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The content of minerals in milk of small ruminants

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Abstract. The aim of this study was to determine and compare the content of sodium, potassium, calcium, magnesium, zinc, copper, lead, and cadmium in sheep and goat milk of different breeds from 9 farms in the Czech Republic (herds of 18–330 goat´s heads and 30–380 sheep heads). Pool samples of milk were collected once a month (April - September) during lactation in the years 2011–2013. The content of minerals was determined using atomic absorption spectroscopy. Most of the analyses of the contents of Cd and Pb were below the limit of detection. Other determined values of these two contaminants were lower than maximal tolerable amount according to previously valid regulation No. 298/1997 Sb of the Ministry of Health of the Czech Republic given for cow's milk. The contents of each element in the whole of the reference period were in a relatively wide range. Determined levels of Ca, Mg, K, Na, Zn and Cu in goat milk related to the weight of lyophilized milk powder varied from 1.40–8.08 g kg^{-1}, 0.16–1.42 g kg^{-1}, 8.16–31.10 g kg^{-1}, 0.72–5.43 g kg^{-1}, 7.59–44.10 mg kg^{-1}, and 0.21–1.46 mg kg^{-1} respectively. Determined levels of Ca, Mg, K, Na, Zn and Cu in sheep milk varied from 1.69–9.13 g kg^{-1}, 0.21–1.36 g kg^{-1}, 3.53–11.90 g kg^{-1}, 0.65–5.05 g kg^{-1}, 13.70–34.30 mg kg^{-1}, and 0.15–2.10 mg kg^{-1} respectively. Statistically higher ($P < 0.05$) content of potassium was determined in goat milk in comparison with sheep milk. The contents of all followed minerals in milk samples from each farm collected during the lactation period were very variable, but it is not possible to find any direct relationship between the content of studied elements and the date of sampling. It was found that the year has statistically significant influence especially on the content of Ca and Mg in milk of small ruminants.

Key words: goat milk, sheep milk, Ca, Cd, Cu, K, Mg, Na, Pb, Zn.

INTRODUCTION

The milk and milk products of different ruminant species comprise a food of outstanding importance for human nutrition throughout their lives. Milk can be considered a source of macro- and micronutrients including the mineral elements, and also contains a number of active compounds that play a significant role in both nutrition and health protection (Sanz Ceballos et al., 2009). Recently in the Czech Republic the production of goat and sheep milk increases as well as all over the world. Goats and sheep are mostly bred in small scale in private farms where milk is also subsequently processed (mainly to the cheese and yoghurt). Breeding of sheep and goats is by general public associated with a friendlier attitude towards animals and nature, so that milk of small ruminant is considered as organic. With the increasingly growing network of farmers' markets is much easier to use these products also in cities. In addition, due to the better digestibility of goat milk proteins this milk plays an important role in the diet of people suffering from allergies (Høst, 2002; Viñas et al., 2014). For these all reasons, the consumption of sheep and goat milk continues to grow.

Goat and sheep milk is constantly compared to cow's milk, whose representation in the total consumption of milk is still dominant.

An evaluation of goat and sheep milk in comparison with cow milk from the point of view of macro- and microelements contents is not uniform. While Gajewska et al. (1997) consider the nutrient composition of cow and goat milk being comparable, according to broad monograph devoted to sheep and goats (Park et al., 2007), sheep and goat milk has around 0.9%, respectively 0.8% total minerals (ash) compared to 0.7% in cow milk. Overall, goat and sheep milk have more Ca, P and Cl, and less Na and S than cow milk. Higher amount of these all elements was found in sheep milk than in goat milk (Park et al., 2007).The content of K in goat milk is higher than in cow milk, on the contrary the content of K in sheep milk is lower than in cow milk. The content of Fe, Cu, and Zn is comparable in all three kind of milk.

Relatively high content of macro- and microelement in sheep milk in comparison with cow milk was found by Hampel et al. (2004) that gave the following values: Ca 2.07 g kg^{-1}, Mg 0.24 g kg^{-1}, K 1.64 g kg^{-1}, P 1.50 g kg^{-1}, Fe 0.51 mg kg^{-1}, Cu 0.09 mg kg^{-1}, Zn 5.10 mg kg^{-1}. In goat milk were determined higher amounts of all elements except Fe and Cu than in sheep milk, which reported Kondyli et al. (2007). These authors reported mean mineral content of raw goat milk of the indigenous Greek breed the widespread breed in Greece, the first among European countries in goat population, 1.30 g kg^{-1} for Ca, 0.16 g kg^{-1} for Mg, 1.50 g kg^{-1} for K, 0.59 g kg^{-1} for Na, 0.98 g kg^{-1} for P, 0.60 mg $kg^{-1}$for Fe, 3.70 mg kg^{-1} for Zn and 0.80 mg $kg^{-1}$for Cu.

The composition of the milk produced by small ruminants depends on the breed, feeding, lactation state, individual animal, status of udder health and other environmental conditions (Antunovic et al., 2001; Aganga et al., 2002; Morand-Fehr et al., 2007; Park et al., 2007; Sanz Ceballos et al., 2009; Zervas & Tsiplakou, 2011).

There are not many studies focused at the investigation of mineral content in sheep and goat milk not only in the Czech Republic, especially in real life. These studies also do not mostly distinguish between different breeds.

The aim of this study was to determine and compare the content of sodium, potassium, calcium, magnesium, zinc, copper, lead, and cadmium in sheep and goat milk of different breed from 9 private farms in the Czech Republic.

MATERIALS AND METHODS

Experimental material

Goat and sheep pooled milk samples were obtained from 9 different farms (F1-F9) of central, south and east Bohemia. The basis of feed on all the farms was the pasture ad libitum, replenished mainly by hay and silage. Mineral licks were also added. Water was available at all times.

Individual farm characteristic. Farm F1: family farm, herd of 100 heads, breed White short haired goat. Feeding: full-day pasture, hay, silage, pressed barley, mineral licks BIOSAXON. **Farm F2:** small family farm, herd of 50 heads, breed Brown short haired goat. Feeding: full-day pasture, hay, silage, pressed barley, branches of pine, oak, beech, birch, pine branches dominance, mineral licks ALMAGEROL and salt licks. **Farm F3:** small family farm, herd of 40 heads, breed Anglo-Nubian goat. Feeding: full-day pasture, hay, silage, pressed barley, oats. Mineral licks MILLAPHOS Z-V. **Farm F4:** small family farm, herd of 65 heads, breed Lacaune sheep. Feeding: full-day pasture, hay, silage, pressed grains, molasses. Mineral licks SANO. **Farm F5:** big commercially farm, herd of 380 heads of East Friesian sheep, 330 heads of White short haired goat, and 120 heads of Brown short haired goat. Feeding: full-day pasture, hay, silage, pressed grains, corn. Mineral licks: RUMIHERB, NATURMIX. **Farm F6:** big family farm, herd of 130 heads, breed Romanov sheep. Feeding: full-day pasture, hay, alfalfa silage, scrap lupine, pressed grains. Mineral licks: MILLAPHOS and BIOSAXON. **Farm F7:** small family farm, herd of 18 head breed Brown short haired goat. Feeding: full-day pasture, hay, silage, and oat. Mineral licks Schauman – LECKSTEN. **Farm F8:** family farm, herd of 85 heads, breed Lacaune sheep. Feeding: full-day pasture, hay, silage, pressed barley, corn and wheat. Mineral licks SANO. **Farm F9:** small family farm, herd of 30 heads, breed East Friesian sheep. Feeding: full-day pasture, hay, silage, pressed barley, mineral licks RUMIHERB, NATUMIX.

Sampling and chemical analysis

Sampling. Pool samples of goat and sheep milk were collected repeatedly once a month (April – September) during lactation in the years 2011–2013. Unfortunately, a complete set of samples from all of the farms failed to provide (numbers of analyzed samples are presented in Table 1–6. Statistical analysis was performed for the corresponding set of samples). Samples were collected to the clean, plastic sampling flasks of 100 ml volume, cooled on 4–6 °C, transferred in thermo boxes to the lab and without added preservatives stored at -20 °C in the freezer until analysis. For the determination of Ca, Cd, Cu, K, Mg, Na, Pb, and Zn in goat and sheep milk, aliquots of frozen milk samples (50 ml) were lyophilized using a LYOVAC GT 2 (LEYBOLD-HERAEUS, GmbH, Germany) and then approx. 0.8 g of lyophilized milk was mineralized by dry ashing (Mader et al., 1997; Mader et al., 1998). Analyses were carried out in triplicate.

Analysis. Concentrations of K, Na, Ca, Mg, and Zn in the digests were determined by flame atomic absorption spectrometry (FAAS) using a Varian SpectrAA 110 instrument (Varian, Inc., Mulgrave, Victoria, Agilent Technologies Inc., Palo Alto, CA, USA) in an acetylene-air flame at wavelengths 766.5 nm (K), 589.0 nm (Na), 422.7 nm (Ca), 285.2 nm (Mg) and 213.9 nm (Zn), respectively. The widths of spectral intervals were 1 nm (K, Na and Zn) and 0.5 nm (Ca and Mg) respectively. During the measurement of Zn and Mg the background was corrected by a deuterium lamp. In the determination of Ca and Mg, 1% solution of lanthanum nitrate was added as a releasing agent. SIPS (Sample Introduction Pump System) was used for the creation of calibration dependence.

Concentrations of Cd, Cu and Pb in the digests were measured by electrothermal atomic absorption spectrometry (ETAAS) using a Varian AA 280Z (Varian, Belrose, Australia) with graphite tube atomizer GTA 120 and PSD 120 programmable sample dispenser. Wavelengths for individual metals were 228.8 nm (Cd), 324.8 nm (Cu) and 283.3 nm (Pb), respectively. Detailed temperature programs for the determination of Cd, Cu and Pb in milk are described in the Technical Report (Mader et al., 2000).

Standard solutions ASTASOL (Analytika, CR) of Ca, Cd, Cu, K, Mg, Na, Pb and Zn were used in the preparation of a calibration curves for the measurements. Concentration of the standards is 1 g l^{-1}. The background of laboratory and used chemicals was monitored by analysis of 14.2% blanks prepared under the same conditions, but without samples, and experimental data were corrected by mean concentration of the elements in blanks, and compared with detection limit (mean ± 3SD of blanks) which were 0.348 mg l^{-1} for Ca, 0.007 mg l^{-1} for Mg, 0.023 mg l^{-1} for Zn, 0.007 mg l^{-1} for K, 0.039 mg l^{-1} for Na, 0.07 μg l^{-1} for Cd, 0.70 μg l^{-1} for Cu, and 0.21 μg l^{-1} for Pb. The quality of analytical data was assessed by simultaneous analysis of certified reference material CRM 063R (Skim milk powder) (3.3% of all the samples). Analytical data obtained for all determined elements were found to be within the confidence interval given by the producer of the CRM for each element.

Statistical evaluation. Experimentally obtained data were statistically evaluated by ANOVA method of one and two factor analysis of variance separately for each element; the SAS computer program, version 9.1 (StatSoft, 2011) at the level of significance $P < 0.05$ was used.

RESULTS AND DISCUSSION

Monitoring of risk elements Cd and Pb in sheep and goat milk

The contents of the risk elements of Cd and Pb in the sheep and goat milk were established only in the years 2011–2012. 75.8% of the analyses on the contents of the Cd and 66.7% of the analyses on the contents of the Pb were below the limit of detection (0.177 and 0.520 μg kg^{-1}, respectively). Other determined values of these two contaminants were lower than maximal tolerable amount (MTA) according to regulation No. 298/1997 Coll. of the Ministry of Health of the Czech Republic given for cow milk (Cd – 10 μg kg^{-1}, Pb – 20 μg kg^{-1}), which is stringent than the later regulation No. 305/2004 Sb. and sets down the hygienic limit not only for Cd but also for Pb in milk. The highest content of Cd (3.13 μg kg^{-1} d.w.) was determined in sheep milk (Lacaune breed) and the highest content of Pb (7.3 μg kg^{-1} d.w.) was determined in goat milk (White short haired breed). For these reasons, the analysis of these risk elements was not carried out in the following year 2013. The fact that all levels of contaminating chemical elements measured are below the hygienic limits (regulation No. 298/1997 Sb.)) is very positive. Hejtmánková et al. (2002) reported the maximum determined content in raw goat milk 1 μg kg^{-1} for Cd, and 26.5 μg kg^{-1} for Pb. Higher content of Cd and Pb also determined Coni et al. (1996) and Rodriguez et al. (1999). In agreement with recent still lower content of Cd in milk mentioned Elmastas et al. (2005) in goat milk the value 0.085 μg l^{-1}.

Monitoring of nutritional elements K, Ca, Na, Mg, Zn, and Cu in sheep and goat milk

Average values and the range of the determined contents (2011–2013) of selected macro– and microelements for individual farms are summarized in Table 1–6. The values are related to lyophilized milk powder. The content of macro-elements potassium and sodium in milk was determined only in years 2012 and 2013. The contents of each element in the whole of the reference period (2011–2013) moved in a relatively wide range. Multiple differences in content of some elements in milk are given also by Aganga et al. (2002) and Mayer & Fiechter (2012).

Determined levels of Ca in goat and sheep lyophilized milk powder varied from 1.40 to 8.08 g kg^{-1} and from 1.69 to 9.13 g kg^{-1}, respectively. The average content of Ca in goat lyophilized milk powder was 4.99 ± 2.49 g kg^{-1}, respectively 5.27 ± 2.25 g kg^{-1} in sheep lyophilized milk powder.

Determined contents of Ca in the milk of small ruminants occur on the lower border of the listed values are extremely low. Low is also average content of Ca as in goat milk, so in sheep milk. Only Khan et al. (2006) shows such low levels of Ca in the milk. These authors indicate 551 ± 12.9 mg l^{-1} in sheep milk in the winter period. Only the maximum values of the Ca content in goat and sheep milk are approaching the values of Ca content in small ruminant milk reported by some authors. Trancoso et al. (2010) reported 10.9 ± 0.8 g kg^{-1} d.w in goat milk, Khan et al. (2006) determined 701 ± 4.1 mg l^{-1} in goat milk in winter period, respectively 961 ± 16.9 mg l^{-1} in summer period, and 900 ± 12.5 mg l^{-1} in sheep milk in summer period. The highest contents of Ca in sheep milk 2.42 g l^{-1} mentioned Mayer & Fiechter (2012), 207 ± 18 mg 100 g^{-1} determined Hampel et al. (2004) and Aganga et al. (2002), 1.397 g 100 g^{-1}. The highest content of Ca in goat milk is also given by Aganga et al. (2002), that is 1.097 mg 100 g^{-1}. Most of the authors are given the content of Ca in milk of small ruminants in range 1–2 g kg^{-1} (Hejtmánková et al., 2002; Kondyli et al., 2007; Sanz-Ceballos et al., 2009; Kedzierska-Matysek et al., 2013.). In accordance with Park et al. (2007), Mayer & Fiechter (2012) and Aganga et al. (2002) the slightly higher content of Ca was found in sheep milk than in goat milk.

Table 1. Calcium content (g kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2011	12	100	3.10–4.90	3.98	3.95	0.66
F1	White short haired goat	2012	18	100	4.31–7.85	6.69	7.65	1.45
F2	Brown short haired goat	2011	18	50	2.50–4.60	3.58	3.60	0.81
F2	Brown short haired goat	2012	18	50	5.83–7.53	6.83	7.02	0.58
F3	Anglo-Nubian goat	2011	18	40	3.90–5.40	4.65	4.75	0.55
F3	Anglo-Nubian goat	2012	18	40	7.15–8.08	7.65	7.68	0.38
F4	Lacaune sheep	2012	18	65	5.72–9.13	7.57	7.89	1.17
F5	East Friesian sheep	2012	18	380	5.82–8.53	7.39	7.46	0.84
F5	Brown short haired goat	2013	15	120	1.79–5.17	3.02	2.71	1.16
F5	White short haired goat	2013	15	330	1.40–2.69	2.29	2.38	0.46
F6	Romanov sheep	2011	18	130	3.30–5.10	4.35	4.70	0.72
F6	Romanov sheep	2012	18	130	4.79–8.66	6.17	5.90	1.21
F7	Brown short haired goat	2013	15	18	1.62–2.66	2.22	2.26	0.33
F8	Lacaune sheep	2013	15	85	1.79–3.40	2.27	2.03	0.62
F9	East Friesian sheep	2013	15	30	2.52–3.32	2.98	3.05	0.32
Average**/ total* of all goats			147*	848*		4.55**	4.67**	0.71**
Average**/ total* of all sheep			102*	820*		5.12**	5.17**	0.81**

n – number of samples;
N – number of heads of herd on farm.

Determined levels of Mg in goat lyophilized milk powder were in range 0.16–1.42 g kg^{-1}, respectively 0.21–1.36 g kg^{-1} in sheep lyophilized milk powder. The average content of Mg in goat lyophilized milk powder was 0.94 ± 0.36 g kg^{-1}, respectively 0.91 ± 0.31 g kg^{-1} in sheep lyophilized milk powder.

Average content of Mg in goat milk determined in this study is consistent with the values reported by Trancoso et al. (2010), and Khan et al. (2006), lower than the content given by Aganga et al. (2002), Park et al. (2007), Kondyli et al. (2007), Mayer & Fiechter (2012) and Kedzierska-Matysek et al. (2013) On the contrary, lower content of magnesium (752–757 mg kg^{-1} d.w.) in goat milk mentioned Coni et al. (1996). Average content of Mg in sheep milk determined in this study is consistent with the values reported by Khan et al. (2006), lower than the content given by Aganga et al. (2002), Hampel et al. (2004), Park et al. (2007), Mayer & Fiechter (2012). On the other hand, lower content of magnesium (588–653 mg kg^{-1} d.w.) in sheep milk mentioned repeatedly Coni et al. (1996).

Table 2. Magnesium content (g kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2011	12	100	0.16–0.48	0.32	0.31	0.12
F1	White short haired goat	2012	18	100	0.70–1.11	0.89	0.87	0.14
F2	Brown short haired goat	2011	18	50	0.42–0.76	0.55	0.52	0.13
F2	Brown short haired goat	2012	18	50	0.95–1.20	1.08	1.11	0.10
F3	Anglo-Nubian goat	2011	18	40	0.35–0.64	0.54	0.56	0.10
F3	Anglo-Nubian goat	2012	18	40	1.10–1.39	1.24	1.24	0.10
F4	Lacaune sheep	2012	18	65	0.72–1.08	0.92	0.93	0.12
F5	East Friesian sheep	2012	18	380	0.92–1.33	1.15	1.15	0.12
F5	Brown short haired goat	2013	15	120	1.16–1.42	1.32	1.39	0.10
F5	White short haired goat	2013	15	330	1.21–1.41	1.31	1.32	0.07
F6	Romanov sheep	2011	18	130	0.21–0.49	0.36	0.35	0.09
F6	Romanov sheep	2012	18	130	0.71–1.13	0.89	0.89	0.14
F7	Brown short haired goat	2013	15	18	1.01–1.27	1.15	1.18	0.10
F8	Lacaune sheep	2013	15	85	0.83–1.21	1.02	1.07	0.14
F9	East Friesian sheep	2013	15	30	1.11–1.36	1.19	1.15	0.10
Average**/ total* of all goats			147*	848*		0.93**	0.94**	0.11**
Average**/ total* of all sheep			102*	820*		0.92**	0.92**	0.12**

n – number of samples;
N – number of heads of herd on farm.

Determined levels of K. in goat lyophilized milk powder ranged from 8.16 to 31.10 g kg^{-1}, the average content was 18.15 ± 5.03 g kg^{-1}. In sheep lyophilized milk powder were recorded levels of K 3.53–11.90 g kg^{-1}. The mean level was 7.48 ± 2.59 g kg^{-1}. Average content of K in goat milk determined in this study is consistent with the values reported by Kondyli et al. (2007), Park et al. (2007), and Kedzierska-Matysek et al. (2013). Higher value of K content 4.87 g kg^{-1} in raw goat milk determined Aganga et al. (2002). On the contrary, lower average content of potassium in goat milk 12.20 ± 2.00 g kg^{-1} d.w. determined Trancoso et al. (2010), and Khan et al. (2006). The average content of K in sheep milk determined in this study is lower than value reported by Aganga et al. (2002), Hampel et al. (2004), Park et al. (2007) and Mayer & Fiechter (2012). On the contrary, Khan et al. (2006) reported lower content of K (1.079–1.166 mg l^{-1}) in sheep milk than it is given in this study. In this study statistically higher ($P < 0.05$) content of potassium was determined in goat milk in comparison with sheep milk. Higher content of potassium in goat milk than in sheep milk also reported Aganga et al. (2002), Park et al. (2007) and Mayer & Fiechter (2012). By contrast, Khan et al. (2006) determined higher content of potassium in sheep milk than in goat milk (1.122 mg l^{-1} vs 480 mg l^{-1}).

Table 3. Potassium content (g kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2012	18	100	13.21–17.75	15.44	16.31	1.91
F2	Brown short haired goat	2012	18	50	8.16–15.32	13.50	14.57	2.50
F3	Anglo-Nubian goat	2012	18	40	12.32–17.20	14.04	12.72	2.04
F4	Lacaune sheep	2012	18	65	4.17–8.00	6.16	6.10	1.46
F5	East Friesian sheep	2012	18	380	5.11–9.73	6.84	6.74	1.54
F5	Brown short haired goat	2013	15	120	19.23–22.39	21.32	21.55	1.15
F5	White short haired goat	2013	15	330	19.27–31.11	24.20	22.48	4.18
F6	Romanov sheep	2012	18	130	3.53–6.26	4.77	4.50	0.90
F7	Brown short haired goat	2013	15	18	20.42–25.86	22.72	23.23	1.98
F8	Lacaune sheep	2013	15	85	7.87–11.90	9.72	9.35	1.35
F9	East Friesian sheep	2013	15	30	10.33–11.65	10.87	10.83	0.44
Average**/ total* of all goats			99*	658*		18.54 **	18.48**	2.21**
Average**/ total* of all sheep			84*	690*		7.67*	6.25**	0.12**

n – number of samples;
N – number of heads of herd on farm.

Determined levels of Na in goat and sheep lyophilized milk powder varied from 0.72 to 5.43 g kg^{-1} and from 0.605 to 5.05 g $kg^{-1,}$ respectively. The average content of Na in goat and sheep lyophilized milk powder was 2.33 ± 1.51 g kg^{-1} and 1.78 ± 0.13 g kg^{-1}, respectively. Average content of Na in goat milk determined in this study is similar to the values (2.83 ± 0.4 g kg^{-1} d.w.) reported by Trancoso et al. (2010) and 0.27 g kg^{-1} reported by Aganga et al. (2002) and other authors (Mayer & Fiechter, 2012; Kedzierska-Matysek et al., 2013). Slightly higher content of Na mentioned Khan et al. (2006), Park et al. (2007), and especially Kondyli at al. (2007). Average content of Na in sheep milk determined in this study is lower than other values given in the literature (Khan et al., 2006; Park et al., 2007; Aganga et al., 2002; Hampel et al., 2004; Mayer & Fiechter, 2012). In summary, it can be said that the content of Na in small ruminant milk was relatively low in this study, but it was moving in a larger range from 0.07–0.17 in goat milk, respectively 0.13–0.33 in sheep milk. Even though the ratio in sheep milk is higher than in goat milk, average Na/K value in sheep milk 0.23 (0.12 in goat milk) is consistent with the ratio (0.23) reported by Trancoso et al. (2010) and lower than reported by Kondyli et al. (2007), Park et al. (2007) and Raynal-Ljutovac et al. (2008). This low Na/K ratio might be of interest from the human nutrition point of view, especially for people suffering from high blood pressure or under dialysis (Trancoso et al., 2010).

Table 4. Sodium content (g kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2012	18	100	0.74–1.27	1.02	0.99	0.18
F2	Brown short haired goat	2012	18	50	0.72–1.04	0.95	0.99	0.11
F3	Anglo-Nubian goat	2012	18	40	0.83–1.49	1.08	1.02	0.22
F4	Lacaune sheep	2012	18	65	0.89–1.28	1.04	1.02	0.14
F5	East Friesian sheep	2012	18	380	0.71–1.03	0.88	0.92	0.12
F5	Brown short haired goat	2013	15	120	3.05–4.54	3.81	3.78	0.48
F5	White short haired goat	2013	15	330	3.46–5.43	4.00	3.71	0.73
F6	Romanov sheep	2012	18	130	0.65–0.93	0.82	0.84	0.10
F7	Brown short haired goat	2013	15	18	3.48–4.25	3.88	4.05	0.32
F8	Lacaune sheep	2013	15	85	1.64–4.31	3.11	3.17	0.86
F9	East Friesian sheep	2013	15	30	2.81–5.05	3.56	3.15	0.83
Average**/ total* of all goats			99*	658*		2.46**	2.42**	0.34**
Average**/ total* of all sheep			84*	690*		1.88**	1.82**	0.41**

n – number of samples;
N – number of heads of herd on farm.

Determined levels of Zn in goat lyophilized milk powder were in range 7.59–44.1 mg kg^{-1}, respectively 13.7–34.3 mg kg^{-1} in sheep lyophilized milk powder. The average content of Zn in goat lyophilized milk powder was 26.5 ± 7.24 mg kg^{-1}, respectively 24.2 ± 4.94 mg kg^{-1} in sheep lyophilized milk powder. Average content of Zn in goat milk determined in this study is nearly identical to the value (26.00 ± 4.90 g kg^{-1} d.w.) reported Trancoso et al. (2010) in the Saanen goat milk, and the value 27.00 mg kg^{-1} d.w. is given by Haenlein & Anke (2011). Slightly higher value of Zn content reported also Kedzierska-Matysek et al. (2013). The contents of Zn in goat milk above 5.0 g kg^{-1} reported Hejtmánková et al. (2002), Elmastas et al., (2005) and Park et al. (2007). Contrarily lower values (16.80–19.30 mg kg^{-1} d.w.) were reported by Coni et al. (1996). The Zn content in sheep milk described in the literature is different. Average content of Zn in sheep milk determined in this study is nearly identical to the interval of Zn content (21.20–2.60 mg kg^{-1} d.w.) reported by Coni et al. (1996). The contents of Zn in sheep milk above 5.0 g kg^{-1} reported Aganga et al. (2002), Hampel et al. (2004) and Park et al. (2007). The highest content of Zn in sheep milk (10.40 ± 0.01 mg l^{-1}) mentioned Elmastas et al. (2005). On the contrary, only 0.56 ± 0.06 mg l^{-1} in sheep milk determined Khan et al. (2006) in summer period in semiarid region of Pakistan, respectively 1.29 ± 0.05 mg l^{-1} in winter period.

Determined levels of Cu in goat lyophilized milk powder ranged from 0.21 to 1.46 mg kg^{-1}, the average content was 0.57 ± 0.31 mg kg^{-1}. In sheep lyophilized milk powder were recorded levels of Cu 0.15–2.10 mg kg^{-1}. The mean level was 0.60 ± 0.47 mg kg^{-1} Average content of Cu in goat milk determined in this study corresponds to the value 0.04–0.08 mg kg^{-1} in raw White short haired goat milk determined in two herds in the Czech Republic (Hejtmánková et al., 2002). It is also similar to the content of Cu in goat milk reported by Coni et al. (1996), Elmastas et al. (2005), Trancoso et al. (2010), Haenlein & Anke (2011), Kedzierska-Matysek et al. (2013). Higher contents of Cu in milk are given by Sanz Ceballos (2009), Khan et al. (2006), Kondyli et al. (2007), Park et al. (2007), and Aganga et al. (2002). The contents of Cu in raw goat milk are 0.40 mg kg^{-1}, 0.30 mg kg^{-1}, 0.40–1.10 g.l^{-1}, 0.5 mg kg^{-1} and

1.007–2.007 mg kg^{-1} respectively. Average content of Cu in sheep milk determined in this study is similar to the range of Cu content (0.453–0.784 mg kg^{-1} d.w.) reported by Coni et al. (1996) in sheep milk. Slightly higher value of Cu in sheep milk reported Hampel et al. (2004) and Elmastas et al. (2005). Park et al. (2007) in raw milk mentioned the value 0.40 mg kg^{-1} and Aganga et al. (2002) even the value 2.007 mg kg^{-1}.

Table 5. Zinc content (mg kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2011	12	100	17.70–29.70	21.70	19.60	4.73
F1	White short haired goat	2012	18	100	14.92–27.62	22.52	23.74	5.05
F2	Brown short haired goat	2011	18	50	24.60–44.10	29.20	26.65	6.79
F2	Brown short haired goat	2012	18	50	28.19–39.31	32.67	32.27	3.85
F3	Anglo-Nubian goat	2011	18	40	25.00–38.40	32.28	32.20	4.58
F3	Anglo-Nubian goat	2012	18	40	27.41–38.90	31.54	30.82	3.76
F4	Lacaune sheep	2012	18	65	17.71–34.27	25.86	27.29	5.80
F5	East Friesian sheep	2012	18	380	24.26–31.51	27.15	26.55	2.48
F5	Brown short haired goat	2013	15	120	18.37–30.93	23.39	21.77	4.34
F5	White short haired goat	2013	15	330	7.59–27.67	18.27	21.77	7.22
F6	Romanov sheep	2011	18	130	20.70–30.75	26.41	27.00	3.33
F6	Romanov sheep	2012	18	130	13.69–26.08	19.85	19.05	4.58
F7	Brown short haired goat	2013	15	18	15.54–30.00	23.07	23.03	4.63
F8	Lacaune sheep	2013	15	85	16.57–24.33	20.33	19.99	2.48
F9	East Friesian sheep	2013	15	30	20.18–29.44	25.25	26.36	3.22
Average**/ total* of all goats			147*	848*		26.07**	25.76**	4.99**
Average**/ total* of all sheep			102*	820*		24.14**	24.37**	3.65**

n – number of samples;
N – number of heads of herd on farm.

According to former regulation No. 298/1997 Coll. of the Ministry of Health of the Czech Republic valid for cow milk the maximal tolerable amount for Cu was 0.40 mg kg^{-1} respectively 10.0 mg kg^{-1} for Zn. From this point of view, the relatively low contents of Cu in both goat and sheep milk determined in this study seems to be positive and also the content of Zn in milk meets the former strict rules.

To determine the influence of breed on the mineral contents in milk of small ruminants, the milk of White short haired goat and Brown short haired goat coming from the same farm (F5) in the year 2013 was used (Table 1–6). No statistical difference ($P < 0.05$) between the two goat breeds was found.

To monitor the effect of a specific character of individual farms, goat milk of the same breed from different farms was used, specifically Brown short haired goat (farms F7, F5) (Table 1–6). No statistical difference ($P < 0.05$) between these two farms was found. Slightly higher content of monitored minerals were found in Brown short haired goat milk bred in farm F7.

To determine the influence of the year the milk samples from three goat breeds, namely White short haired goat (farm F1), Brown short haired goat (farm F2), and Anglo-Nubian goat (farm F3) and one sheep breed, namely Romanov sheep (farm F6), were collected in the years 2011–2012. It was found that the year has statistically significant (P < 0.05) influence on the content of Ca and Mg in milk of small ruminants. The contents of these elements were higher both in goat and sheep milk in the year 2012.

Table 6. Cooper content (mg kg^{-1}) in milk of small ruminants

Farm	Breed	Year	n	N	Range	Average	Median	St.dev.
F1	White short haired goat	2011	12	100	17.70–29.70	0.39	0.39	0.08
F1	White short haired goat	2012	18	100	14.92–27.62	0.34	0.35	0.05
F2	Brown short haired goat	2011	18	50	24.60–44.10	0.27	0.27	0.04
F2	Brown short haired goat	2012	18	50	28.19–39.31	0.43	0.51	0.14
F3	Anglo-Nubian goat	2011	18	40	25.00–38.40	0.58	0.44	0.30
F3	Anglo-Nubian goat	2012	18	40	27.41–38.90	0.43	0.45	0.03
F4	Lacaune sheep	2012	18	65	17.71–34.27	0.25	0.25	0.06
F5	East Friesian sheep	2012	18	380	24.26–31.51	0.53	0.35	0.31
F5	Brown short haired goat	2013	15	120	18.37–30.93	0.87	0.99	0.23
F5	White short haired goat	2013	15	330	7.59–27.67	1.07	1.01	0.20
F6	Romanov sheep	2011	18	130	20.70–30.75	0.31	0.32	0.09
F6	Romanov sheep	2012	18	130	13.69–26.08	0.41	0.27	0.30
F7	Brown short haired goat	2013	15	18	15.54–30.00	0.89	0.88	0.07
F8	Lacaune sheep	2013	15	85	16.57–24.33	1.10	0.90	0.50
F9	East Friesian sheep	2013	15	30	20.18–29.44	1.15	1.11	0.29
Average**/ total* of all goats			147*	848*		0.53**	0.59**	0.13**
Average**/ total* of all sheep			102*	820*		0.63**	0.53**	0.26**

n – number of samples;
N – number of heads of herd on farm.

Changes during lactation period

The influence of the lactation period on content of minerals in sheep and goat milk was also monitored. The samples of milk were taken once a month during lactation (April – September) from all farms. The contents of all followed minerals in milk samples from each farm collected during the lactation period were very variable. Variability ranged from 4.05% (K, F9, East Friesian sheep, 2013) to 73.2% (Cu, F6, Romanov sheep, 2012.). The highest average variability of the content of all measured minerals during the lactation period was observed in the year 2013 (22.5%). The average variability observed in the years 2011 and 2012 was very similar 17.4% respectively 18.4%. Slightly higher variability was observed in the sheep milk than in goat milk (20.8% vs 17.4%). As regards the evaluation of the whole study period it could be said that the contents of measured minerals mostly varied significantly ($P < 0.5$) during lactation period.

According Aganga et al. (2002), Hejtmánková et al. (2002), and Kondyli et al. (2007) Ca and Cu showed significantly higher content at the beginning of the lactation period. In this study, the higher content of Ca at the beginning of the lactation period was not confirmed unlike the Cu content, which was mostly the highest at the beginning of the lactation period, especially in the sheep milk. With some deviation the increasing content of Mg in milk of small ruminants according to previous study (Hejtmánková et al., 2002) was observed. Generally, in accordance with Hejtmánková et al. (2002) it is not possible to find any direct relationship between the content of studied elements and the date of sampling.

CONCLUSION

The contents of risk elements Cd and Pb in milk from all tested farms were very low and met the requirements for hygienic limits according to Regulation No. 298/1997. The levels of Ca, Cu, K, Na, Mg, and Zn in both goat and sheep milk were variable not only during the lactation period, but also during the entire study. The contents of determined elements in this study were average or rather below average in the comparison with the contents of these elements in milk of small ruminants reported in literature. The highest average variability of the content of all measured minerals during the lactation period was observed in the year 2013 (22.5%). An important factor of variability apart different lactation stage proved to be a year, which may be related to the quality of feed and pasture, which is associated with fluctuations in vegetation and climate conditions. The year had significant influence on the content of Ca and Mg in milk of small ruminants, but it is not possible to find any direct relationship between the content of studied elements and the date of sampling. Generally, due to the great variability of elements in milk of small ruminants the differences in the mineral composition between goat and sheep milk were not demonstrated, with the exception of the potassium content.

Significantly higher content of potassium was determined in goat milk than in sheep milk. It is not possible to decide whether statistically different contents of Ca, Cu, Na, Mg and Zn in the milk of small ruminants detected in the same year are the result of a different breed or reflect the specificity of the individual farms.

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