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## ZINC AND COPPER CONCENTRATION IN MILK OF DAIRY COWS IN THE SOUTH BOHEMIA REGION

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#### Key words: copper, zinc, milk, dairy cows.

#### Introduction

Milk is an important source of minerals including trace elements for suckling as well as for human nutrition. It can be assumed that lactogenic secretions of trace elements fluctuate significantly by their intake. Knowing the content of trace elements in the milk as a function of their concentration in the milk and their intake prevents either insufficient and excessive quantity of trace elements from being supplemented. The content of micro-elements in the milk can be an important indicator whether the animals are being saturated with these elements and a parameter of the milk's biological quality as a nutrient.

#### Material and methods

In 2004, 50 pool samples of milk from Southern Bohemian diary farms, collected in May and June, were analysed. The content of zinc and copper was determined using the method of mass spectrometry with induction-combined plasma (ICP-MS), after pressure microwave degradation with nitric acid and hydrogen peroxide. In addition, determined in the milk samples were selected quality parameters including selenium and manganese (ICP method). The content of zinc and copper was assessed in relation to the selected qualitative parameters of the milk, including selenium and manganese. Correctness of the result was checked on a continuous basis by means of a certified reference material, BCR-NIST 1549 (Non Fat Milk Powder). The following values were selected as reference values: zinc: 4 - 5 mg/l (Illek 2000), copper: 50 µg/l (Novák, 1982).

#### **Results and discussion**

The content of copper in the pool milk samples was characterised by the following parameters: arithmetic mean 43.80  $\mu$ g/l, coefficient of variation (V%) 144.00, minimum 4.00, maximum 269.00, median 5.00  $\mu$ g/l. The minimum is at the limit of detection by the selected analytical method. The average content of copper in the milk and the high coefficient of variation suggest an uneven level of copper supplementation of the diary cows. The lowest

values of 5.00 µg/l and less were detected mainly in three counties - České Budějovice, Český Krumlov and Prachatice. The highest values were found in pool samples from diary farms in the Jindřichův Hradec county (269.00 µg/l). The greatest variability in the content of copper was identified in diary farms from the České Budějovice county (V% 215.00). The upper permissible limit of copper content in milk of 400 µg/l (Slanina et al., 1992) was not exceeded in any of the analysed samples. The generally low content of copper in the analysed samples was characterised by 57% of samples showing the value of  $5.00 \mu g/l$  or less (Table 1), with 14% of samples showing 5 - 50 µg/l and only 28% samples had the content higher than 50  $\mu$ g/l. The found average values of copper content in milk are close to the values published by Novák (1982), who claims a level of 50 µg/l concentration for mature milk and a value around 500 µg/l for colostrum. According to this author, the content of copper in the last stages of lactation drops down to as low as 10 µg/l. In comparison to the copper content found in goat milk in the course of a seven-month lactation (Khaled, Illek, Pechová, 1998) which was much more even (48.29 - 61.64  $\mu$ g/l), the values identified by our study are merely approaching their lower limit. The predominantly low content of copper in the milk is in line with the data which shows that copper saturation of animals in the Czech Republic is insufficient in all cattle, and in diary cows in particular (Illek et al., 1999).

Table 1: Relative representation of copper concentration in milk pool samples

Content of copper in milk ( $\mu$ g/l) ( $\mu$ g · l <sup>-1</sup> )	< 5.0	5.0 - 50.0	50.1 - 100	100.1 - 150	> 150
Relative representation (%)	57.14	14.29	8.16	16.33	4.08

The content of zinc in milk pool samples is characterised by the following parameters: arithmetic mean 4.67 mg/l, standard deviation 0.64 mg/l, V% 13.80, minimum 2.07, maximum 5.92, median 4.65 mg/l. These values indicate a lower variability in the zinc content in the milk compared to copper content. The average zinc value of 4.67 mg/l is within the limits of what is regarded as adequate quantity in cow milk, i.e. 3.8 - 4.7 mg/kg (Reilly, 1991 in Kvasničková, 1998). Cow milk contains greater quantity of zinc than human breast milk. Pilecki *et al.* (1999) found zinc concentration in human milk to be  $2.93 \pm 2.11$  mg/l. An average content of zinc in the milk by county was within a narrow range of values (4.42 - 5.12 mg/l). The lowest average value was found in the České Budějovice county ( $4.42 \pm 0.50$  mg/l), the highest in the Český Krumlov county ( $5.12 \pm 0.42$  mg/l). Values below 3 mg/l were found only in 2% of the samples. More than 61% of the samples were within the

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physiological range, i.e. 4 - 5 mg/l (Illek, 2000) (Table 2). 26.5% of the samples exceeded the upper limit.

Content of zinc in milk (mg/l)	< 3	3.0 - 4.0	4.1 - 5.0	> 5
Relative representation (%)	2.04	10.20	61.22	26.53

Table 2: Relative representation of zinc concentration in milk pool samples

Table 3 below illustrates the content of Zn and Cu as a function of daily milk production on the diary farm. The Zn concentration in the milk was highest on farms with the production in excess of 7000 litres of milk a day ( $4.96 \pm 0.21 \text{ mg/l}$ ), and lowest on farms with production up to 1000 litres of milk a day. The higher content of zinc in the milk from large diary cow herds (by 11.3%) indicates better zinc supplementation to the animals on bigger farms.

Table 3: Comparison of diary farms by daily milk production

Daily milk production (l)	Cu (µg/l)	Zn (mg/l)	
	$\mathbf{x} \pm \mathbf{s}_{\mathbf{X}}$	$\mathbf{x} \pm \mathbf{s}_{\mathbf{X}}$	
up to 1000	$64.80 \pm 59.10$	$4.18 \pm 1.30$	
1001 - 3000	$49.41 \pm 76.44$	$4.67 \pm 0.40$	
3001 - 5000	$29.08 \pm 45.59$	$4.71 \pm 0.60$	
5001 - 7000	$18.42 \pm 37.83$	$4.91 \pm 0.56$	
above7000	$51.25 \pm 49.75$	$4.96 \pm 0.21$	

The content of copper in the milk closely correlates with the content of manganese ( $r_{x,y}$  0.59), and the content of zinc with selenium ( $r_{x,y}$  0.40), with manganese (0.28), with fat-free dry matter, with milk proteins and lactose (0.26 - 0.36). The expected relation between the content of zinc and the number of somatic cells in the milk (Šimek *et at.*, 1995 in Šiške, 1997) has not been confirmed. The relation between the concentration of zinc and the milk production (Šimek *et al.*, 2001; Rešová, 2000) is expressed by the value  $r_{x,y}$  0.25. The relation between the nutritional standard on the diary farm represented by urea and the content of zinc in the milk is expressed by the value  $r_{xy}$  0.52. The remaining monitored relationships such as between Cu and Zn, between Cu and Se and between Cu and milk fat, fat-free dry matter, milk proteins and lactose, were insignificant.

## Conclusions

The content of copper in the milk showed high variability which is linked to the different level of copper supplementation to the diary cows. The insufficient animal saturation is demonstrated by the more than 57 % of the samples in which the value was 5  $\mu$ g/l or less. The concentration of copper in the milk closely correlates with the content of manganese. Unlike with copper, the content of zinc in the milk did not show high variability, and its average value was within the recommended limit for zinc content in consumer milk. The quantity of zinc in the milk correlates with the content of urea, which reflects the nutrition standard at the diary farm.

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