

Heavy metals and other elements in faeces of wild ruminants in the area of paper mill industry

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Abstract. This study compared the content of heavy metals and other elements in faeces of red deer (*Cervus elaphus*) and roe deer (*Capreolus capreolus*) from Mních Hill (closely located to paper mill factory), Ružomberok, and in Jastrabá, mid Slovakia (control locality). Together 130 samples were collected, dried, milled and analysed by XRF spectroscopy. Results showed that throughout the year potassium, chromium, iron, barium, and lead (K, Cr, Fe, Rb, Ba Pb) were present in higher concentrations in red deer than in roe deer. Sulphur, calcium, copper and molybdenum (S, Ca, Cu, Mo) concentrations were higher in autumn than in winter, and throughout the year they were at higher levels in the town of Ružomberok compared to the Jastrabá area. Inverse interrelations among some clusters of elements were revealed: in autumn, Cu, Zn, and Pb all increased and Cl and K decreased, while in winter, Cl and K increased and Cu, Zn, and Pb decreased. Both Cl and Mo as well as Ca and Zn ratios increased in autumn, and Ca and Zn ratios decreased in winter. The ratio of Cl and Mo to Ca and Zn was higher in roe deer than in red deer throughout the year. Lead values were higher in autumn compared to winter.

Key words: heavy metals, faeces of ruminants, red deer, roe deer

Introduction

Toxic metals (e.g. Pb, Cd and Hg) are natural components of the Earth's crust and their increased concentrations in the environment are often caused by human activity, including combustion of fossil fuels, mining and smelting of non-ferrous metals, and waste incineration (Czaban *et al.* 2013, Norgate *et al.* 2007, Pacyna *et al.* 2007). Increased concentrations of toxic elements have been found in all environments including soils (Chrastný *et al.* 2012, Šajn *et al.* 2013, Durkalec *et al.* 2015). Toxicity of some elements causes damage to the crops, forest ecosystems, livestock, as well as humans (Lazor *et al.* 2007). Animals that consume plant food with the increased content of heavy metals have more toxic elements in hair, callous tissues, inner organs, and in the liver and kidneys. These increased concentrations may be also found in milk

and muscle tissues mainly in species with higher longevity (Šalgovičová and Zmetáková 2005).

Lead is a blue-grey, shiny, very soft, malleable, non-noble metal. When the exposure to lead is higher than the organism can eliminate, bioaccumulation occurs and up to 90% of lead is stored and detained in the bones and kidneys. Lead affects the entire body, but the circulatory system, central nervous system, and digestive systems are very sensitive. Lead causes destruction of red blood cells, which leads to anaemia (Bencko *et al.* 1995, Fergusson 1990). Lead and all of the soluble compounds are highly toxic. Via blood circulation it gets into the organs, damaging muscles, blood vessels, brain, lungs and kidneys. Ions of lead inhibit the biosynthesis of proteins, nucleic acids, hemoglobin, and hormones as well as increase egestion of potassium from the cells. Lead accumulates in the body and is excreted in a very difficult way. The only effective defence is to supply the body with a high amount of calcium, magnesium, vitamin A and C as well as to consume large quantity of carrots and cabbage because the pectin has the ability to bind up to 80% of heavy metals and excrete them from the body (Šalgovičová and Zmetáková 2005).

Lead is absorbed in the gastrointestinal tract by a process which has two steps. Firstly, it is absorbed from lumen and then excreted into the intestinal fluid (Sobel *et al.* 1938). Upon oral ingestion about 5 to 10% of lead is absorbed and usually less than 5% of what is absorbed is retained (Goyer 1996). About 99.5% of total ingested lead is excreted through faeces. 90% of this is excreted without being absorbed and 9.5% is excreted after being absorbed and metabolized, leaving only 0.5% to be deposited in various body tissues (Gupta 2012). The load of lead in faecal matter almost exceeded what is present in the food material (Gupta 2012). For example, lead, cadmium, chromium, copper and zinc concentrations were found in a considerable amount in the biological samples (faecal matter/feed) and non-biological (soil/water) samples collected from Udaipur Zoo. Concentrations of metals particularly in faecal matter samples from the zoo were much higher than in wild animals like white tailed deer feeding near the smelter (Ipsen and Feigel 1970). Metal concentration in faeces normally equals that in food (Leonzio and Massi 1989). Obviously, the additional exposure occurred through inhalation. The load of lead in faecal matter almost exceeded what is present in the food material (Gupta 2013). In case of Slovakia, the spatial analysis of lead accumulation in tissues of wild ruminants showed that the highest average values of lead were found in the Trenčín region, Banská Bystrica region and Prešov region, where the samples exceeded limits (Šalgovičová and Križová 2004).

Zinc, copper, cadmium

The uptake of micronutrients like zinc and copper is dependent on the animal's demands. Critical concentrations in tissues are expected only when there are high levels in the diet (Gutleb *et al.* 1998). Chronic cadmium, zinc, and lead poisoning in domestic and laboratory animals has been investigated in many studies. High intakes of cadmium can cause anaemia, enteropathy, and kidney damage. Signs of zinc toxicosis include anaemia, poor bone mineralization, and arthritis (NRC 1980). In some studies, faecal analysis was a useful way to detect gross exposure, and showed that some deer living close to the smelters were ingesting potentially dangerous quantities of zinc and cadmium. For example, cadmium accumulated with age in the kidneys of the Palmerton deer. This has been shown also in other deer herds (Munshower and Neuman 1979, Kocan *et al.* 1980). In many species a concentration of 200 ppm wet weight in the kidney cortex is associated with tubular damage (Sileo and Beyer 1985). Deer livers are often consumed by hunters, and those livers having the highest concentrations of cadmium should probably be considered unfit for human consumption (Srebočan *et al.* 2012).

Sulphur

Sulphur dioxide stays in the atmosphere for 2-6 days after it is exhaled. It is subject to various photochemical oxidative, catalytic and other reactions. It is among the most common contaminant of the atmosphere. It gets there via the combustion of fossil fuels, but also through volcanic activity and can also be produced by soil microorganisms. In our conditions the major pollutant is SO₂, which is responsible for most damage to agricultural production. All fossil fuels (coal, oil, natural gas) contain different forms and varying amounts of sulphur compounds. These are oxidized in combustion mainly to SO₂. The natural content in the atmosphere is about 1-3 ppm SO₂ per m³ of air (Lazor *et al.* 2007). Sulphur contamination may affect human health. For example, some authors found that the incidence of nasal symptoms, cough, eye symptoms, and headache were increased in severely polluted communities, but were not statistically significant. The authors concluded that exposure to malodorous sulphur compounds may affect the health of children (Drimal *et al.* 2010).

Chlorine

Chlorine is an element soluble in water, which irritates the upper and lower airways and lungs. Chlorine reacts with water to form hydrochloric acid and free oxygen radicals. It is non explosive, greenish yellow and heavier than air at room temperature and atmospheric pressure. In today's society it occurs relatively frequently and the greatest risks of poisoning threat are industrial accidents (Dobiáš 2008). Chlorine occurs in various forms in the chemical, paper and textile industries, as well as in water and mineral water in the form of cleaning products in households. Deaths from chlorine intoxication occurs with an incidence of about 1-2 per 10,000 people (Dobiáš 2008).

The aim of this study was to compare the content of selected elements including heavy metals in the faecal pellets of wild ruminants in red deer (*Cervus elaphus*) and roe deer (*Capreolus capreolus*) from the polluted area in the town of Ružomberok and the control location in the Kremnica Mountains. Due to the similarities and differences in measured values we can compare the variability of environmental conditions in the localities. The first site is located near the Mondi paper production factory in the town of Ružomberok, and animals in this area are constantly in contact with emissions and increased noise, which can cause major differences in the results. The evaporator factory passed a modernization process in 2014, which resulted in the decreased amount of hazardous substances released into the atmosphere compared to the past. The second site is located in a relatively unpolluted area where factories or other anthropogenic factors do not have such a significant impact.

Material and Methods*Locality*

The town of Ružomberok is a historically industrialized town and it is located in northern Slovakia. The local industry has been dominated by a large textile company, and a pulp and paper mill. The textile manufacturer stopped production in 2006. The paper pulp mill used the kraft pulping process, which had a considerable influence on the ambient air quality in and around the town. The kraft process results in the release of malodorous emissions partly due to the use of sodium sulphide in combination with sodium hydroxide for the digestion of wood chips. The combined effect of these two compounds allows for the rapid delignification of wood while allowing the cellulose fibres to keep their strength. However, this process results in the release of reduced sulphur compounds (Drimal *et al.* 2010).

The climate of the studied area is characterised by wet summers and mild winters. The vegetation of the study area is dominated by coniferous forests, but there are also deciduous trees and meadow habitats with herbs and grasses (Husáriková *et al.* 2015).

Data collection

Faecal samples of wild ruminants - red deer and roe deer - were collected. The data collection occurred near the town of Ružomberok on the Mních Hill and its surroundings (Choč Mts.) and started in December 2014. Samples were collected between Likavka village a Lisková village, north of Ružomberok (Fig. 1).

In this locality, a total of 78 samples were collected. 42 faecal samples were from roe deer and 36 samples were from red deer.

In October 2015, samples collected control locality in the Kremnické vrchy Mts. near the Jastrabá village, between the Ostrá Hora Peak and Jas-trabská Skala Rock (Fig. 2). In this locality, 52 samples were collected from roe deer and 22 from red deer.

Data collection

Faecal samples were collected in plastic sealable bags and stored in a freezer (temperature -18° C) at the Institute of High Mountain Biology in Tatranská Javorina. Samples were collected at both sites until March 2016.

Sample preparation

Sample processing in the laboratory begun in January 2016 at the Institute of High Mountain Biology in Tatranská Javorina. Samples were first put into a Petri dish and dried in the Memmert Incubator IF160 dryer for 10 – 15 hours at a temperature of 75° C. Dried samples were homogenized to powder using Retsch CryoMill. After homogenization, samples were pre-

pared for an X – ray spectrometry analysis. Elements in samples were analysed using XRF spectrometer DELTA CLASSIC. The presence and amounts of the following elements were measured: Cd, Sn, Sb, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Ba, Hg and Pb.

Statistic

For this task we used the software Statistics Version 10.1. Using measured data, the data matrix was created. For statistical analysis only samples containing all of the relevant elements were used, so that multifactorial analysis of variance (MANOVA) could be calculated. Therefore, 105 out of 130 samples were used for further analyses. Samples were investigated to find factors which influence

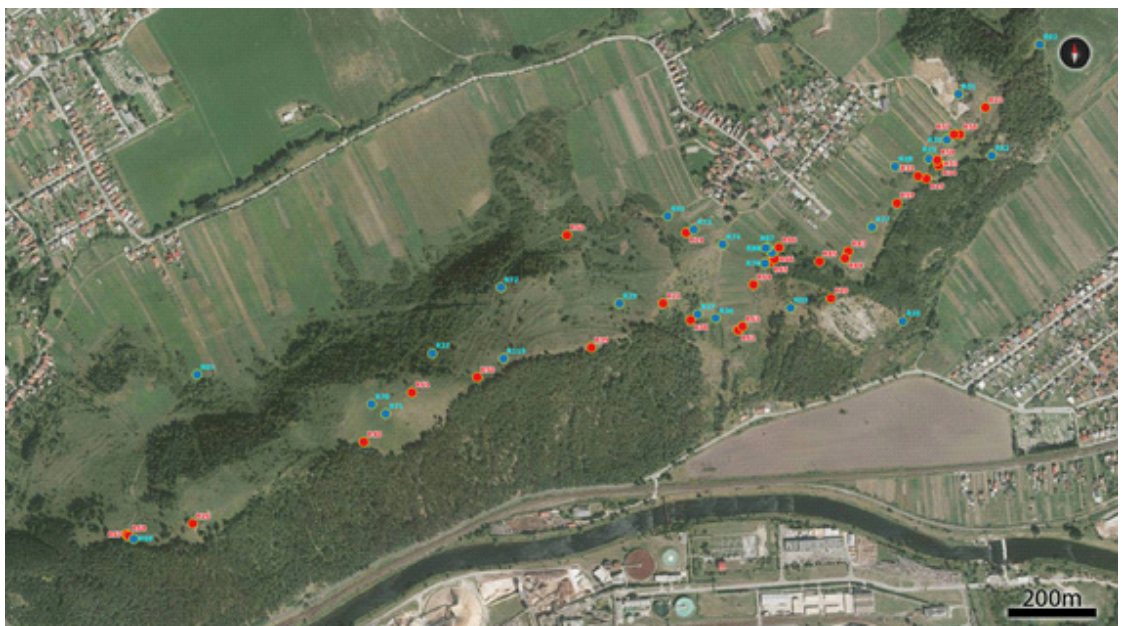


Fig. 1. Map of the studied location near the town of Ružomberok with GPS coordinates of faecal samples red deer (red dots) and roe deer (blue dots).



Fig. 2. Map of the locality Jastrabá with GPS coordinates of faecal samples from red deer (red dots) and roe deer (blue dots).

the concentration of measured elements or groups of elements. Common factors were: species, season and locality.

Results

The average concentrations of the elements found in all samples are presented in Table 1. In most of the samples we also found other elements. Chlorine was present in 120 samples (above the detection limit of Delta spectrometer), and the average value was 530.5 ppm. Titanium was present in 124 samples with an average of 582.9. Chromium was present in 129 samples with an average value of 19.6 ppm. Copper was found in 128 samples with an average of 19.2 ppm. Strontium was found in 128 samples with an average of 85.6 ppm. Zirconium was found in 110 samples with an average measured value 23.1 ppm. Molybdenum was found in 128 samples with an average value of 5.2 ppm. Finally, lead was found in 122 samples with an average value of 8.2 ppm.

Cobalt, nickel, selenium, silver, and mercury were also measured, but these elements were not found (below the detection limit of Delta) in any of the measured samples.

Phosphorus was found in five samples with an average of 525.0 ppm, all from the Ružomberok site; two samples from roe deer and three from red deer. Arsenic was found in seven samples, averaging 6.9 ppm. Each sample with the presence of arsenic was collected in the area of Ružomberok. The comparison of this element between seasons or game species did not show significant differences. Cadmium was found in two samples collected in early February 2016 at the Jastrabá village. One sample was from red deer (8 ppm), and one from roe deer (9 ppm). Tin was found in 13 samples with an average value of 14.3 ppm regardless of location, time or game species. Antimony was found in 68 samples with an average value of 11.8 ppm and its incidence did not depend on location, annual period or game species.

Factor data analysis - the method of principal components

Multivariate analysis

For the data analysis we selected 111 of 130 collected samples and each of them contained 13 elements (S, Cl, K, Ca, Cr, Mn, Fe, Cu, Zn, Rb, Mo, Ba and Pb). The

factor analysis revealed 13 factors that show mutual relations of elements in the samples. Three of these factors had a percentage higher than 10%, and we considered the eight most important factors that influence the content of heavy metals and other elements in the faeces of wild ruminants. Each of them had a proportion of variance greater than 3% (Table 2).

The first factor describes mutual variation of potassium, chromium, iron, rubidium, barium and lead concentrations. The second factor is also a so called unipolar vector which describes mutual increase or decrease of sulphur, calcium, copper and molybdenum. The third factor shows the antagonistic interdependence between chlorine/ potassium and copper/zinc/lead. Other factors had the proportion of variance lower than 10%. Factor eight reflects the variation of lead in the faeces (Table 2).

The synergic increase or decrease of potassium, chromium, iron, rubidium, barium and lead concentration in scats (Table 2, Factor 1) was independent of location and seasons. In red deer the increase of elements over the year is more significant in contrast to roe deer (Fig. 3). The concentrations of this group of elements did not differ between localities and was also similar in autumn and winter.

The mutual rise or fall of sulphur, calcium, copper and molybdenum (Table 2, Factor 2) was the same in red deer as in roe deer. However, the concentrations of these elements were higher at the Ružomberok site than in Jarabá ($F(1,105)=3.7$, $p=0.05$), and at both localities these elements increased in the faeces in autumn ($F(1,105)=27.2$, $p=0.0000$) (Fig. 4).

Bipolar vector copper, zinc, lead versus chromium and potassium (Table 2, Factor 3). In winter, the ratio of chromium and potassium to copper, zinc, and lead increased, and then decreased in autumn. (Fig. 5). This phenomenon is independent of species or locality.

The relationship between the mutual decrease of chlorine and molybdenum, and the increase of calcium and zinc (Table 2, Factor 7), or vice versa, was not dependent on different locations. Roe deer had proportionately more chlorine and molybdenum, while red deer had more calcium and zinc ($F(1, 105)=4.4$, $p=0.038$). Importantly, in both species there was proportionally more chlorine and molybdenum in faeces in autumn, while in winter, there was an increased amount of calcium and zinc ($F(1, 105)=6.56$, $p=0.012$) (Fig. 6).

Lead and seasons. The amount of solitary varied lead (Factor 8) did not vary between species or locations, but the amount of lead tended to be higher in autumn than in winter (Fig. 7).

	Count	Average of S	Average of K	Average of Ca	Average of Mn	Average of Fe	Average of Zn	Average of Rb	Average of Ba
Jastrabá	52	1043.46	6572.77	25635.19	2131.33	1856.50	133.29	27.72	121.12
CC	30	1000.77	6229.47	27210.63	2288.67	1655.50	130.60	29.61	126.07
CE	22	1101.68	7040.91	23486.86	1916.77	2130.59	136.95	25.15	114.36
Ružomberok	78	1144.81	10263.13	38922.26	242.41	6430.22	126.32	29.65	128.80
CC	42	1168.22	9795.62	38473.45	239.60	6280.83	128.38	29.07	123.13
CE	36	1117.50	10808.56	39445.86	245.69	6604.50	123.92	30.31	135.42
Grand Total	130	1104.27	8786.98	33607.43	997.98	4600.73	129.11	28.88	125.73

Table 1. Average values (ppm) of elements which were present in each of the collected samples, divided by locality and ruminant species (CE - *Cervus elaphus*, CC - *Capreolus capreolus*).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
S	0.0418	-0.4904	-0.0319	0.3749	0.2110	-0.1202	-0.0476	-0.1472
Cl	-0.1074	-0.1815	0.4270	0.3270	-0.4736	-0.4903	-0.2014	0.0651
K	-0.3393	-0.1411	0.4122	0.1749	-0.1000	0.2167	-0.0034	-0.0954
Ca	0.0681	-0.4644	-0.0317	-0.0813	0.3374	-0.3311	0.4482	-0.0952
Cr	-0.4569	-0.0368	-0.1747	-0.1303	0.0232	-0.1289	0.0668	0.2535
Mn	0.1511	0.2880	-0.2734	0.6509	0.2052	-0.0859	-0.2387	0.1944
Fe	-0.4492	-0.0962	-0.0402	-0.1794	0.1475	-0.1787	-0.0450	0.3036
Cu	-0.1251	-0.3599	-0.4061	0.2933	-0.0133	0.2763	0.0241	-0.1553
Zn	0.1175	-0.1464	-0.3969	0.0266	-0.7173	0.0639	0.3498	0.1805
Rb	-0.3755	0.0578	0.1858	0.2353	0.0058	0.5255	0.2304	-0.1621
Mo	0.0216	-0.4285	-0.1324	-0.2765	-0.0628	0.2587	-0.6978	0.0819
Ba	-0.4166	0.1294	-0.2593	0.1268	0.0645	-0.1170	-0.0173	0.2925
Pb	-0.2986	0.2068	-0.3118	-0.0892	-0.1417	-0.3089	-0.1720	-0.7658
	31.34%	20.73%	14.04%	7.47%	7.09%	5.13%	4.86%	3.01%

Table 2. Eigenvectors of the first eight principal components.

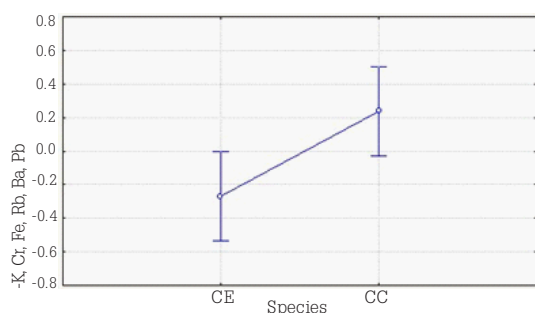


Fig. 3. The comparison of the mutual increase of potassium, chromium, iron, rubidium, barium and lead (Factor 1) in faeces of roe deer and red deer. (Y – axis, lower numbers mean higher concentrations). The higher concentrations occurred in red deer (CE) than in roe deer (CC). $F(1,105)=7.2134$, $p=0.008$.

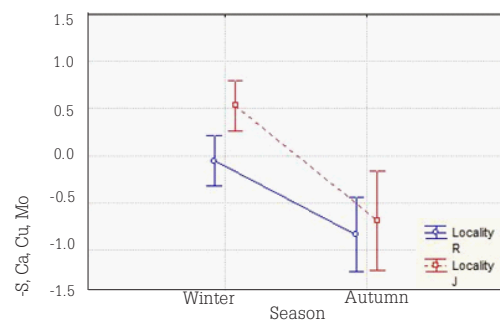


Fig. 4. The comparison of sulphur, calcium, copper, molybdenum (Factor 2) between seasons (Y axis – lower values mean higher concentrations). The amount of the elements increased in winter at both localities but at the locality near pulp mill industry was higher than in the control. The concentrations did not differ between species. $F(1,103)=1.3082$, $p=0.255$.

Discussion

Elemental sulphur, potassium, calcium, manganese, iron, zinc, rubidium, and barium were detected in faeces of roe deer and red deer at both locations. All these elements are to some level common in nature, but their content also depends on the extent of pollution and the distance from industrial zones and frequented roads (Wei and Yang 2010). For example, the study of Way and Schroder (1982) showed that the

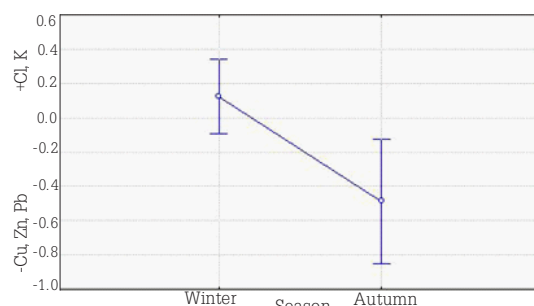


Fig. 5. Content of copper, zinc and lead (Factor 3) versus chlorine and potassium. In winter ratio of Cl and K to Cu, Zn, Pb increased. $F(1, 105)=8.1902$, $p=0.005$.

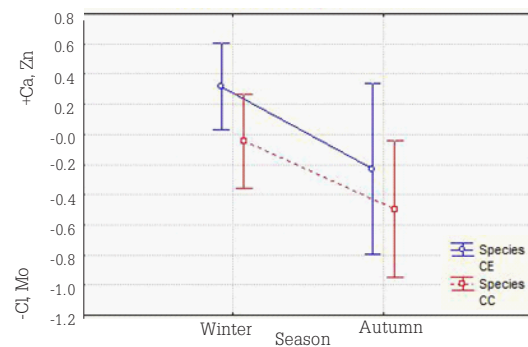


Fig. 6. Bipolar interdependence of chlorine/molybdenum and calcium/zinc (Factor 7). This phenomenon was independent of locality. The ratio Cl, Mo/Ca, Zn was significantly higher in roe deer (CC) than red deer (CE) and also higher in autumn than in winter. $F(1,103)=0.05011$, $p=0.82332$.

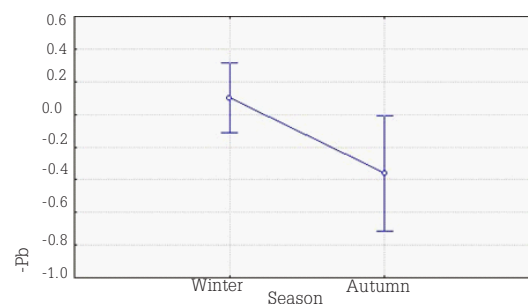


Fig. 7. Lead (Factor 8) in faeces in different seasons. Concentration of this type of lead were higher in autumn than in winter. $F(1, 105)=4.9321$, $p=0.02851$.

concentration of lead in the body of rats was directly proportional to the distance from the highway. This may be the reason why the average values of sulphur, potassium, calcium, iron, rubidium and barium in the urbanized and industrialized area of the town of Ružomberok were higher than in the Jastrabá rural area (Table 1). For example, the study by Gupta (2012) revealed that animals from localities farther from urbanized areas showed only background concentrations of heavy metals. Ružomberok is located near the Mondi factory and also near a busy road connecting the east and west of Slovakia. The area where the samples were collected is on the windward side of Ružomberok. According to Mráz and Šoltés (2015) the concentration of sulphur and lead is higher on the windward site of the Mondi paper mill.

It is interesting to note that the proportion of manganese is significantly higher in the Jastrabá area when this locality is much farther from the roads, as well as from towns. The increase in the proportion of manganese may be caused by the ZSNP and Slovalco factories in the town of Žiar nad Hronom, which is located about 10 km southwest. For example, Jamnická *et al.* (2007) measured 0.24 mg/g-1 of manganese in the upper soil layer (1-10 cm) in the Permanent Monitoring Plot Žiar nad Hronom, and 0.14 mg/g-1 in the Beech Ecological Experimental Station Kremnické vrchy Mts. The Jastrabá locality is leeward from the aluminium factory in the town of Žiar nad Hronom.

Higher concentrations of potassium, chromium, iron, rubidium, barium and lead were found in red deer than in roe deer, which is shown in the first factor (Fig. 3). This can be caused by differences in the diet and possibly by differences in metabolism (Prins and Geelen 1971). Variations in digestion between different ruminant species have been already studied by several authors (Mine *et al.* 1978, Holand 1994).

The second factor had a significant connection to season and locality. It was confirmed that sulphur, calcium, copper and molybdenum in the faeces of wild ruminants were found at higher concentrations in autumn compared to winter in both sites. This decrease in the concentration of these elements in winter may be caused by the intake of elements by plants during the year because these elements are accumulated from spring till autumn, but no longer in winter, and thus they are not passed to the ruminants via the food web. The diet of ruminants changes during the year. For example, the variation in the diet composition of roe deer throughout the year was studied by Tixier and Duncan (1996), and a variation in the accumulation of selected elements by different plant species was investigated by Deng *et al.* (2004).

The second factor shows a higher concentration of detected elements throughout the year in the urbanized area of Ružomberok. This dependence is probably related to the increased pollution in this area, mainly due to the Mondi paper mill in close proximity and the road (Fig. 4). For example, Fazeli *et al.* (1991) found concentrations of heavy metals (Cu, Pb, Zn, Ni, Co, Cd) in different parts of coconut trees irrigated directly by wastewaters of a paper mill near Nanjangud in India in higher concentrations than the limits suggested by the World Health Organization. An increased concentration of heavy metals and other elements near the town of Ružomberok has already been measured by several authors (Mráz and Šoltés 2015, Korčeková *et al.* 2015, Hudák *et al.* 2015). The

concentration of elements in the faeces usually corresponds to a concentration in food and additional rate is by inhalation (Gupta 2012).

The third factor shows seasonal dependence and suggests that similarly to the second factor, copper, zinc and lead accumulate in plants during their growth. Therefore their ratio to chlorine and potassium was higher in autumn than in winter. The values of chlorine and potassium increased proportionally in winter most probably because they get to the surface of dry plants from the air or are being captured from snow and the snow melting process (Fig. 5).

The eighth factor proved the seasonal dependence of the lead content in the faeces of ruminants. This is probably also related to the absorption of lead or physiological processes of plants and not the binding of lead to the surface of dry plants by aerosols in winter (Fig. 7). For example, the seasonal variation in accumulation of heavy metals in the leaf, wood and bark of different trees was studied by Laureysens *et al.* (2004). Šalgovičová and Křížová (2004) found that the content of lead that gets into the digestive tract by food is higher than the content received from the air or water.

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References

- Bencko, V., Cikrt, M. and Lener, J. 1995: Toxické kovy v životním a pracovním prostředí člověka. Grada Publishing, Praha.
- Czaban, S., Kolacz, R., Dobrzanski, Z., Bubeľ, F., Opalinski, S., Durkalec, M. and Gruszczynski, M.F. 2013: Mercury content in the area of the "Želazny Most" tailings pond. *Przemysl Chemiczny*, **92**: 1268-1271.
- Deng, H., Ye, Z.H. and Wong, M.H. 2004: Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. *Environmental Pollution*, **132**: 29-40.
- Dobiáš, V. 2008: Intoxikácia chlóróm (Cl⁻) a čpavkom (NH₃). *Via pract.*, **5**: 85-86.
- Drimal, M., Lewis, Ch. and Fabiánová, E. 2010: Health risk assessment of environmental exposure to malodorous sulfur compounds in central Slovakia (Ružomberok area). *Carpathian Journal of Earth and Environmental Sciences*, **5**: 119 - 126.
- Durkalec, M., Szkoda, J., Kolacz, R., Opalinski, S., Nawrocka, A. and Zmudzki, J. 2015: Bioaccumulation of Lead, Cadmium and Mercury in Roe Deer and Wild Boars from Areas with Different Levels of Toxic Metal Pollution. *International Journal of Environmental Research*, **9**: 205-212.
- Fazeli, M.S., Sathyanarayan, S., Satish, P. N. and Muthanna, L. 1991: Effect of paper mill effluents on accumulation of heavy metals in coconut trees near Nanjangud, Mysore District, Karnataka, India. *Environmental Geology and Water Sciences*, **17**: 47-50.
- Fergusson, J.E. 1990: The Heavy Elements, Chemistry. Environmental Impact and Health Effect. Pergamon press, New Zealand.
- Goyer, R.A. and Clarkson, T.W. 1996: Toxic effects of metals. In: *The Basic Science of Poisons, Fifth Edition.* (ed. C.D. Klaassen), pp. 811-867. Casarett & Doull's Toxicology,

- McGraw-Hill Health Professions Division, New York.
- Gupta, V. 2012: Mammalian Scat as a Bio-indicator of Heavy Metals Contamination in Western Rajasthan, India. *International Journal of Scientific and Research Publications*, **2**(12): 1-7.
- Gupta, V. 2013: Feces of captive wild mammal use as bio-indicator of heavy metal pollution in urban air. *International Journal of Innovative Research in Science, Engineering and Technology*, **2**(6): 2-9.
- Gutleb, C.A., Kranz, A., Nechay, G. and Toman, A. 1998: Heavy Metal Concentrations in Livers and Kidneys of the Otter (*Lutra lutra*) from Central Europe. *Bulletin of Environmental Contamination and Toxicology*, **60**: 273-279.
- Holand, Ø. 1994: Seasonal dynamics of digestion in relation to diet quality and intake in European roe deer (*Capreolus capreolus*). *Oecologia*, **98**: 274-279.
- Hudák, M., Randis, M., Bartaloš, T., Kmeťová, M., Kosová, I. and Horník, M. 2015: The preliminary study of the selected environmental effects around the paper industry. *Oecologia Montana*, **24**(2): 78-83.
- Husáriková, M., Janiga, M. and Kufelová, M. 2015: Howell-Jolly bodies in peripheral blood of Yellow-necked mouse (*Apodemus flavicollis*) living in the vicinity of pulp mill industrial complex. *Oecologia Montana*, **24**(1): 9-20.
- Chrastný, V., Vaněk, A., Teper, L., Cabala, J., Procházka, J., Pechar, L., Drahotka, P., Penížek, V., Komárek, M. and Novák, M. 2012: Geochemical position of Pb, Zn and Cd in soils near the Olkuszmine/smelter, South Poland: Effects of land use, type of contamination and distance from pollution source. *Environmental Monitoring and Assessment*, **184**(4): 2517-2536.
- Ipsen, J. and Feigel, P. 1970: In Bancrofts Introduction to Biostatistics. 2nd edition, Harper & Row, New York.
- Jamnická, G., Bučinová, K., Havranová, I. and Urban, A. 2007: Current state of mineral nutrition and risk elements in a beech ecosystem situated near the aluminium smelter in Žiar nad Hronom, Central Slovakia. *Forest Ecology and management*, **248**(1): 26-35.
- Kocan, A.A., Shaw, M.G., Edwards, W.C. and Eve, J.H. 1980: Heavy metal concentrations in the kidneys of white-tailed deer in Oklahoma. *Journal of wildlife diseases*, **16**: 593-596.
- Korčeková, R., Klemmová Gregušková, E., Kmeťová, M. and Janiga, M. 2015. In situ monitoring of air pollutants in the Ružomberok area - vascular plants as indicators. *Oecologia Montana*, **24**(2): 50-59.
- Laureysens, I., Blust, R., De Temmerman, L., Lemmens, C. and Ceulemans, R. 2004: Clonal variation in heavy metal accumulation and biomass production in a poplar coppice culture: I. Seasonal variation in leaf, wood and bark concentrations. *Environmental Pollution*, **131**(3): 485-494.
- Lazor, P., Tóth, T., Tomáš, J. and Melicháčová, S. 2007: Imisná záťaž lesných ekosystémov slovenska zlučeninami sýry. In: *Klima lesa* (eds. J. Rožnovský, T. Litschmann and I. Vyskot), Křtiny.
- Leonzio, C. and Massi, A. 1989: Metal bio-monitoring in bird eggs: A critical experiment. *Bulletin of Environmental Contamination Toxicology*, **8**: 280-288.
- Milne, J.A., Macrae, J.C., Spence, A.M. and Wilson, S. 1978: A comparison of the voluntary intake and digestion of a range of forages at different times of the year by the sheep and the red deer (*Cervus elaphus*). *The British journal of nutrition*, **40**(2): 347-357.
- Mráz, M. and Šoltés, R. 2015: *Fallopia japonica* (Houtt.) Ronse Decr. as bioindicator of pollution in the experimental study area Ružomberok. *Oecologia Montana*, **24**: 41-49.
- Munshower, F.F. and Neuman, D.R. 1979: Metals in soft tissues of mule deer and antelope. *Bulletin of environmental contamination and toxicology*, **22**(1): 827-832.
- NRC (National Research Council) 1980. Mineral Tolerance of Domestic Animals. National academy of sciences, Washington, D.C.
- Norgate, T., Jahanshahi, S. and Rankin, J.W. 2007: Assessing the environmental impact of metal production processes. *Journal of Cleaner Production*, **15**(8): 838-848.
- Pacyna, E.G., Pacyna, J.M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., Nitter, S., Pregger, T., Pfeiffer, H. and Friedrich, R. 2007: Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmospheric Environment*, **41**(38): 8557-8566.
- Prins, R.A. and Geelen, M.J.H. 1971: Rumen characteristics of red deer, fallow deer, and roe deer. *The Journal of Wildlife Management*, **35**(4): 673-680.
- Sileo, L. and Beyer, W.N. 1985: Heavy metals in white-tailed deer living near a zinc smelter in Pennsylvania. *Journal of Wildlife Diseases*, **21**(3): 289-296.
- Srebočan, E., Janicki, Z., Crnić, A. P., Tomljanović, K., Šebečić, M. and Konjević, D. 2012: Cadmium, lead and mercury concentrations in selected red deer (*Cervus elaphus* L.) tissues from north-eastern Croatia. *Journal of Environmental Science and Health, Part A*, **47**(13): 2101-2108.
- Sobel, A.E., Gawron, O. and Kramer, B. 1938: Influences of vitamin D in experimental lead poisoning. *Experimental Biology and Medicine*, **38**(3): 433-435.
- Šajn, R., Aliu, M., Stafilov, T. and Alijagić, J. 2013: Heavy metal contamination of topsoil around a lead and zinc smelter in Kosovska Mitrovica/Mitrovicë, Kosovo/Kosovë. *Journal of Geochemical Exploration*, **134**: 1-16.
- Šalgovičová, D. and Krížová, S. 2004: Olovo v svalovine vysokej zveri v Slovenskej republike. Rizikové faktory potravného reťazca IV, pp. 217-219, Nitra.
- Šalgovičová D. and Zmetáková Z. 2005: Lead in the venison's and deer's musculature. O ekológii vo vybraných aglomeráciách Jelšavy - Lubenika a stredného Spiša, XIV, Hrádok pri Jelšave.
- Tixier, H. and Duncan, P. 1996: Are European roe deer browsers? A review of variations in the composition of their diets. *Rev. Ecol. (Terre Vie)*, **51**: 3-17.
- Way C.A. and Schroder, G.D. 1982: Accumulation of lead and cadmium in wild population of the commensal rat, *Rattus norvegicus*. *Arch. Environ. Contam. Toxicol*, **11**: 407-417.
- Wei, B. and Yang, L. 2010: A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical Journal*, **94**(2): 99-107.

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