*Letter to Editor*

# The Content of Microelements and Trace Elements in Raw Milk from Cows in the Silesian Region

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### Abstract

The content of 38 microelements and trace elements in raw milk of cows from Lower Silesia (LS) and Upper Silesia (US) were examined. Analytical method of mass spectrometry (ICP-MS) with microwave sample digestion was used in this study. Statistically significant differences were detected in the case of iodine, rubidium, cesium, tungsten and thorium (more in the US region) as well as aluminum, titanium, manganese, gallium, selenium, germanium, cobalt (more in LS). No statistically significant differences were observed in the case of: Zn, Ba, Cu, Cr, V, Ni, As, Mo, Pt, Sb, Au, Hf, Ce, U, Re, Tl, Ru, Rh, Ir, Ta and Be. For La, Nb, Ag, In and Y statistical differences were not calculated since in the majority of samples concentrations were below detection limit.

**Keywords**: raw milk, microelements, trace elements, Lower and Upper Silesia

## Introduction

Cow milk and its products are basic foodstuffs and constitute an important source of nutrients in the daily diet of humans. The content of protein, fat, carbohydrates, vitamins and minerals determine biological and technological properties of milk.

As far as the fundamental composition of cows milk is known, its elemental composition is generally unknown. It has been reported that the content of the main mineral components, such as Ca, P, K, Na, Mg, Cl, S, is not diversified and undergoes only slight changes depending on the lactation phase and the quality of nutrition [1], in particular under the influence of applied mineral additives or environmental conditions, mainly chemical pollutants [2]. Flynn [3] reported that in cow milk the content of mineral components averaged 7.3 g/l, but Hurley [4] pointed out that macroelements (Ca, P, Mg, Na, Cl and S) in milk are present in quantities ca. 0.578% and their concentration is not diversified. Similarly, the concentration of nickel (0.027), iron (0.45 mg/l) or silicon (1.43 mg/l) that is on a low level is not changed under the influence of feeds supplementation. However, Wnuk et al. [5] stated that in the case of mineral deficiency in feed, some ranging of macroelements concentration in milk such as Ca, P, Mg, Na and K were observed.

The content of microelements and trace elements in cow milk was recently more widely studied, in particular in industrialized and polluted regions, since it is considered a good bioindicator of pollution of the agricultural environment [6,7]. Therefore, the quality of milk is continuously monitored by the National Veterinary Institute, and some elements, in particular toxic metals, such as As, Cd, Hg, Pb are controlled in milk. Their permissible levels are regulated by the Regulation of the Minister of Health in 2003 [8].

The aim of the present work is to asses the concentration of microelements and trace elements in milk from cows kept in farms located in an industrialized region of the Silesian macro-region.

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## Material and Methods

The studies were carried out on a population of cows in full lactation period, 4-12 years old kept in the industrialized region of Lower (LS) and Upper (US) Silesia.

In the first region (LS), the animals were exposed to impact copper industry and to a lower extent the chemical industry (Legnica-Głogów Copper Region). Some authors [2, 9, 10] have reported that in the process of flotation of copper ore and pyrometallurgical processing of copper concentrates, various chemical substances, includining Ag, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Si, V, Zn, are emitted to the environment.

In the US (Silesian Voievodship), extractive industry dominate, mainly coal mining, industrial power as well as iron and steel metallurgy. These industries are a source of large amounts of industrial wastes, including hazardous [11], and environmental emission of various pollutants (dusts). Pastuszka et al. [12] has reported that 19 elements (i. e. Al, Cd, Cu, F, Fe, I, Pb, Si, Ti, Zn, etc.) were present in air aerosol in the center of Upper Silesia.

Milk was sampled a single time into sterile containers, hand stripping from 4 teats of udder in the afternoon hours (evening milking) in the autumn season, when animals where pastured.

The samples of milk were transported into the Wrocław University of Technology laboratory (ITNiNM), they where were analyzed with mass spectrometry method (ICP-MS) using the use of Varian Ultramass-700 aparate. The samples were digested with microwave method with the use of microprocessor station MCS-2000 [13]. Analytical blanks (acids used for samples digestion) were employed during ICP-measurements of elemental composition. Totally, 24 samples of milk, that is 12 from US and LS regions were analyzed for the content of 17 microelements and 21 trace elements, excluding heavy metals (Cd, Hg, Pb – the subject of another paper.)

The results were elaborated statistically, by calculating mean values ($\overline{X}$), standard deviations (SD), significance of differences between the content of elements in regions LS and HS (with the use of Statgraphics ver. 5.0 software). The means of the levels from US and LS were elaborated by t- test.

## Results

The results of analyses of 18 studied microelements are shown in Table 1. The highest concentrations of microelements were detected in the case of zinc (3.09-3.16 mg/l), iodine (0.53-0.59), aluminum (0.23-0.32), rubidium (0.29-0.84) and barium (0.19-0.22 mg/l). Cu, Cr, Ti, Mn, Ga, V, Ni, Se, Ge and As were in the concentration range 29-104 µg/l. It was shown that the concentration of Mo and Co was below 10 µg/l.

Table 1. The content of microelements in raw milk from cows from Lower (LS) and Upper (US) Silesia (µg/l).

| Element | Lower Silesia Mean ± SD | Upper Silesia Mean ± SD | Significance of differences |
|---|---|---|---|
| Zinc (Zn) | 3163.68 ± 710.61 | 3085.42 ± 589.85 | |
| Iodine (I) | 530.40 ± 23.54 | 588.85 ± 73.69 | * |
| Aluminum (Al) | 323.01 ± 113.13 | 227.78 ± 85.00 | * |
| Rubidium (Rb) | 291.77 ± 53.87 | 839.35 ± 544.76 | ** |
| Barium (Ba) | 191.21 ± 65.75 | 224.85 ± 113.75 | |
| Copper (Cu) | 89.85 ± 125.14 | 65.37 ± 85.30 | |
| Chromium (Cr) | 88.13 ± 59.33 | 75.06 ± 44.80 | |
| Titanium (Ti) | 104.42 ± 24.70 | 54.48 ± 28.90 | ** |
| Manganese (Mn) | 101.84 ± 25.63 | 51.24 ± 14.49 | ** |
| Gallium (Ga) | 91.97 ± 20.86 | 37.09 ± 15.15 | ** |
| Vanadium (V) | 74.18 ± 30.05 | 99.09 ± 52.10 | |
| Nickel (Ni) | 53.54 ± 25.55 | 68.84 ± 34.67 | |
| Selenium (Se) | 39.20 ± 14.17 | 22.44 ± 10.73 | ** |
| Germanium (Ge) | 37.81 ± 16.50 | 19.75 ± 15.99 | * |
| Arsenic (As) | 29.31 ± 7.26 | 35.47 ± 21.08 | |
| Molybdenum (Mo) | 10.65 ± 5.69 | 10.39 ± 5.09 | |
| Cobalt (Co) | 8.34 ± 3.55 | 5.16 ± 2.79 | * |

Data are the means ± standard deviation * $p<0.05$, ** $p<0.01$

Table 2 presents concentrations of trace elements. The following elements were found in trace concentrations: Pt, Sb, Au, Hf, Cs, U, Re, W and Th, and below the level 1 μg/l Ce, Tl, Ru, Rh, Ir, Ta, Be, La, Nb, Ag, In and Y.

Statistically significant differences were found in the case of iodine, rubidium, cesium, thorium (more in HS region) as well as aluminum, tungsten and titanium, manganese, gallium, selenium, germanium and cobalt (more in LS). No significant differences were found in the content of: Zn, Ba, Cu, Cr, V, Ni, As, Mo, Pt, Sb, Au, Hf, Ce, U, Re, Tl, Ru, Rh, Ir, Ta, Be. For La, Nb, Ag, In and Y statistical differences were not calculated, since in the majority of samples concentrations were below detection limit.

## Discussion of Results

The content of mineral components and trace elements in milk is determined by a variety of factors, including mainly the content of a given element in soil, the content of energy in feed, the level of such organic components as fats, vitamins, protein, changes in absorption and retention of a given element [14]. Important factors that influence the occurrence of many trace elements, including toxic ones, is environmental pollution, mainly of anthropogenic origin [2]; as well as phenomena of inter-element interactions [15]. Therefore, in the literature available different data are reported. Flynn [3] reports the following elemental composition of milk: I – 0.1 – 0.77, B – 0.5 – 1.0, Fe – 0.5, Si – 3.0, Zn – 3.5 mg/l and Cr – 2.0, Sc – 10, F – 20, Ni – 26, Mn – 30, As – 20 – 60, Mo – 50 and Cu – 90 μg/l. It could also contain bismuth [16] or lithium [17]. Relatively wide elemental composition of milk was reported by Hurley [4]: Al – 0.46, As – 0.05, B – 0.27, Br – 0.6, Cr – 0.015, Cu – 0.13, F – 0.15, I – 0.043, Fe – 0.45, Mn – 0.022, Mo – 0.073, Ni – 0.027, Se – 0.04 – 1.27, Si – 1.43, Ag – 0.047, Sr – 0.171, Zn – 3.9 mg/l, Co – 0.6 and V – 0.09 μg/l. These values differ from the results of our own studies, in particular in the case of Ag, Co, Cr, Cu, Mn, Ni and V, that might point out on anthropogenic influence, mainly by industrial emissions. This fact can also explain why differences of 12 elements content in milk between milk from cows of

Table 2. The content of trace elements in raw milk from cows from Lower (LS) and Upper (US) Silesia (μg/l).

| Element | Lower Silesia Mean ± SD | Upper Silesia Mean ± SD | Significance of differences |
|---|---|---|---|
| Platinum (Pt) | 6.02 ± 2.21 | 7.05 ± 2.12 | |
| Antimony (Sb) | 5.47 ± 1.87 | 4.73 ± 1.99 | |
| Gold (Au) | 4.30 ± 7.81 | 4.92 ± 8.07 | |
| Hafnium (Hf) | 2.01 ± 2.24 | 4.14 ± 3.68 | |
| Cesium (Cs) | 1.49 ± 0.57 | 4.63 ± 2.94 | ** |
| Uranium (U) | 1.39 ± 0.74 | 1.59 ± 0.49 | |
| Rhenium (Re) | 1.09 ± 1.06 | 1.10 ± 0.95 | |
| Tungsten (W) | 0.83 ± 0.42 | 1.41 ± 0.91 | * |
| Cerium (Ce) | 0.96 ± 1.73 | 0.34 ± 0.52 | |
| Thallium (Tl) | 0.73 ± 0.44 | 0.84 ± 0.81 | |
| Ruthenium (Ru) | 0.66 ± 0.10 | 0.77 ± 0.37 | |
| Rhodium (Rh) | 0.62 ± 0.49 | 0.43 ± 0.37 | |
| Iridium (Ir) | 0.48 ± 0.68 | 0.44 ± 0.53 | |
| Tantalum (Ta) | 0.40 ± 0.07 | 0.70 ± 0.61 | |
| Thorium (Th) | 0.30 ± 0.28 | 1.98 ± 1.34 | ** |
| Beryllium (Be) | 0.38 ± 0.06 | 0.42 ± 0.07 | |
| Lanthanum (La) | <0.04 | 0.47 ± 0.85 | nc |
| Niobium (Nb) | <0.04 | 0.41 ± 0.58 | nc |
| Silver (Ag) | <0.15 | <0.15 | nc |
| Indium (In) | <0.20 | <0.20 | nc |
| Yttrium (Y) | <0.10 | <0.10 | nc |

Data are the means ± standard deviation; * $p<0.05$; ** $p<0.01$; nc - not calculated the LS and US regions were statistically significant. Monkiewicz et al. [18] and Kołacz et al. [19], who observed an increase in the content of Zn and Cu (as well as As, Cd, Hg and Pb) in a region polluted by the copper industry. However, Żmudzki et al. [7] studied the composition of cow milk for the content of microelements, including toxic elements, in Zgorzelec-Bogatynia region (brown coal power plants). In milk, the average content of heavy metals was: Cd – 0.001, Hg – 0.002, Pb – 0.065 and As – 0.002 mg/kg, and other elements: Cu – 0.04, F – 0.23, Fe – 0.62 and Zn – 4.59 mg/kg. Pyś [20] reported that there are 25 trace elements present in milk. Their concentration may vary and depend on local environment. He found some influence of impact of sulfur industry (Tarnobrzeg) on the content of Cu, Cr, Fe, Mn, Pb, Zn in milk, but these concentrations were within the range of physiological values.

Licata et al. [21] studied the content of heavy metals and other elements in milk in various farms in cows in south of Italy. Among microelements, the highest concentration was detected for Se – 13.24 and Zn – 2016 µg/kg; however, the lowest for Cr – 2.03 and Cu – 1.98 µg/kg. Rodriquez et al. [22] studied the mineral composition of raw milk from Spain (Canary Islands). They reported the content of Se – 16.44, Cu – 76 µg/l and Fe – 0.515, Zn – 4.41 mg/l. In the range of these few elements (Cr, Cu, Se, Zn) there exist significant differences when compared with the results of our own studies, that suggests the influence of local environment on the content of microelements in milk.

There is not much data concerning trace elements in raw milk. Therefore, it was worthy to cite data from the manuscript of Muramatsu and Parr [19], although they concern powdered milk. The average contents of some elements were evaluated as follows: Al – 2, Br – 12, Cu – 0.7, F – 0.20, Fe – 1.78, I – 3.38, Mn – 0.26, Mo – 0.34, Rb – 11, Se – 0.11, Si – <50, Sn – <0.02, Zn – 46.1 mg/kg and As – 1.9, Cd – 0.5, Co – 4.1, Cr – 2.6, Hg – 0.3, Pb – 19, Sb – 0.27 µg/kg.

As it was found, cow milk is a good source of microelements and trace elements in human diet, although the biological role of the majority of them is still not fully understood [15]. It was found that the location of the cows determines their concentration, in particular when related to elements with elevated concentrations (over 20 µg/l).

## Conclusions

1. The location of cows has a significant impact on the content of many microelements and trace elements in milk.
2. In cows from Lower Silesia, there were statistically significant higher levels of aluminum, titanium, manganese, gallium, selenium, germanium, and cobalt; however, lower content of iodine, rubidium, cesium, tungsten and thorium when compared with the Upper Silesia region.
3. No statistically significant differences were observed in the case of Zn, Ba, Cu, Cr, V, Ni, As, Mo, Pt, Sb, Au, Hf, Ce, U, Re, Tl, Ru, Rh, Ir, Ta, Be, but in the case of La, Nb, Ag, In and Y in the majority of samples the concentration was below detection limit.

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