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Heavy metals and other elements in the different types of precipitation - Ružomberok experimental area, Liptov, Slovakia

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Abstract. From the acquired results of environmental monitoring and analyses of 117 samples of air water, 50 samples of rain water and 29 samples of solid water sampled from the sample plot Lisková, situated almost 2 km from the company Mondi SCP, a.s. (Ružomberok), we may assume the following concluding points: From the chosen elements of S, P, Cl, Ca, K, Ti, Mn, Cr, Fe, Ni, Co, Cu, As, Zn, Rb, Zr, Sr, Mo, Cd, Ag, Sn, Ba, Sb, Pb and Hg the acquired concentrations (ppm) were higher than the detection limits of the used X-ray fluorescence spectrometry only in cases of Cl, Ca, K, Ti, Mo, Rb, Sb, S and Sn. One factor ANOVA also showed that the concentration of K in samples of snow decreased with the increasing age of snow or temperature at sampling. This relationship remains unconfirmed from a statistic point of view for the other elements. Higher levels of chlorine were present in a liquid form - rain water, air water. In solid water (ice, snow) the levels were lower. Chlorine occurred more in places where sulphur was not detected, which was in contrast with the places, where sulphur was detected. Chlorine cumulated in an increased manner in an environment where CO_2 levels were higher, temperature was higher and there were higher levels of O_3 in the air. Less chlorine occurred in an environment at times when the air was very humid and partly accompanied with increased dustiness. The variance of potassium amount did not correlate with this phenomenon. Sulphur correlated almost absolutely with an increasing or decreasing amount of PM_{10} particles.

Key words: solid water, air humidity, rain, inorganic pollutants, alloys, pollution, deposition, Ružomberok, X-ray fluorescence spectometry

Introduction

This work is focused on retaining inorganic pollutants in snow, fog, frost cover, air humidity and rain. The main objective was to evaluate the impact of Mondi SCP, a.s. within the distribution of inorganic substances, especially metals from snowfall, fog, rain, frost cover and air humidity at places lying close to the Ružomberok - Lisková area.

Mondi SCP, a.s. in the town of Ružomberok is one of the biggest Slovak plants. It is the largest manufacturer of paper and pulp in Slovakia and its production capacity is 560,000 metric tons of uncoated paper, 66,000 metric tons of wrapping paper and 100,000 metric tons of market pulp (www.mondigroup.com 2016).

The processing industry of paper and pulp demands a lot of water and energy, which causes releasing of different inorganic substances or organic compounds into atmosphere and water sources. In regard to the fact that fog, air humidity, snow and rain are active mediums, which can bring over gases and particulates from atmosphere in the land, rain, snow, air humidity and fog can also be an appropriate indicator of different particulates and compounds, accumulations and deposits. In this respect accumulations reflect the chemistry of atmosphere.

Heavy metals, which originate in human activities, become various environmental components and they are considered as a serious problem because they are not biologically decomposed, they are toxic and get in food chains. The agency for toxic substances and the register of diseases recorded arsenic (As) on the first position, plumbum (Pb) on second place and mercury (Hg) on third place in the register of the most dangerous substances on the basis of frequencies, toxicity and occurrence in environment, which can consequently affect human health (ATSDR 2016). Thanks to that monitoring is growing because of the adverse effects from heavy metals on the mentioned human health and ecosystems as such.

This study is focused on retaining inorganic pollutants in snow, fog, frost cover, air humidity and rain. The main objective was to evaluate the impact of Mondi SCP, a.s. in the distribution of inorganic substances, especially metals from snowfall, fog, rain, frost cover and air humidity at places lying near the Ružomberok – Lisková area.

The aim of this study is to find out the anthropogenic impact on environment and to improve the quality and impact of the company Mondi SCP. This work coincides with the scientific research of the Institute of High Mountain Biology, University of Zilina, Slovakia.

Material and Methods

Description of sampling sites and samples obtaining snow samples

The samples of solid water, rain water and air humidity (Table 1) were collected from the selected locality of the Lisková village (N49° 05´ 26´´ and E19 ° 20´ 56´´), next to the company Mondi SCP, Inc. (altitude above sea-level: 480 m; coordinates: N49° 04′43′′ and E19° 18′30′′V). The location is marked on the satellite image by the yellow star. The company Mondi SCP, Inc. is marked by the

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	Air water	Rain water	Solid water
March 2015	6	-	-
April 2015	3	-	-
May 2015	6	6	-
June 2015	15	5	-
Jule 2016	16	8	-
August 2015	18	3	-
September 2015	15	7	-
October 2015	15	4	-
Novemer 2015	7	7	4
December 2015	8	1	3
January 2016	-	4	13
February 2016	5	1	6
March 2016	3	4	3

Table 1. Number of samples in different months - locality Lisková.

red rectangle (Fig. 1). Snow samples were collected from the surface under snow in glass jars and subsequently rendered at 4° C in the refrigerator. Icing coating was curbed from glass dimensions 0.5 x 0.5 m. Humidity was collected in DeLonghi DEM 8,5 dehumidifier and then stored in the refrigerator. Rain water was collected directly into glass bottles, and all types of samples were stored in the fridge at 4° C ready for the analysis. Table 1 shows the types of samples from the locality of the Lisková village. 50 samples of rain, 117 samples of humidity and 29 samples of solid water were collected. The samples were taken in the period March 3, 2015 – March 22, 2016.

X-ray fluorescence spectrometry

For the elemental analysis of rain water, solid water and air humidity samples a hand-held X-ray fluorescence (XRF) spectrometer DELTA CLASSIC (USA) was used. This approach of the elemental analysis of atmospheric waters was also applied by other authors (Muia *et al.* 1991). The analysis of the sample of snow water with known weight to calculate the concentration of a given element was carried out in a closed protective box of XRF spectrometer during 180 s. The following elements were determined: S, P, Cl, Ca, K, Ti, Mn, Cr, Fe, Ni, Co, Cu, As, Zn, Rb, Zr, Sr, Mo, Cd, Ag, Sn, Ba, Sb, Pb and Hg. The Factory Grade Library utilized analytical models consisting of a set of minimum and maximum values for each element in an alloy. If the content of an element was smaller or bigger then the detection limit, it was classified as "not detected - ND" element. For the purposes of accuracy was each sample measured three times and subsequently averaged.

Data analysis and statistics

To evaluate the relationships between parameters describing the sampling conditions (age of snow, day temperature, and O_3, CO_2, t, rH, PM_{10}) and/or concentration of Cl, Ca, K, Ti, Rb, SN and Sb in samples of rain, snow, air humidity, the principal component analysis (PCA) methods of multivariate analysis were applied. In addition, one-way analysis of variance (ANOVA) was also performed to analyse significant differences between studied

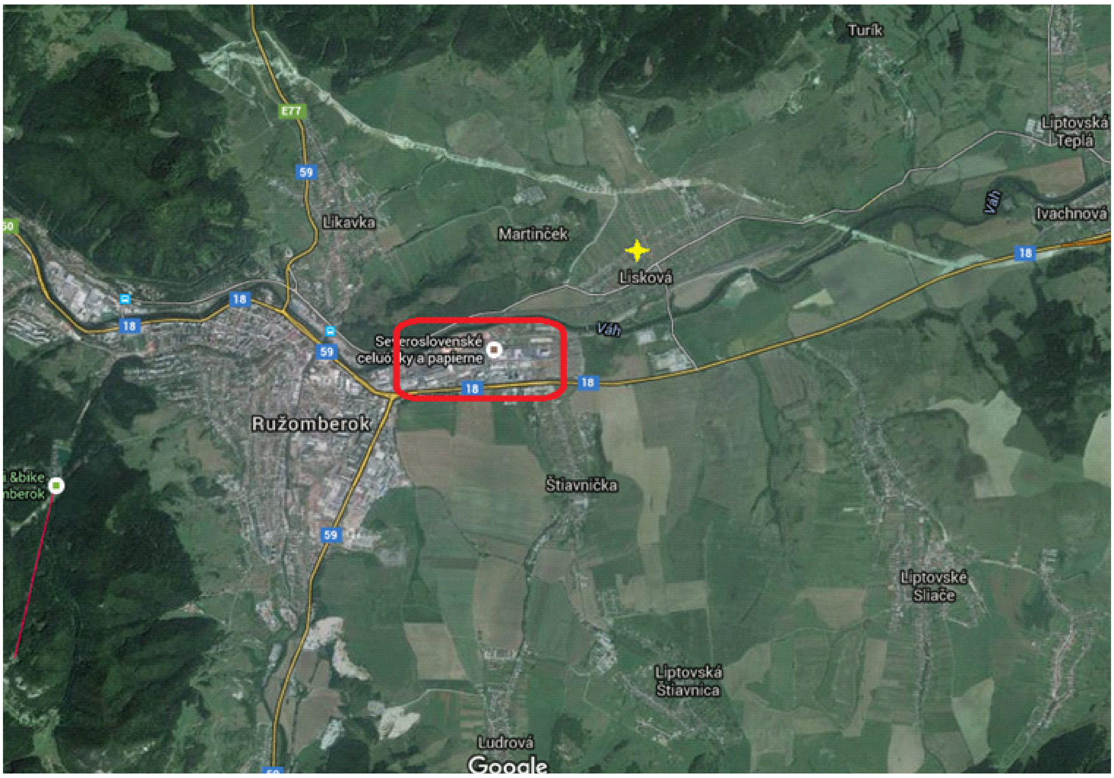

Fig. 1. Localization of sampling site (denoted by star) for obtaining samples - selected locality Lisková within the vicinity of company Mondi SCP Inc. (Satellite imagery obtained from Google Earth).

precipitation types on the basis of the determined concentrations of Cl, Ca, K, Ti, Rb, SN and Sb. The mentioned data analyses were carried out while using the statistical and data visualization program soft STATISTICA Centurion ver. 15 (StatPoint Technologies, Inc., Warrenton, VA, USA).

Results

On the basis of the samples of solid water, rain water and air water the following elements were surveyed by the means of X-ray fluorescence spectrometry: S, P, Cl, Ca, K, Ti, Mn, Cr, Fe, Ni, Co, Cu, As, Zn, Rb, Zr, Sr, Mo, Cd, Ag, Sn, Ba, Sb, Pb and Hg. We concluded that some elements are not, or almost not transported in the given types of measured samples. P, Cr, Co, Zn, As, Se, Sr, Hg, Ba, Ag, Zr are the undetected elements in the samples. Mn, Fe and Cu occurred once in air water. Cd occurred only in four samples of air humidity as well as Pb, which except for this case occurred in two samples of rain. The frequencies of occurrence of chosen elements in different types of samples are shown in Tables 2 to 7.

The relationship between S and PM_{10} levels is shown in Fig. 2. Due to the small number of samples this graph may serve as an inspiration for further research on this issue.

In the studying of the element composition of H_2O we have focused on chlorine and potassium, which were detected in all samples (XRF). The occurrence of Cl and K was studied in relation to measured values of pH in the water medium and also in relation to the values of PM_{10}, O_3, CO_2, temperature, relative humidity of the environment, where the samples of the Lisková location were collected. The subsequent data matrix was transformed into a correlation matrix to find out the correlations. The next step was to use the correlation matrix to process the data by the method of principal components. Found factors and the score of individual samples for these factors were compared with a one-factor analysis of variance presented earlier. The main eigenvector matrix is presented in Table 8. Two most significant factors explaining more than 50% of the data variance correlated with the accumulation of chlorine. The first one, very significant (39%), describes the increased accumulation of chlorine in correlation to the environment, where there also was an increased amount of CO_3, increased temperature, and where higher levels of O_3 were present in the air, too. Less chlorine accumulated in the environment in times when the air was very humid and partly accompanied by increased dustiness. The variance of potassium levels did not correlate with this phenomenon at all. It is possible that this type of chlorine - tied to a certain warmer weather typology in precipitation - is of the anthropogenic origin. The second type of chlorine, explained by Factor 2 was in the environment when the levels of potassium were highly increased and the levels of CO_2 partly decreased. The accumulation of this type of chlorine correlated less with weather and did not correlate at all with O_3 or dustiness. We may assume that this type of chlorine occurred in other chemical compounds and since it was manifested accordingly with potassium, it is possible that its origin lies in an organic compound in the environment.

Other factors (Table 8) describe the variability of weather and dustiness in the air with evidence that the levels of large particles in the atmosphere varied only slightly with the levels of chlorine or potassium in water. For these reasons we assess mainly the first two significant factors.

Rb	D	ND	D%
Air water	49	68	41.88
Rain water	19	31	38.00
Solid water	1	28	3.45

Table 2. Rb occurred in 69 samples. (D - determined, ND - non-determined, D% - relative number of samples in which the element was found).

S	D	ND	D%
Air water	12	105	10.26
Rain water	10	40	20.00
Solid water	13	16	44.83

Table 3. S was detected in 35 samples from a total amount of 196 samples. It occurred most often in solid water.

Sb	D	ND	D%
Air water	71	46	60.68
Rain water	33	17	66.00
Solid water	26	3	89.65

Table 4. Sb was detected in 72.11% of samples. It occurred most often in solid water - 89.65% of the samples.

Ti	D	ND	D%
Air water	49	68	41.88
Rain water	19	31	38
Solid water	1	28	3.45

Table 5. We may assume that Ti does not bond at all to water of solid form, since it was present only in 1 sample out of 29. On the other hand it was present in rain water in 38% of the samples a in 41.88% of samples of air water.

Sn	D	ND	D%
Air water	22	95	18.8
Rain water	11	39	22
Solid water	9	20	31.03

Table 6. Sn, unlike titan, was concentrated most often in solid water while it reached lower concentrations in rain and air water.

Mo	D	ND	D%
Air water	81	36	69.23
Rain water	30	20	60
Solid water	17	12	58.62

Table 7. Mo was detected stably in all surveyed types in an average of 62.6% samples.

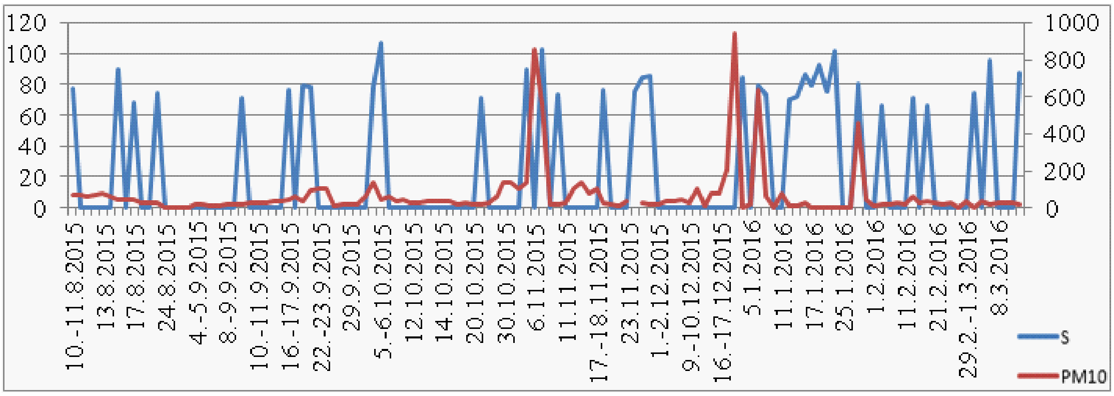

Fig. 2. Chart showing levels of S and PM_{10} during sampling.

Higher levels of chlorine occurred in the liquid form - in rainwater, air water. In solid water (snow, ice) the levels were lower (F=11,31, P=0,0). In addition, chlorine occurred more in places where sulphur was not detected compared to places where sulphur was detected (F=4,76, P=0,031). There was a correlation in influencing chlorine in precipitation between the factor of sulphur and the factor of water typology (F=0,48, P=0,619). In other words, chlorine accumulates in liquid water more than in solid water, whether it is at a place with detected sulphur or not. From this point of view we may assume that sulphur and this type of detected chlorine have a different origin. These findings are graphically presented in Fig. 3.

This phenomenon is also interesting by the fact that chlorine accumulated more in the samples in which titan was detected (Fig. 4). It seems that chlorine correlates with a certain type of industrial pollution, in which titan also occurs. The same is true for another element – rubidium. Chlorine occurred mainly at those places, where rubidium was detected (Fig. 5).

The accumulation of chlorine did not correlate with molybdenum. Its levels where approximately the same at places where molybdenum was not detected. Levels of chlorine decreased where Sb was not detected (Fig. 6)

In this first phenomenon we may assume that it is inorganic chlorine produced by the industrial sphere, occurring in waters with higher levels of titan and rubidium, and more in liquid water than in solid water.

Factor 2 denotes a different typology of accumulation of chlorine and suggests its mutual accumulation with potassium. Such increased levels of both elements occur at the same time more-or-less without any relation to weather (O_3, rH, PM_{10}) and partly take place at a time when the levels of CO_2 decrease, and marginally also temperatures (Table 1). The increased accumulation of chlorine and potassium in snow and ice is depicted in Fig. 7.

The increased accumulation of Cl and K did not depend on the situation if sulphur was detected in the samples or not (F=0.66, p=0.1) This type of chlorine compounds probably occurs along with potassium on places, where a higher amount of titan was also detected (Fig. 8). The Cl/K accumulation did not significantly differ in samples in which Rb, Mb or Sb were or were not detected. However, the occurrence of Cl and K in water, where Sb was not detected, was higher (Fig. 9).

The lower correlation between the accumulation of chlorine and potassium with several industrial elements and its accumulation mainly in the solid form of water (snow - compare with Cl described in the first factor, which accumulated more in the liquid form) suggests that it may be because of the organic compounds with chlorine and potassium.

Discussion

The determination of alloys in atmospheric water and snow can provide information about the processes in the air, its accumulation and ways in the ecosystem,

Eigenvectors of correlation matrix

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
pH	0.181	0.138	-0.113	0.876	-0.297	0.276	-0.029	-0.023
Cl	-0.347	-0.503	0.096	-0.058	0.030	0.751	0.198	-0.089
K	-0.042	-0.711	0.216	0.140	-0.446	-0.460	-0.109	0.049
CO_2	-0.348	0.387	0.489	-0.05	-0.413	0.037	0.266	0.492
rH	0.445	0.037	0.125	-0.34	-0.378	0.376	-0.607	0.102
t	-0.493	0.255	0.180	0.007	-0.197	-0.062	-0.348	-0.702
O_3	-0.489	-0.046	-0.227	0.169	0.275	-0.009	-0.600	0.491
PM_{10}	0.201	-0.042	0.768	0.237	0.531	0.003	-0.164	-0.026
	39%	18%	13.50%	12.5%	7.3%	5.3%	3.1%	

Table 8. Eigenvectors for the measured environmental variables.

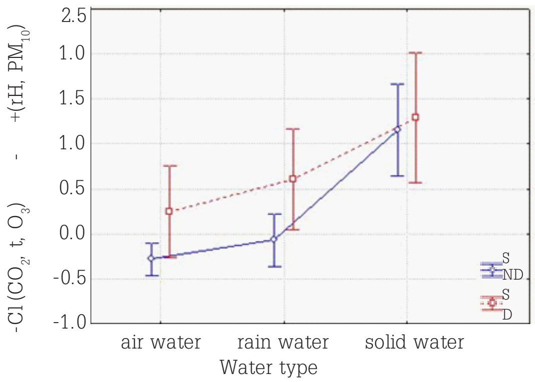

Fig. 3. S-ND - S not detected, SD - S detected, there was no significant interaction between these two groups - two way ANOVA (F (2, 169)= .48245, p=0.618).

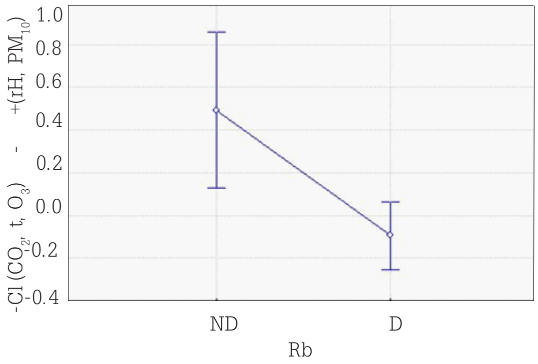

Fig. 5. Rb-ND – rubidium not detected, Rb-D – rubidium detected. A significant correlation (F (1, 173)=8.4288, p= 0.00417).

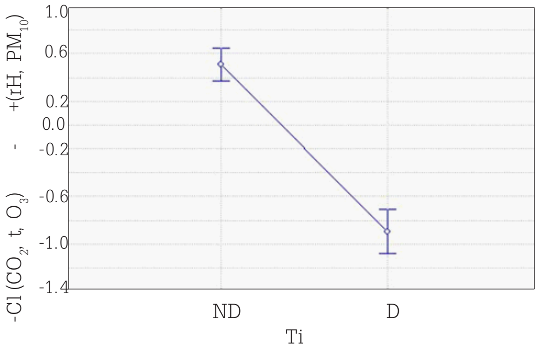

Fig. 4. -ND - titan not detected, Ti-D - titan detected. A significant correlation (F (2, 173) = 144.29, p = 0.0000).

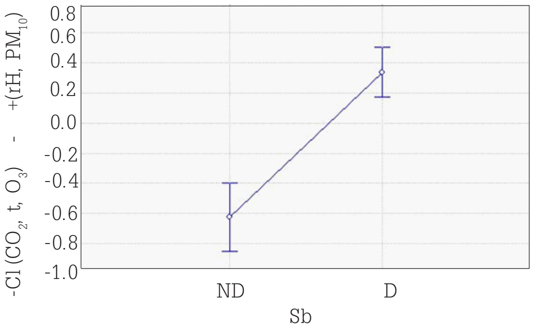

Fig. 6. Sb-ND – antimony not detected, Sb-D – antimony detected. A significant correlation (F (1, 173) =46.182, p=0.00000).

find out the sources and ways of the transportation of elements in a local and global sense. Snow analyses were successfully used to determine the load on ground and water ecosystems during wintertime (Benassai *et al.* 2005; Ming et al. 2007). The accumulation of atmospheric pollution in snow cover depends on temperature, type of ground and wind conditions.

Samples from the Lisková locality showed that from the analysed elements (S, P, Cl, Ca, K, Ti, Mn, Cr, Fe, Ni, Co, Cu, As, Zn, Rb, Zr, Sr, Mo, Cd, Ag, Sn, Ba, Sb, Pb and Hg) differences in the bonding of elements occur based on a sample type (rain water, solid water, air water). Rb bonds best in all types of atmospheric humidity - up to 79,3% of samples, 104 times of 117 samples occurred in the samples of air humidity. S, Sb and Sn bond best in solid water. Sb was even detected with 90% probability. Mo and Ti bond better in air water. In this comparison we could say that samples of rain water are average, considering the bonding of elements.

By comparing sulphur with PM_{10} particles we discovered a quite high correlation; to determine it more accurately we would, however, need more samples.

The disadvantage of this type of measuring is that it needs a lot of variables. However, it offers an accurate analysis when these requirements are met; an analysis that describes environmental proceedings in nature. That is why it would be beneficial to continue in the research and collect the largest possible amount of physical-chemical data to define the pollution in atmospheric water more accurately.

X-ray fluorescence spectrometry enables the detection of a wide variety of elements, that is why it is convenient for monitoring and the determination of basic data.

To evaluate the relationships between the parameters describing the conditions during sampling we assessed data that were measured for all of these samples: pH, CO_2, rH, t, O_3 and PM_{10} with elements detected also in all of these samples - Cl and K.

The occurrence of Cl and K was studied in relation to measured values of pH in the water medium and also in relation to the values of PM_{10}, O_3, CO_2, temperature, relative humidity of the environment. The next step was to use the correlation matrix to process the data by the method of principal components. The defined factors and score of individual samples for these factors were compared with the analysis of one factor of variance, which is how we defined the two most important factors explaining more than 50% of variance of our data in correlation to Cl accumulation. First of them, very significant (39%), describes the increased accumulation of Cl in correlation to the increased levels of CO_3, increased temperature, and where the air with higher levels of O_3 was present. Cl accumulated in the environment at times when it was very humid and partly accompanied by increased dust in the air. The variance of K levels does not correlate with this factor at all. It is possible that this type of Cl, related to a certain warmer typology of weather, is of an anthropogenic origin. The second type of Cl explained by factor 2 occurs in an environment where the level of K was very increased and the level of CO_2 was partly decreased. The accumulation of this type of Cl correlated less with the weather and did not correlate at all with O_3 and dust nuisance. We may assume that this type of Cl

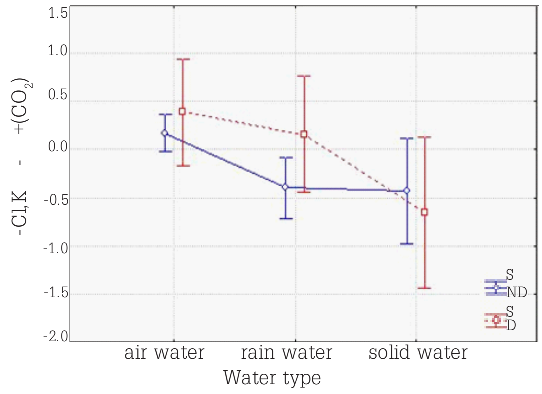

Fig. 7. Graph showing the different accumulation of Cl, K in ice and snow (solid water). An insignificant correlation (F (2, 169)=0.86902, p=0.42123).

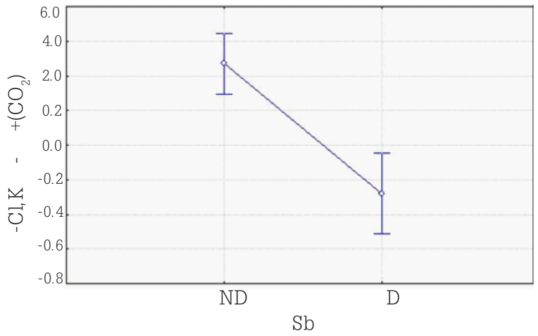

Fig. 8. Graph showing the correlation between Ti occurrence and Cl, K and CO2 levels. A significant correlation, (F (1, 173)=25.966, p=0.0001).

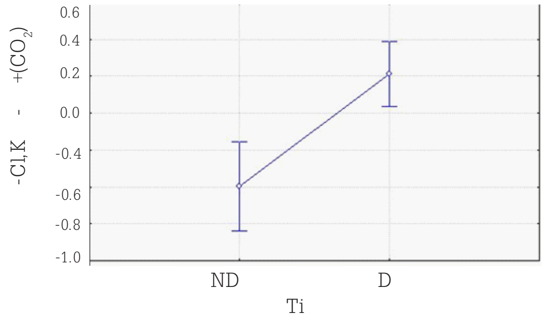

Fig. 9. A graph showing the correlation between Sb occurrence and levels of Cl, K and CO$_2$. A significant correlation (F (1, 173) = 15.968, p = 0.00010).

	O$_3$ (μg/m^3)	**PM$_{10}$ (μg/m^3)**
Chopok	52	4.8
Topoľníky	51	15.5
Starina	55	12.6
Stará Lesná	56	13.3
Lisková	19.8	55.8

Table 9. Annual averages of O$_3$ and PM$_{10}$ levels in SHMÚ monitoring stations and Lisková (www.shmu.sk 2014).

originates in other compounds and occurs accordingly with K. It is possible that its origin lies in the organic compounds in the environment.

The concentrations of snow pollution in the Lisková village were compared to chosen localities (Topoľníky, Chopok, Starina, Bratislava – Koliba and Stará Lesná) according to the annual report of SHMÚ and we found that K and Cl reach concentrations twice as high and Pb reaches higher concentrations than the average values measured at the Chopok Hill (Hudák 2015).

In our geographical – climatic conditions the variance of the chemical consistency of the snow cover reflect most of all the origin of air masses, the synoptic situation, the amount of precipitation (in case of snow cover its water values), global, regional and local pollution of atmosphere, the length of snow cover and the air temperature changes.

The findings of a quite low pH of melted snow are important. The snow subsequently reacts first with the vegetation cover and soil, then with the geological environment, during which its chemical consistency metamorphoses a lot and negative changes occur mainly in the soil profile.

Based on the findings we may say that the average pH measured during the time period of March 2015 – March 2016 is in accordance with the demands on the surface water quality (Nariadenie vlády SR č. 269/2010).

When we compare the annual average of O$_3$ and PM$_{10}$, we see that there are significant differences in the SHMÚ monitoring stations (Topoľníky, Chopok, Stará Lesná, Starina) and Lisková (Table 9).

Ackonwledgements

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