Oecologia Montana 2017, **26,** 55-58

REPORTS

A contribution to the knowledge of selected element contents in food products and sycamore leaves near the paper mill industry

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The environmental pollution in Ružomberok, Sloavkia is mainly caused by two major sources of pollution: The Mondi SCP, Inc. paper mill and heavy traffic. This is one of the primary reasons for the town being declared as an area highly exposed to environmental pollution (Drimal *et al.* 2010). The process of pulp production at Mondi SCP, INC. uses sulphates and other basic chemicals including sodium hydroxide (NaOH) and sodium sulphide (Na_2S). During the processing of organic mass (wood), by-products of these sulphur compounds, particularly hydrogen sulphide, dimethyl disulphide, dimethyl sulfide and methyl mercaptan, are released into the environment (Drimal *et al.* 2010). Hydrogen sulphide is a colourless gas, and has the distinct odour of rotten eggs (Weil *et al.* 2006). Endogenous H_2S plays an important role in the central nervous system, cardiovascular system, and immune system, but long time exposure to ambient levels of this gas can cause ophthalmic lesions, and malignant disorders (Saeedi *et al.* 2015). Several studies (Struve *et al.* 2001; Blackstone *et al.* 2005; Volpato *et al.* 2008; Al-Magableh *et al.* 2015) show that exposure to hydrogen sulphide can affect brain neurochemistry, physiology and behaviour in rats. A study by Saeedi *et al.* (2015) has shown higher mean methemoglobin concentrations and lower mean sulfhemoglobin concentrations in workers exposed to hydrogen sulphide. The industrial complex and paper mill operated by Mondi SCP is the largest pollutant in the area. In this study, we examined concentrations of elements in food products from private farmers in the village of Lisková, located in close proximity to the mill.

Material and Methods

The milk of free-range goats and cows was sampled from July to November, 2015. Between October and December, 2015, samples were taken from stabled goats and cows. Chicken eggs were sampled between August and October, 2015. Apples were sampled in November 2015 and the fallen dried leaves of sycamore were sampled in March 2015. All samples were collected in different locations around the industrial complex of the paper mill. All samples were dried using the Memmert Universal Oven UF160 Plus., and eggs, apples and leaves were milled using the CryoMill Retsch GmbH 2015. We used X-ray fluorescence spectrochemical analysis with the XRF DELTA Classic spectrometer to measure the concentration of elements. The analysis was repeated three times and an average was calculated. Descriptive statistics was recorded in IBM SPSS Statistics 23 (IBM Corp. 2015). The chemical elements were measured in the $mg.kg^{-1}$.

Results

Mean concentrations of seven elements in the milk of goats and cows are given in Table 1 and Table 2. Total mean concentrations ($mg.kg^{-1}$) of elements in the milk measured in the following order: K>Ca>Cl>S>Sb>Rb>Mo. The order was the same between free-range and stabled goats and cows. Concentrations of Sb were higher in free-range goats, while Mo and Sb were higher in free-range cows than in stabled. Concentrations of all other elements were higher in stabled goats and cows. Total concentrations of all elements, except Mo, were higher in the milk of goats than in the milk of cows. Higher concentrations of Ca and Mo were found in the milk of free-range cows than in the milk of free-range goats. All other element concentrations were higher in the free-range goats. All concentrations of all elements in the milk were higher in the stabled goats than in the stabled cows. The most significant variance between element concentrations in free-range and stabled goats was found in Ca and Mo levels. In cows, the largest difference in element concentrations between free-range and stabled animals was Cl.

The mean concentrations of S, Cl, K, Ca, Rb, Mo and Sb in the whites and yolks of chicken eggs are presented in Table 3 and Table 4. Sn was detected only in the egg whites, and Zn was detected only in the egg yolks. Total mean concentrations of elements in the egg whites were recorded as follows: K>Cl>S>Ca>Sn>Sb>Rb>Mo. The ranking of element concentrations during summer was the same, but the order of autumn concentrations was K>Cl>Ca>S>Sn>Sb>Rb>Mo. Total mean concentrations of elements in the yolk were K>Ca>Cl>S>Zn>Sb>Rb>Mo. The ranked order of sum-

Element	N	Total ± (SD)	Feeding	
			Free-ranged	Stabled
S	11	115.91 ± 15.97	110.14 ± 13.56	126 ± 16.39
Cl	15	876.53 ± 197.82	839.73 ± 219.06	977.75 ± 63.45
K	15	1,400.6 ± 487.45	1,320.64 ± 552.55	1,620.5 ± 56.7
Ca	15	985.07 ± 381.82	871.09 ± 384.57	1,298.5 ± 93.42
Rb	15	3.81 ± 1.07	3.75 ± 1.24	4 ± 0.41
Mo	5	1.36 ± 0.22	1.23 ± 0.15	1.55 ± 0.07
Sb	12	10.2 ± 3.68	10.57 ± 4.39	9.33 ± 1.16

Table 1. Mean concentrations (mg.kg^{-1}) of elements in the milk of free-ranged and stabled goats (*Capra aegagrus hircus*) sampled between July and November 2015.

Element	N	Total ± (SD)	Feeding	
			Free-ranged	Stabled
S	10	97.5 ± 20.77	92.67 ± 17.94	104.75 ± 25.3
Cl	14	602.79 ± 88.9	572.4 ± 77.64	678.75 ± 73.41
K	14	1,158.14 ± 281.53	1,123.5 ± 330.14	1,244.75 ± 49.78
Ca	14	979.29 ± 245.92	938.4 ± 283.8	1,081.5 ± 30.62
Rb	14	2.04 ± 0.53	1.96 ± 0.56	2.23 ± 0.46
Mo	7	1.47 ± 0.28	1.52 ± 0.3	1.35 ± 0.21
Sb	12	9.25 ± 1.71	9.5 ± 1.93	8.75 ± 1.26

Table 2. Mean concentrations (mg.kg^{-1}) of elements in the milk of free-ranged and stabled cows (*Bos taurus*) sampled between July and December 2015.

Element	N	Total ± (SD)	Season	
			Summer	Autumn
S	16	355.81 ± 62.51	363 ± 76.86	343.83 ± 29.18
Cl	16	916.75 ± 122.69	910.4 ± 144.48	927.33± 85.83
K	16	1,248.56 ± 171.54	1,280.1 ± 213.51	1,196 ± 30.2
Ca	16	353.94 ± 335.45	315.9 ± 275.3	417.3 ± 439.81
Rb	16	2.23 ± 0.33	2.32 ± 0.3	2.25 ± 0.6
Mo	6	1.37 ± 0.33	1.38 ± 0.41	1.35 ± 0.07
Sn	5	9.4 ± 0.56	9.33 ± 0.58	9.5 ± 0.71
Sb	13	9 ± 1.47	9.1±1.52	8.67 ± 1.53

Table 3. Mean concentrations (mg.kg^{-1}) of elements in chicken egg whites (*Gallus gallus domesticus*) in summer and autumn seasons sampled between August and October 2015.

Element	N	Total ± (SD)	Season	
			Summer	Autumn
S	13	354.31 ± 52.48	360.78 ± 42.89	344.6 ± 44.74
Cl	13	922 ± 67.96	902.25 ± 76.94	953.6 ± 38.31
K	13	1,120.15 ± 165.44	1,096.13 ± 147.71	1,158.6 ± 202.31
Ca	13	1,042.64 ± 245.28	1,111.38 ± 212.87	932.2 ± 276.58
Zn	13	29.15 ± 7.44	29 ± 6.39	29.4 ± 9.71
Rb	13	2.75 ± 0.4	2.65 ± 0.38	2.9 ± 0.41
Mo	10	1.46 ± 0.25	1.52 ± 0.28	1.38 ± 0.19
Sb	11	8.91 ± 1.58	9 ± 1.63	8.75 ± 1.71

Table 4. Mean concentrations (mg.kg^{-1}) of elements in the yolks of chicken (*Gallus gallus domesticus*) eggs in summer and autumn seasons sampled between August and October 2015.

Elements	N	Flesh ± (SD)	Seeds ± (SD)	Total ± (SD)
S	24	124.5 ± 24.32	2141.83 ± 1,158.15	628.83 ± 1,043.2
Cl	20	286.94 ± 31.86	285 ± 36.77	286.75 ± 31.3
K	24	7,805.39 ± 1,273.61	26,923.5 ± 15,279.39	12,584.92 ± 11,111.36
Ca	24	504.28 ± 77.17	9,333.67 ± 5,623.22	2,711.63 ± 4,704.37
Cr	16	3.32 ± 0.44	63.15 ± 49.16	25.76 ± 41.24
Mn	24	8.73 ± 2.42	141.17 ± 68.88	41.84 ± 66.84
Fe	7	47	641.33 ± 723.89	556.43 ± 697.96
Zn	6	x	34.67 ± 14.32	34.67 ± 14.32
Rb	24	12.86 ± 4.05	19.37 ± 4.79	14.49 ± 5.04
Mo	24	3.17 ± 0.38	6.47 ± 1.09	4 ± 1.58
Sn	7	10.33 ± 1.63	18	11.43 ± 3.26
Sb	16	10.6 ± 1.81	13	10.75 ± 1.84
Ba	6	x	90.67 ± 70.46	90.67 ± 70.46
Pb	18	4.01 ± 0.87	11.4 ± 2.75	6.06 ± 3.72

Table 5. Mean concentrations ($mg.kg^{-1}$) of elements in the flesh and seeds of apples (*Malus pumila*) sampled in November 2015.

Elements	N	Mean ± (SD)
P	18	6,409.06 ± 858.89
S	18	578.06 ± 91.47
Cl	18	323.33 ± 72.48
K	18	1,948.78 ± 492.39
Ca	18	37,732 ± 9,181.34
Ti	18	59.39 ± 25.09
Cr	5	6.4 ± 1.14
Mn	18	157.72 ± 46.39
Fe	18	1,063.67 ± 645.16
Co	18	15.22 ± 2.98
Ni	18	14.11 ± 0.9
Cu	7	11.57 ± 4.54
Zn	18	77.67 ± 21.19
Rb	18	8.02 ± 1.11
Sr	18	38.15 ± 10.52
Mo	18	5.32 ± 1.93
Ag	18	7.78 ± 0.43
Sn	18	12.33 ± 0.49
Ba	18	11.5 ± 1.25
Pb	18	8.04 ± 1.52

Table 6. Mean concentrations (mg.kg-1) of elements in the dried leaves of sycamore (*Acer pseudoplatanus*) sampled in March 2015.

mer concentrations was Ca>K>Cl>S>Zn>Sb>Rb>Mo, while autumn concentrations showed greater concentrations of K>Cl>Ca>S>Zn>Sb>Rb>Mo. Concentration of S, K, Rb, Mo and Sb in egg whites and S, Ca, Mo and Sb in egg yolks were higher in summer than in autumn. Concentrations of Cl, Ca and Sn in egg whites and Cl, K, Zn and Rb in egg yolks were higher in autumn. Total concentrations of S, K and Sb were higher egg whites than in yolks, while concentrations of Cl, Ca, Rb and Mo were higher in the yolks than in the whites. Summer concentrations of S, Cl, K and Sb were higher in the egg whites than in the yolks, while summer concentrations of Ca, Rb and Mo were higher in the egg yolks than in the egg whites. All autumn concentrations of elements, except K, were higher in the egg yolk than in the egg whites. Between summer and autumn, concentrations of Cl, Rb, Mo, Sn and Sb in the egg whites and S, Zn, and Sb in the egg yolks showed only a slight variation. The major difference was in the summer and autumn concentrations of Ca in egg whites.

The mean concentrations of fourteen elements in sampled apples are presented in Table 5. Mean concentrations of elements in apples were ranked as follows: K>Ca>S>Fe>Cl>Ba>Mn>Zn>Cr>Rb>Sn>Sb>Pb>Mo. Zn and Ba were detected only in apple seeds. Concentrations of elements in the flesh of apples measured as follows: K>Ca>Cl>S>Fe>Rb>Sb>Sn>Mn>Pb>Cr>Mo, while concentrations in seeds vary slightly: K>Ca>S>Fe>Cl>Mn>Ba>Cr>Zn>Rb>Sn>Sb>Pb>Mo. Concentrations of Cl, Sn and Sb were higher in the flesh than in the seeds of apples. Concentrations of all other elements were higher in seeds. There was a slight difference in the concentration Cl between sampled apple flesh and seeds, but a significant variance in concentration was detected in S, Ca, Cr and Mn found in flesh and seeds.

The mean concentrations of twenty elements in the dried leaves of sycamore are given in Table 6. Mean concentrations of elements were in the following order: Ca>P>K>Fe>S>Cl>Mn>Zn>Ti>Sr>Co>Ni>Sn>Cu>Ba>Pb>Rb>Ag>Cr>Mo.

Discussion

Essential elements were the most abundant in the milk of goats and cows, when compared to other food samples, and the order of concentration was the same. Goat and cow milk is very similar in composition, but goat milk is distinguished by a higher concentration of essential elements, and therefore has higher nutritional content. These findings are in accordance with the referenced literature (Raynal-Ljutovac *et al.* 2008, Park *et al.* 2007, Zamberlin *et al.* 2012, Kapadiya *et al.* 2016, Belewu and Aiyegbusi 2002, Forson *et al.* 2011). Higher concentrations of elements in the milk of stabled goats and cows could be explained by nutritional supplementation in their diet while stabled.

The most abundant elements found in chicken eggs were the essential elements, as the trace element Zn was detected only in yolk. Mo concentration was also higher in yolk samples. Forson *et al.* (2011) also detected greater trace element concentrations in yolk samples. Concentrations of Cl, and especially Ca, were higher in yolks, while concentrations of K were higher in whites. The higher concentration of Ca in egg yolks indicates that they have a higher nutritional content than egg whites. These findings are in agreement with the referenced literature (Guardia and Garrigues 2015). Element concentrations differed between seasons, which could occur as a result of seasonal differences in diet, as suggested by the referenced literature (Waegeneersa *et al.* 2009).

Acknowledgements

The research was supported by projects ITMS (Grant No. 26210120006) and ITMS (Grant No. 26110230078).

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Received 3 August 2017; accepted 25 October 2017.