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Concentrations of toxic heavy metals and trace elements in raw milk of Simmental and Holstein-Friesian cows from organic farm

Renata Pilarczyk · Jerzy Wójcik · Paweł Czerniak · Piotr Sablik · Bogumiła Pilarczyk · Agnieszka Tomza-Marciniak

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Abstract Concentrations of toxic heavy metals (cadmium (Cd), lead (Pb)) and major nutritional and trace elements (Ca, Mg, P, Cu, Fe, Mn, Se, Zn) were analyzed in the milk of Simmental ($n=20$) and Holstein-Friesian ($n=20$) cows from an organic farm. Elements were determined using inductively coupled plasma emission atomic spectrometry. The conducted research showed that the milk of Simmental cows was characterized by the more advantageous mineral composition and lower concentration of noxious heavy metals compared to the milk of Holstein-Friesian cows. In the milk of Simmental cows, significantly lower concentrations of Pb and Cd ($P<0.001$) and Cu ($P<0.05$) and significantly higher concentrations of Fe and Mg ($P<0.05$) as well as nonsignificantly higher concentrations of Ca, Mn, and Se were found. In the milk of both breeds, very low Cu concentrations were recorded. The higher-than-recommended concentration of Pb in milk was also found. In the milk of both breeds, the significant positive correlations between concentrations of the following elements were observed: Pb–Cd, Pb–Se, Cd–Se, Cd–Mn, Zn–Cu, Zn–P, Ca–P, Ca–Mg, and Mg–P. The correlations between other elements within each of the analyzed breeds separately were also found.

Keywords Cow's milk · Breeds · Heavy metals · Trace elements · Correlations

R. Pilarczyk (✉) · J. Wójcik · P. Czerniak · P. Sablik
Department of Ruminant Science, West Pomeranian University of Technology in Szczecin,
Judyma 10 Street,
71-460 Szczecin, Poland
e-mail: renata.pilarczyk@zut.edu.pl

B. Pilarczyk · A. Tomza-Marciniak
Department of Animal Reproduction Biotechnology and Environmental Hygiene, West Pomeranian University of Technology in Szczecin,
Judyma 6 Street,
71-460 Szczecin, Poland

Introduction

Milk as an excretion of the mammary gland can carry numerous xenobiotic substances, which constitute a technological risk factor for dairy products and, above all, for the health of the consumer. Determination of the residual concentrations of metals in milk could be an important "direct indicator" of the hygienic status of the milk, as well as an "indirect indicator" of the degree of pollution of the environment in which the milk was produced (Licata et al. 2004; González-Montaña et al. 2012).

In the last few years, the contamination of milk is considered as one of the main dangerous aspects. Trace metals are a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm. This term is widely recognized and usually applied to the elements such as cadmium (Cd), Cu, Fe, lead (Pb), and Zn which are commonly associated with pollution and toxicity problems (Malhat et al. 2012). One of the main problems with metals is their ability to bio-accumulate. Metal residues in milk are of particular concern because milk is largely consumed by infants and children (Tripathi et al. 1999).

The food chain is an important source of Cd and Pb accumulation, especially for plants grown on polluted soils. Significant amounts of Cd and Pb can be transferred from contaminated soil to plants and grass, causing accumulation of these potentially toxic metals in grazing ruminants, particularly in cattle (López Alonso et al. 2003; Miranda et al. 2005). Accumulation of Cd and Pb in ruminants causes toxic effects in cattle, but also in humans consuming meat and milk contaminated with toxic metals (González-Weller et al. 2006; Vromman et al. 2008; Cai et al. 2009).

Cd and Pb are amongst the elements that have caused the most concern in terms of adverse effects on human health. This is because they are readily transferred through food chains and are not known to serve any essential biological function. Lead is a pervasive and widely distributed environmental pollutant with no beneficial biological roles. The poisoning is more common in farm ruminants, which are considered most susceptible to the toxic effects of lead (Swarup et al. 2005). For that reason, the concentration of Cd and Pb in cow's milk should be monitored to ensure the consumers' health (Jen et al. 1994).

In most studies, the concentrations of toxic heavy metals and trace elements were determined in the milk obtained most frequently from Holstein-Friesian cows. It seems justified to compare the concentration and the relationships between the levels of individual elements in the milk of Simmental and Holstein-Friesian cows, kept in the same environment and fed identically, which allows finding breed differences in the concentration of elements and assimilability of heavy metals. Therefore, the aim of this study was the comparison of the concentrations of toxic heavy metals and trace elements in the milk of Simmental and Holstein-Friesian cows kept on an organic farm.

Material and methods

The research material comprised milk obtained from 20 Simmental dairy cows and 20 Holstein-Friesian cows kept on an organic farm with a total area of 4,000 ha of arable land including 3,000 ha of grassland, located in the northwestern part of the Lubuskie Province in Poland (Fig. 1). Approximately 1,000 ha is located in the "Mouth of Warta" National Park. The remaining area is a part of Natura 2000 land. Grasslands are situated in the basin of Odra and Warta Rivers. This farm, i.e., specializing in milk production, as the only one in this area maintained the Holstein-Friesian and Simmental cows under the same conditions, grazing them in the park area and its buffer zone.

The animals were kept in a loose barn with a free access to the stockyard located along the long walls of the building. Winter feeding of cows was based on the preserved feeds obtained from the farm (maize silage, wilted silage, ensilaged sugar beet pulp, hay, and concentrates), whereas during the summer feeding, cows additionally used the pasture.

Milk samples from a total of 40 cows (20 samples from each breed) at the amount of 50 mL from one cow were taken in September 2008. Each group, within the evaluated breed, consisted of cows of the similar milk yield (3,800–4,000 kg), similar age (3–7 years old), and similar lactation stage (100–150 day post-calving).

Elements (Cd, Pb, Ca, Mg, P, Cu, Fe, Mn, Se, Zn) were determined using inductively coupled plasma emission atomic spectrometry by means of an Optima 2000 DV instrument (PerkinElmer Inc.), after mineralization in a microwave system using the Anton Paar microwave oven. Measurements were made along the plasma in an axial direction. The analyzed elements were quantified using calibration curves plotted from analytical standards (Merck, Darmstadt, Germany). The limit of detection was as follows: Cd 0.1 μg/L; Pb, 1.0 μg/L; Ca, 0.05 μg/L; P, 4 μg/L; Mg, 0.04 μg/L; Cu, 0.4 μg/L; Fe, 0.1 μg/L; Mn, 0.1 μg/L; Se, 4 μg/L; and Zn, 0.2 μg/L.

The correctness of the analytical procedure was tested by determining the analyzed elements in reference material Seronorm (Trace Elements Serum, Sero AS) (n=3) together with the samples. The results agreed within ±10 % of the certified values. The analytical procedure was also checked by analysis of the blank samples. Blank digests (n=4) were run with a series of milk samples, and no major interferences were found in the quantitative element analysis.

Statistical analysis of the data was performed using Statistica software (Statsoft Inc., version 10.0). Prior to analyses, data were investigated to determine their distribution using the Shapiro–Wilk W test. The

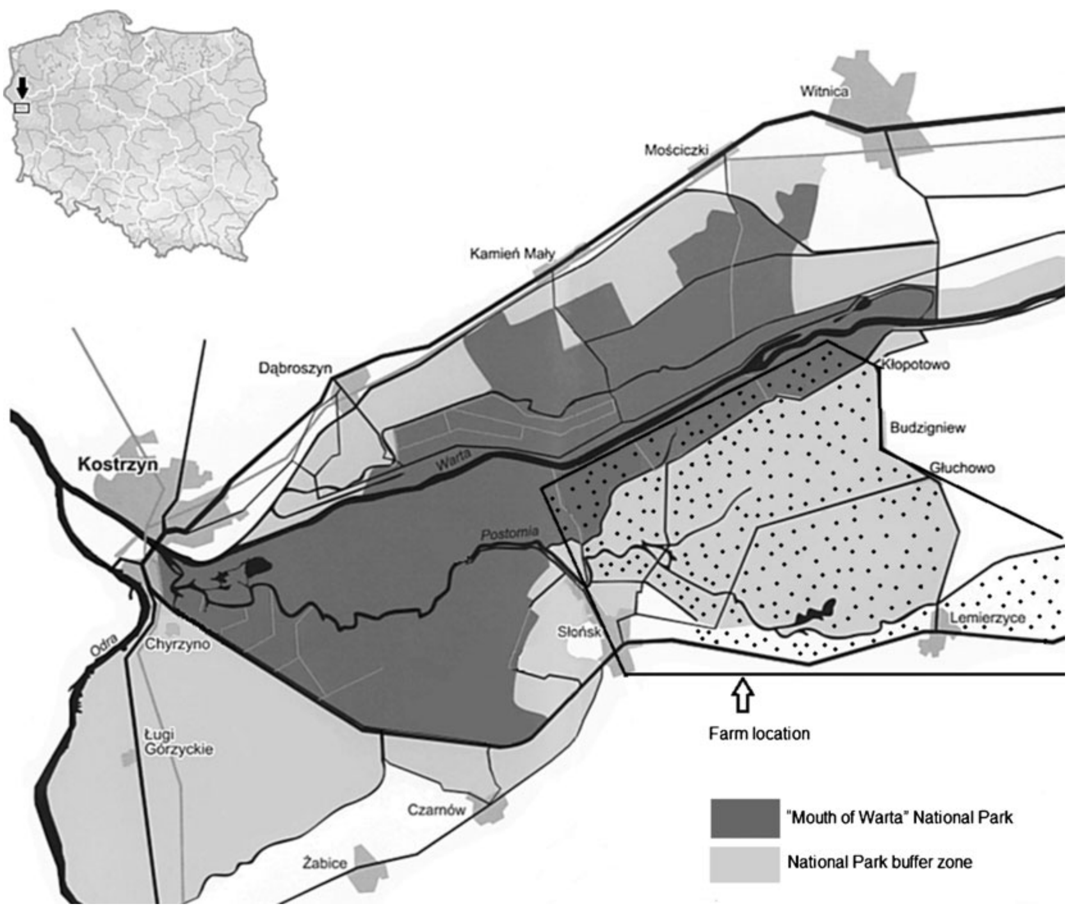

Fig. 1 Location of the province and the farm

concentrations of elements were log transformed to attain or approach a normal distribution of the data. Concentration of the analyzed elements in cow's milk between Simmental and Holstein-Friesian breeds was compared by the Student's *t* test. Differences were considered significant at the level of $P<0.05$, $P<0.01$, and $P<0.001$. The relationships between the levels of individual elements in the milk of examined animals were calculated using Spearman rank correlation analysis. Statistical significance of coefficients of correlation was tested at the levels of $P<0.05$, $P<0.01$, and $P<0.001$. All data are expressed throughout as an arithmetic mean, geometric mean, minimum values, maximum values, quartile deviation, and also standard error mean.

Results and discussion

The concentration of toxic heavy metals and trace elements in milk samples is given in Table 1. The milk of Simmental cows had significantly lower concentration of Pb and Cd ($P<0.001$) and Cu ($P<0.05$) and significantly higher concentration of Fe and Mg ($P<0.05$) than did the milk of Holstein-Friesian cows. In the milk of Simmental cows, higher concentrations of Mn, Se, and Ca and lower concentrations of Zn and P were also found; however, these were not statistically significant differences.

Concentration of Mg, P, Fe, Mn, Se, and Zn in the milk of cows of both breeds was within the standards proposed by Gaucheron (2005) and Hunt and Nielsen (2009), that of Ca was higher than the given range 1,043–1,283 μg/mL, whereas that of Cu was at least 50 % too low in relation to the suggested normal concentration of 0.1–0.35 μg/mL. Unfortunately, the Pb content in the milk of cows of both breeds was two times higher than the permissible concentration of 0.02 μg/mL in the raw milk given by the standards of the European Commission Regulation (2006) establishing the highest permissible levels of some pollutants in foodstuffs.

Table 1 Content of mineral elements and toxic heavy metals in milk of Simmental and Holstein-Friesian cows

Elements	Concentration, μg/mL												P value
	Simmental						Holstein-Friesian						
	Mean	GM	Min.	Max.	SEM	QD		GM	Min.	Max.	SEM	QD	
Ca	1,701.33	1,689.15	1,409.86	2,156.45	47.332	323.301	1,606.67	1,600.37	1,273.21	1,949.81	32.430	149.985	0.11
Mg	130.87	129.84	96.66	161.32	3.726	20.498	119.72	119.18	93.66	149.99	2.622	10.666	0.02*
P	980.90	975.61	719.93	1,186.55	22.904	86.658	1,008.90	1,004.25	813.25	1,216.55	22.076	116.655	0.38
Cu	0.0377	0.0329	0.0147	0.1420	0.00592	0.01572	0.0453	0.0426	0.0221	0.0993	0.00377	0.01816	0.02*
Fe	0.2576	0.2340	0.1283	0.7066	0.03108	0.07083	0.1984	0.1884	0.1400	0.4966	0.01785	0.06833	0.04*
Mn	0.0215	0.0210	0.0116	0.0325	0.00103	0.00592	0.0201	0.0191	0.0098	0.0407	0.00156	0.00655	0.46
Se	0.0198	0.0160	0.0100	0.1187	0.00523	0.00335	0.0162	0.0160	0.0115	0.0209	0.00058	0.00402	0.49
Zn	3.027	2.967	2.026	4.433	0.1403	0.92657	3.277	3.209	2.043	4.800	0.1510	0.8266	0.23
Pb	0.0366	0.0364	0.0316	0.0440	0.00082	0.00600	0.0412	0.0411	0.0363	0.0477	0.00081	0.00667	<0.001***
Cd	0.0035	0.0035	0.0028	0.0041	0.00007	0.00049	0.0040	0.0040	0.0033	0.0047	0.00007	0.00052	<0.001***

GM geometric mean, *Min.* minimum values, *Max.* maximum values, *QD* quartile deviation, *SEM* standard error mean

Differences in trace mineral metabolism between breeds of cattle have been reported. Fisher et al. (1970) conducted a study in which Ayrshires and Holsteins were treated identically. The magnesium and calcium content of the milk from Ayrshires was higher than that from Holsteins. In an experiment by Hermansen et al. (2005), a total of 480 samples of milk from 10 organically and 10 conventionally producing dairy farms in Denmark were analyzed for 45 trace elements and 6 major elements. The dairy cattle breeds were Danish-Holstein or Jersey. Compared with the Holsteins, Jerseys produced milk with higher concentrations of Ba, Ca, Cu, Fe, Mg, Mn, Mo, P, Rh, and Zn and with a lower concentration of Bi. In the study by Barłowska et al. (2006) on five Polish dairy cattle breeds (Simmental, Polish Red, Whitebacks, Polish Holstein-Friesian of Black-and-White and Red-and-White variety), the milk from Simmental cows was characterized by a significantly higher Fe, Mg, and Zn content and a lower Mn content compared with the milk from Polish Holstein-Friesian cows of Black-and-White variety. It was found that the Ca, Mg, and Zn content was higher in the milk from Simmental, Polish Red, and Whiteback cows in comparison with Polish Holstein-Friesian cows of Black-and-White and Red-and-White varieties. The Cu content in the milk from Simmental cows was also very low (only 0.03 μg/mL), two times lower than that in the milk from Polish Holstein-Friesian cows of Black-and-White and Red-and-White varieties as well as Polish Red cows (0.06 μg/mL) and three times lower compared with Polish Holstein-Friesians of Red-and-White variety and Whitebacks (0.09 and 0.10 μg/mL, respectively).

In the milk of Simmental and Holstein-Friesian cows from the organic farm, particularly low Cu concentrations amounting to 0.0377 and 0.0453 μg/mL, respectively, were recorded, indicating the deficiency of this element in animals and thus in environment and feed either. Copper deficiency is a common nutritional problem in ruminants, though Cu excess is also commonly encountered, especially in sheep. It is considered that Cu concentrations between 0.1 and 0.9 μg/mL are the "normal" range in milk (Bilandžić et al. 2011).

Breed effects for efficiency in metabolizing Cu are well documented (Smart and Christensen 1985; Littledike et al. 1995; Ward et al. 1995; Du et al. 1996). In an experiment by Du et al. (1996), Holstein and Jersey primiparous cows and growing heifers were supplemented with either 5 or 80 mg of copper per kilogram dry matter. At the end of the 60-day experiment, the hepatic Cu concentration, plasma Cu concentration, and ceruloplasmin oxidase activity clearly showed a genetic difference in Cu absorption and post-absorption metabolism between Holstein and Jersey breeds. Jerseys had higher liver copper concentrations relative to Holsteins across both treatments. Furthermore, liver copper concentrations increased more rapidly and were higher in the Jerseys compared to Holsteins supplemented with 80 mg of copper per kilogram dry matter. Overall serum ceruloplasmin oxidase activity was higher in Jerseys than Holsteins. Additionally, Jersey cows and heifers had higher liver Fe and lower liver Zn concentrations than did Holstein cows and heifers at the end of the experiment. No differences in plasma Fe and Zn appeared between breeds. These data indicate that Jerseys and Holsteins metabolize Cu, Zn, and Fe differently.

The genetic difference may be related to the efficiency of dietary Cu absorption, the excretion of endogenous Cu, or the amount of feed intake. Gooneratne et al. (1994) suggested that the differences in endogenous Cu excretion also contributed to the genetic differences in the retention of hepatic Cu.

Cu deficiency occurs more frequently in Simmental than in other breeds of cattle (Gooneratne et al. 1994; Ward et al. 1995; Mullis et al. 2003). Bile Cu concentration and bile Cu excretion were higher in Simmental cattle than in Angus cattle (Gooneratne et al. 1994). Ward et al. (1995) conducted a study in which Angus and Simmental steers were placed in metabolism crates to monitor apparent absorption and retention of copper. At the end of the experiment, plasma copper concentrations, apparent absorption, and retention of copper were higher in Angus steers. The authors indicate that Simmental cattle may have a higher copper requirement than Angus cattle and that these different requirements may be related to the differences in copper absorption from the gastrointestinal tract between breeds. Furthermore, it has also been suggested that these breed differences in copper metabolism may not be due solely to differences in absorption, but also to the manner in which copper is utilized or metabolized post-absorption. Simmental steers had also lower serum and liver Cu concentrations and serum ceruloplasmin activity than Angus throughout the study by Mullis et al. (2003). Smart and Christensen (1985) reported that Hereford-sired cows had greater plasma Cu concentrations during gestation than did Simmental-sired cows.

Others have reported differences in serum Mg, Ca, and P. Wiener (1980) found a difference in blood Cu, Ca, P, and Mg concentrations between Friesian and Jersey cattle. Angus had higher serum Mg than did Hereford cows in a study by Greene et al. (1989) and true digestibility of Mg in Angus cows of this herd was higher than that of Hereford. However, Chirase et al. (1988) found that serum Mg, Ca, and P were similar in Angus, Angus × Hereford, Angus × Jersey, Brahman × Hereford, Brahman × Jersey, and Hereford × Jersey cows grazing oat pastures.

Littledike et al. (1995) compared the mineral status of Angus, Braunvieh, Charolais, Gelbvieh, Hereford, Limousin, Red Poll, Pinzgauer, and Simmental breeds consuming similar diets. In adult cattle, liver Cu was higher for the Limousin breed than for all others, except for Angus. Liver Zn concentrations were higher for Limousin than for Pinzgauer, but no other breed differences were observed. Serum Ca concentrations were higher for Angus, Red Poll, and Limousin than for Simmental, and Red Poll had higher concentrations of serum Ca than did Braunvieh. Serum Mg concentrations were higher for Angus than for Hereford. Concentrations of serum Ca were positively correlated with serum concentrations of Cu, Zn, and Mg, but negatively correlated with liver Fe.

In few studies, an effect of breed on the efficiency of Se metabolism was also shown. In an experiment by Sprinkle et al. (2006), Brahman cross (Brahman × Salers or Brahman × Hereford) cows were more efficient in metabolizing Se, having greater whole blood Se than either composite cows (25 % Hereford, Angus, Gelbevieh, and Senepol or Barzona) or Hereford cows. Langlands et al. (1980) reported that Brahman cattle in Australia had greater blood Se than Brahman cross, Africander, Africander cross, Brahman-Africander × Hereford-Shorthorn cross, or Hereford × Shorthorn cross cattle. In evaluating specific sire breeds, they also reported that Brahman × Hereford crosses had greater Se than Hereford × Hereford, Friesan × Hereford, and Simmental × Hereford genotypes.

Cd and Pb are environmental pollutants toxic to humans and animals (Cai et al. 2009). Cd and Pb are nonbiodegradable, and their accumulation in the environment raises agricultural and public health concerns (Olsson et al. 2005; De Vries et al. 2007). In our study, Pb and Cd concentrations in the milk of Simmental cows were significantly lower ($P<0.001$) compared to Holstein-Frisian cows. The Pb concentration in the milk of both breeds exceeded, however, permissible EU standards, amounting to 0.0366 and 0.0412 μg/mL for Simmental and Holstein-Friesian cows, respectively. In the study by Gabryszuk et al. (2010), the Pb concentration in the milk of cows from organic farms was much lower and ranged from 0.0041 to 0.0062 μg/mL.

Heavy metal contamination in milk has been reported also in different countries and regions (Simsek et al. 2000; Licata et al. 2004; Pavlovic et al. 2004). In the study by Bilandžić et al. (2011), mean lead concentrations exceeded the maximum residue levels in the north and the south regions of Croatia (0.0587 and 0.0362 μg/mL, respectively). Levels above 0.020 μg/mL were measured in 35.5 % of samples from the north and 28.3 % of samples from the south regions. In the study by Pavlovic et al. (2004), the Pb level ranged from 0.028 to 0.036 μg/mL, but that of Cd was between 0.005 and 0.006 μg/mL for a majority of 15 farms in Croatia. Sikrić et al. (2003) reported even higher Pb concentration in milk, which amounted to 0.023–0.070 μg/mL.

The interesting aspect in the present study is the interaction between toxic heavy metals (Pb and Cd) and major nutritional and trace elements (Ca, Mg, P, Cu, Fe, Mn, Se, Zn) in milk because the nutritional function of milk is important for health. In the liver or kidney, the interactions of Zn, Cu, Se, Fe, Ca, and Pb or Cd are well known from the earlier literature, but their relation in milk is not clearly reported (Isaac et al. 2012).

In the milk of Simmental and Holstein-Friesian cows, significant very high or high positive correlations (Table 2) were found between the concentrations: Pb–Cd (r=0.86 vs. r=0.87), Pb–Se (r=0.68 vs. r=0.83), Cd–Se (r=0.62 vs. r=0.70), Cd–Mn (r=0.49 vs. r=0.61), Zn–Cu (r=0.57 vs. r=0.46), Zn–P (r=0.46 vs. r=0.57), Ca–P (r=0.64 vs. r=0.81), Mg–P (r=0.55 vs. r=0.66), and Ca–Mg (r=0.89 vs. r=0.62).

Moreover, in the milk of Simmental cows, statistically significant correlations were observed between milk concentrations of: Cd and Mg (r=−0.46), Pb and Ca (r=−0.41), and Pb and Fe (r=0.57). In the milk of Holstein-Friesian cows, the concentration of Pb and Cd was positively and significantly correlated with P (r=0.47 and r=0.49, respectively), Mn (r=0.57 and r=0.67, respectively), Se (r=0.83 and r=0.70, respectively), and Zn (r=0.49 and r=0.55 respectively). In addition, Mn concentration significantly correlated with Ca (r=0.55), P (r=0.65), Se (r=0.48), and Zn (r=0.58), concentration of Zn with Cu (r=0.57) and P (r=0.57), and concentration of Se with P (r=0.54).

A very high, significant, and positive correlation between Ca and Mg (r=0.873) in the milk of cows was reported also by Rodríguez Rodríguez et al. (1999). However, contrary to our results, they found significant negative correlations between Cu and Zn (r=−0.377) and not high positive correlations between Fe and Cu as well as Fe and Zn. In the study by Sikrić et al. (2003), the Cu concentration in milk was significantly positively correlated with the concentrations of Fe (r=0.613) and Zn (r=0.629) and that of Zn with Mn (r=0.731), which was proved in our work. In the milk of both analyzed breeds, the Pb concentration was very highly correlated with Cd concentration (r=0.85 vs. r=0.87), whereas in the study by Pavlovic et al. (2004) no correlation between these metals was found. Stawarz et al. (2007) reported strong positive correlations between Cd and Ca (r=0.220), Cd and Mg (r=0.201), Cd and Zn (r=0.279), and Cu and Ca (r=0.347) and negative correlation between Pb and Ca (r=−0.295) in breast milk.

There is a paucity of earlier literature, particularly concerning animals, to compare the present finding. The correlations between the elements of milk were rarely analyzed (Rodríguez Rodríguez et al. 1999). The available literature describes relationships between different elements, principally in the liver, kidneys, and muscles of animals (López Alonso et al. 2002, 2004; Blanco-Penedo et al. 2006), in the limited number in blood or serum (López Alonso et al. 2002). The largest number of significant correlations between toxic and essential elements is found in the kidneys followed by liver (Tomza-Marciniak et al. 2011), which according to Lopez Alonso et al. (2004) is a reflection that these organs play the main role in trace element metabolism.

Experimental exposure of rats to either lead or cadmium or both concomitantly has been demonstrated to influence the metabolism and tissue concentration of divalent cations like zinc, copper, and iron and tissue-specific changes in the distribution of iron, zinc, copper, cobalt, and manganese have been documented after experimental administration of lead and cadmium in cattle and rats (Patra and Swarup 1998; Oishi et al. 2000; Patra et al. 2001, 2008).

During lactation, Pb and Cd are thought to be transported from maternal plasma to mammary gland and secreted into milk along with Cu and Zn.

Table 2 Spearman rank correlations between milk concentration of different mineral elements

Elements	Mg	P	Cu	Fe	Mn	Se	Zn	Pb	Cd
Simmental									
Ca	0.89***	0.64**	0.22	−0.26	0.08	−0.22	0.38	−0.41*	−0.36
Mg		0.55*	0.13	−0.13	−0.08	−0.26	0.36	−0.40	−0.46*
P			0.28	−0.32	−0.20	−0.09	0.46*	−0.32	−0.29
Cu				0.29	0.19	0.13	0.57**	0.06	0.03
Fe					0.24	0.42	0.03	0.57**	0.28
Mn						0.42	0.15	0.43	0.49*
Se							−0.10	0.68**	0.62**
Zn								−0.30	−0.35
Pb									0.86***
Holstein-Friesian									
Ca	0.62**	0.81***	0.26	0.28	0.55*	0.33	0.35	0.17	0.17
Mg		0.66**	0.09	0.24	0.37	0.17	0.37	0.27	0.27
P			0.20	0.40	0.65**	0.54*	0.57**	0.47*	0.49*
Cu				0.25	0.39	0.12	0.46*	0.24	0.15
Fe					0.33	−0.14	0.35	−0.02	0.05
Mn						0.48*	0.58**	0.57**	0.61**
Se							0.33	0.83***	0.70**
Zn								0.49*	0.55*
Pb									0.87***

***$P<0.001$, **$P<0.01$, *$P<0.05$, statistically significant coefficient of correlation

However, the interaction between toxic heavy metals and trace elements (Ca, Mg, P, Cu, Fe, Mn, Se, Zn) has not been understood clearly, particularly in milk. There is a good level of understanding of the role of major nutritional elements like Ca, Mg, P, Na, and K in milk, but the effects of Pb and Cd on their metabolism have not been sufficiently investigated (Isaac et al. 2012).

Cd and Pb mainly distribute in the liver and kidney, where Cd is bound to metallothionein (MT), a small, cysteine-rich metal-binding protein (Klaassen et al. 1999).

Several studies have suggested that interactions between Cd or Pb and Zn in the organism result in a high degree from an affinity of both metals to MT and their ability to induce its synthesis. They can induce MT synthesis in various tissues, especially in the intestine, liver, and kidney (Brzóska and Moniuszko-Jakoniuk 2001; Cai et al. 2009). Metallothionein, which is synthesized in response to cadmium, lead, zinc, copper, or mercury exposure (MT inducers), contributes to the accumulation of metals by eliminating them from metabolism. Olsson et al. (2010) found a significant relationship between kidney levels of Cd and metallothionein. Another way of eliminating metals from metabolism is through the formation of neutral complexes (e.g., Se–Cd and Se–Pb) by selenium, which are then bound by proteins similar to metallothionein. This is possible because of the high affinity of selenium for these elements (Nehru and Iyer 1994; Tomza-Marciniak et al. 2011). The interaction between Zn and Cu has been extensively reported (Blanco-Penedo et al. 2006; Bremner and Beattie 1995) and is a consequence of the ability of these metals to induce synthesis of metallothioneins and of their competition for metallothionein-binding sites.

Interaction between toxic heavy metals (Pb and Cd) and major nutritional and trace elements was also found in humans, most frequently in blood and serum (Bárány et al. 2002) and in the milk of nursing mothers (Perrone et al. 1994; Krachler et al. 1998; Stawarz et al. 2007). Wang et al. (2012) reported correlations among the toxic (Cd, Pb) and nutritionally essential (Zn, Cu, Fe, Mn, Se) elements in the blood, also urine and feces in the male. In the case of the toxic metals, a significant positive correlation was found for Cd–Pb in blood and a moderate correlation in urine. Cd was positively correlated with most of the essential elements in both urinary and fecal excretion. Moreover, significant direct correlations were found between Cd and either Zn or Se concentration in both urine and feces, whereas a significant negative correlation was found between Cd and Se in blood.

At present, we have no biological explanations to several others of the reported correlations and more studies are needed in this area.

Correlation analysis also showed some differences among the analyzed cow breeds. The correlations between Pb and Zn as well as Cd and Zn are noteworthy. In the milk from Holstein-Friesians (HF) cows, very high positive and significant correlations between these elements were recorded (0.83 and 0.70, respectively), whereas in the milk from Simmental cows, these correlations were negative, weak, and statistically nonsignificant (−0.30 and −0.35, respectively). In Simmental cows, negative correlations were also found between Pb and Cd and Ca, Mg, and P; however, only those between Pb and Ca (−0.41) and Cd and Mg (−0.46) were significant. In HF cows, only correlations between these elements and P were positive and significant (0.47 and 0.49 for Pb–P and Cd–P, respectively). A high positive and significant correlation between Pb and Fe was also observed in Simmental cows, whereas it was low in HF cows. In the milk from HF cows, high positive and significant correlations between Mn and Ca, P, Se, Zn, and Pb as well as between Se and P were additionally found, whereas in Simmental cows, these correlations were nonsignificant and the obtained correlation coefficients much smaller. These correlations confirm differences in trace mineral metabolism between the studied breeds.

Conclusions

The present research showed that the milk of Simmental cows had more favorable mineral composition and lower concentration of toxic heavy metals compared to the milk of Holstein-Friesian cows. In the milk of Simmental cows, significantly lower concentrations of Pb, Cd, and Cu, significantly higher concentrations of Fe and Mg, as well as nonsignificantly higher concentrations of Ca, Mn, and Se were found. In the milk of both breeds, particularly low Cu concentrations (0.0377 vs. 0.0453 μg/mL), at least two times lower than the recommended standards, were recorded, which indicates the deficiency of this element in animals as well as in environment and feed. Also, the Pb concentration in milk that was higher than the recommended standards was found. Simmental and Holstein-Friesian cows remained in the same environment and were identically fed, which allows us to suppose that the differences obtained between these breeds in the content of the examined elements and heavy metals in milk are caused by differences of metabolic background.

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