.78
0.8	0.268	53.87	56.55	28.68	23.58	7.50	28.41	24.12	51.19
1	0.524	83.32	102.70	57.64	39.82	12.58	48.21	30.92	53.45
1.3	1.150	87.40	140.30	77.05	54.05	12.65	54.05	34.50	44.85
1.6	2.145	145.86	233.81	163.02	111.54	45.05	124.41	77.22	94.38
2	4.189	205.26	263.91	280.66	180.13	125.67	255.53	108.91	138.24
2.5	8.181	294.52	351.78	449.96	237.25	188.16	400.87	130.90	171.80
3	14.137	212.06	268.60	438.25	169.64	84.82	339.29	70.69	113.10
3.5	22.449	291.84	314.29	583.67	202.04	134.69	381.63	44.90	134.69
4	33.510	703.71	703.71	1306.89	469.14	402.12	871.26	134.04	301.59
5	65.450	785.40	785.40	1570.80	523.60	392.70	850.85	65.45	196.35
6.5	143.79	575.16	431.37	1150.32	287.58	431.37	575.16	0.00	287.58
7.5	220.89	662.67	662.67	883.56	441.78	441.78	662.67	0.00	0.00
8.5	321.55	643.10	643.10	1607.75	321.55	643.10	643.10	0.00	321.55
10	523.60	1047.20	1047.20	1047.20	523.60	523.60	523.60	0.00	0.00
12.5	1022.65	1022.65	0.00	2045.30	0.00	1022.65	1022.65	0.00	0.00
15	1767.14	0.00	1767.14	0.00	0.00	1767.14	0.00	0.00	0.00
20	4188.79	0.00	0.00	4188.79	0.00	0.00	0.00	0.00	0.00

Table 6. Volumes of deposition of particles of different grain size in the months from March to October.

	I. fraction 0.25-3.5 μm	II. fraction 4.0-10.0 μm	III. fraction 12.5-20 μm
March 18	4,265.89	4,417.28	1,022.65
April 15	5,487.33	4,273.48	1,767.14
May 16	3,082.41	7,566.59	6,234.10
June 18	1,991.53	2,567.27	0
July 16	1,403.45	2,834.70	2,789.79
Aug. 19	3,489.16	4,126.68	1,022.65
Sept. 19	2,740.24	199.49	0
Oct. 15	5,936.58	1,107.09	0

Table 7. The total volume of fractions related to the monthly sampling. μm^3.

is tire wear, motor oil, grease, brake emissions, and corrosion of galvanized parts. The source of Fe includes auto body rust and engine parts. The source of Cu is bearing wear, engine parts, and brake emissions. The source of Cd is tire wear, fuel burning, and batteries. The origin of Cr is air conditioning coolants, engine parts, and brake emissions. Ni comes from air conditioning coolants, engine parts, and brake emissions. Al comes from auto body corrosion, Pb in the environment is a major environmental health hazard though it has had a wide use in a wide variety of commercial products ranging from leaded gas to household paint (Link 2012).

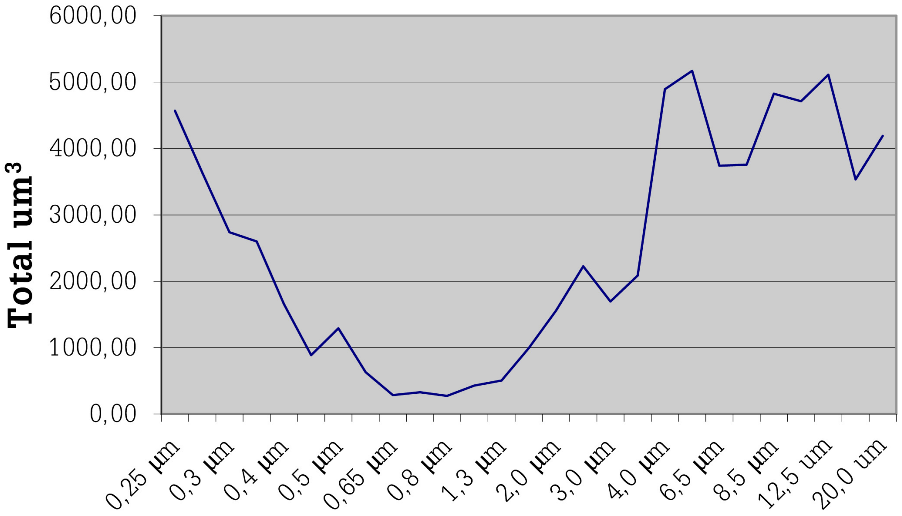

Fig. 5. Structure of total deposition in March – October 2015 (µm^3).

Site 3 and Site 4 are located 300 to 750 meters eastwards (Fig. 1), and are semi-terrestrial. They are exposed to both air and aquatic emissions. Unfortunately, at these sites we did not find the moss species *Brachythecium salebrosum*. Instead. the moss *Brachythecium rivulare* was collected as a bioindicator, *Brachythecium rivulare* creates yellowish-green patches on rocks, soil, logs and tree boles near streams and rivers. It is more hygrophylous than *Brachythecium salebrosum* and therefore found at a higher water level in the river Váh where the sites are flooded. We have taken this into consideration when evaluating the results.

Date	All fractions. total
March 18	9,705.82
April 15	11,527.95
May 16	16,883.10
June 18	4,558.80
July 16	7,027.94
August 19	8,638.49
September 19	2,939.73
October 15	7,043.67

Table 8. Dust depositions. the total during the investigated days (µm^3).

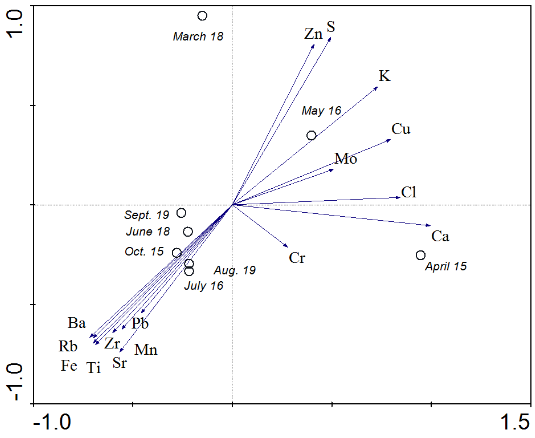

Fig. 6. PCA. *Brachythecium rivulare*. ordination of elements.

Fig. 6 shows significant differentiation in the ordination of the analyzed elements. Group of Zn, S, K, Cu, Mo. Cl, Ca, Cr stands against the group made up of Fe, Rb, Ba, Zr, Ti, Mn, Pb, Sr. It was found that the differentiation consists in the date of sampling. The samples were sorted into two groups according to the date of sampling. Group 1 for spring sampling (March – May). and Group 2, for a summer sampling (June - October) (Table 9).

The differences between ecological groups were tested with one-way analysis of variance (ANOVA) of the component scores. Analysis showed a significant separation of the environmental groups, F = 2834.8, p = 0.00035.

In Group 1, collected during the spring months, Zn, S, K, Ca, Cu, Mo, Cr, Cl of higher concentration were present. On the other hand, in Group 2, in the sampling conducted in June - October, we found higher concentrations of Pb, Mn, Sr, Zr, Ti, Fe, Ba, Rb (Table 9). The largest share of annual rainfall in the area of Ružomberok fell in May 2015 (Lapin 2015). Due to the regulated outflow from the Liptovská Mara dam. the flow in the river Váh does not follow the course of precipitation. Despite the regulated outflow from the dam, we assume that sometime in early June the sampling sites 3 and 4 were flooded. Such a conclusion was drawn from a study of the shore, as the grass was flattened in the direction of the stream. The flooding of sampling sites 3 and 4 is the reason for significant ecological separation of groups 1 and 2.

It is necessary to explain this remarkable phenomenon. The most plausible explanation lies in the fact that the different elements prefer different places to preferentially bind (intercellular, extracellular, and intracellular binding sites). Vázquez *et al.* (1999) studied uptake of heavy metals to the extracellular and intracellular compartments used by the moss species *Fontinalis antipyretica*, *F. polyphyllus* and liverwort *Scapania undulata*. It has been shown that the ranking of the bound elements varied by

	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr	Zr	Mo	Ba	Pb	Predictor
March	1,507	507	21,193	26,899	217	89	198	4,842	19	123	24	25	4	6	117	16	g1
April	1,089	945	21,786	65,366	303	115	235	5,546	24	99	23	39	7	7	112	17	g1
May	1,298	726	21,489	46,133	260	102	216	5,194	21	111	23	32	6	7	114	17	g1
June	679	654	14,186	28,260	1,426	72	882	13,806	10	79	48	85	93	4	214	17	g2
July	573	268	12,849	29,107	1,643	134	1,082	15,171	13	74	55	97	134	6	253	20	g2
Aug.	683	562	14,526	28,916	1,728	71	1,375	15,772	16	87	59	96	151	4	258	20	g2
Sept.	594	489	13,698	26,906	1,176	63	530	12,861	14	72	42	67	66	5	200	20	g2
Oct.	692	454	16,762	26,704	1,373	129	594	17,429	17	89	48	64	60	7	223	24	g2

Table 9. Ecological groups for One-Way Analysis of Variance, matrix Group 1 (g1) - spring sampling; Group 2 (g2) - summer sampling.

different species. Thus, the affinity of the elements relative to *Brachythecium salebrosum* and *Brachythecium rivulare* are different.

Bryophytes containing Na, Mg and Ca may be explained through binding in the cell wall or the outer surface of the plasma membrane. However, most of the K is intracellular. bound within the cell itself (Tipping *et al.* 2008).

Different elements bind to binding sites at different concentrations. Uptake of elements increases with pH at constant total metal concentration. whereas redox potential and colloidal interactions may be significant for some elements in the liverwort *Scapania undulata* (Vincent *et al.* 2001). Flooding sampling sites on the banks of the river Váh caused changes in binding elements. Intercellular metals (dissolved in liquids surrounding cells) were washed away by river water and discarded. Other elements that accumulate in river water bind to intracellular or extracellular binding sites. However. some elements are also released from extracellular or intracellular sites. It appeared that for most metals the release from extracellular compartments was faster than from intracellular compartments (Fernandéz *et al.* 2006).

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