Effect of the application of bioplexes of zinc, copper and manganese on milk quality and composition of milk and colostrum and some indices of the blood metabolic profile of cows

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ABSTRACT: The object of an experiment was inorganic and organic forms of zinc, copper and manganese applied in mineral mixtures to dairy cows. The experiment was carried out on 90 cows with average milk yield for previous lactation of about 9 500 kg milk. The cows received mineral mixtures containing inorganic or organic forms of zinc, copper and manganese for 6 weeks before calving and during the first three months of lactation. The application of microelements as bioplexes in amounts covering 30% of daily requirements of cows had a positive effect on an increase in colostrum dry matter content from 20.9 to 23.35% as well as on the concentration of protein and fat, and the level of minerals – calcium, phosphorus, magnesium, zinc and copper. In cows' milk in the 2nd and 3rd month of lactation there were no differences in contents of minerals. However in the blood serum of cows in the 1st and 2nd month of lactation an increase in calcium concentration from 1.96 to 2.14 g/kg was observed while the content of phosphorus also increased average from 1.76 to 2.22 g/kg in the first trimester of lactation.

Keywords: dairy cows; bioplexes of zinc; copper and manganese; colostrum; milk; blood

High-yielding animals require the application of mixtures which contain all necessary minerals, especially microelements such as zinc, manganese, copper, iodine, cobalt and selenium. The progress of knowledge of the absorption of minerals verified a view concerning the mineral nutrition of animals (Spears, 1996). Taking into consideration various biological functions of minerals and high yield of cows, the interest in different forms of minerals applied in nutrition increased (Iwańska et al., 1999; Strusińska et al., 2003). Organic and inorganic forms of microelements have different levels of absorption and utilization by animals, depending on their solubility in animals' digestive tracts (Peterson et al., 1987; Olson et al., 1999; Huert et al., 2002). It seems to be purposeful to make experiments with the application of organic forms of zinc, copper and manganese in dairy cow feeding.

MATERIAL AND METHODS

The experimental material consisted of 90 dairy cows of Black-and-White Lowland breed upgraded with 70–90% of HF, and with average milk yield for previous lactation of about 9 500 kg. The animals were kept in a stanchion barn without outside run and without pasture all the year round.

The experiment was commenced in the dry period of cows, 6 weeks before calving, and after calving the first three months of lactation were taken into consideration. The cows were divided by an analogue method into three experimental groups (30 animals in each), and the number of lactation, milk yield for previous lactation, percentage proportion of HF genes and calving date were considered. Each group of animals chosen by the analogue method consisted of individuals in the 1st lactation (17 hei-

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Table 1. Composition and nutritive value of diets fed to dairy cows calculated according to INRA system

Feeds	Daily ration (kg)		Dry matter	UFL/kg	PDIN/kg	PDIE/kg	LFU/kg
	25–30 kg milk	dry cows	(%)	DM	DM	DM	DM
Maize silage n = 12	15.0	10.0	32.2	0.88	57	69	1.06
Barley-lucerne silage	17.0	15.0	51.2	0.71	78	70	0.68
Sugar cane silage	7.0	2.0	20.8	0.98	60	92	1.05
Brewers' grains	7.0	2.0	24.9	0.92	190	170	–
Meadow hay	1.5	1.5	84.2	0.67	49	68	1.22
Concentrate	4.0		87.9	1.12	126	125	–
Mineral-vitamin mixture	0.2	0.2	90.0	–	–	–	–
Diet contains							
kg	51.7	30.7					
DM (kg)	21.7	13.3					
UFL	18.27	10.02					
PDIN (g)	1 880	966					
PDIE (g)	1 901	971					
LFU	14.13	10.63					
Ca (g)	143	78					
P (g)	107	62					
Mg (g)	61	40					
Zn (mg)	1 693	917					
Cu (mg)	300	199					
Mn (mg)	1 450	831					

fers), in the 2nd lactation (5 cows) and in the 3rd lactation (4 cows) and in the 4th–5th lactation (4 cows). All cows were fed the same diets during the experiment: maize silage, barley GPS silage, sugar beet pulp silage, brewer's grain, meadow hay and mineral-vitamin mixture. The amount of fodders was different in dry and lactation period (Table 1).

The daily rations of feed covered cows' maintenance requirement and requirement for the production of 19 kg milk. The cows producing more than 19 kg milk/day were additionally fed 1 kg of concentrate per each 2 kg of surplus milk. The concentrate was produced in a local feed mill belonging to an Experimental Station in Pawlowice according to our formula. The basal components were maize grains (50%), soybean meal (15%), wheat bran (10%), cocoa shells (10%), rapeseed meal (6%). The nutritive value of 1 kg of mixture was 1.12 UFL, 196 g of total protein and 126 PDIN. Daily rations for dry cows provided 13.3 kg of dry matter, and 21.7 kg of dry matter for cows producing 25 to 30 kg of milk. Nutrients were balanced according to INRA'88 system (Table 1). The feeding groups were diversified with respect to the supplementary mineral mixtures which contained Zn, Cu, and Mn in sulphate or bioplex forms given individually to the animals at a dose of 200 g/day/head:

Group I – control	Mineral-vitamin mixture contains Zn, Cu and Mn in sulphate forms
Group II – experimental	Mineral-vitamin mixture contains Zn, Cu and Mn in organic forms as bioplexes in an amount covering 20% of the requirement for this element
Group III – experimental	Mineral-vitamin mixture contains Zn, Cu and Mn in organic forms as bioplexes in an amount covering 30% of the requirement for this element

Mineral-vitamin mixtures were produced by Rolimpex Wroclaw according to the formula presented in Table 2. The levels of Zn, Cu and Mn in organic forms calculated per 1 kg of dry matter of fodders did not exceed the levels allowed by the European Union (Directive 70/524). At the beginning of the experiment and during it the basic chemical analyses of feeds were done once a month according to the conventional methods (AOAC, 2005), and the analytical data allowed to calculate the nutritive value of diets for cows according to INRA'88 stan-

Table 2. Mineral and vitamin concentrations per 1 kg of mineral-vitamin concentrates (for the whole time of experiment)

Components	Concentration per 1 kg of mixture		
	group I	group II	group III
Calcium (Ca) (g)	117	117	116
Phosphorus (P) (g)	150	150	148
Magnesium (Mg) (g)	75	75	75
Sodium (Na) (g)	55	55	55
Copper (sulphate) (Cu) (mg)	600	300	–
Copper (chelate) (Cu) (mg)	–	300	600
Zinc (sulphate) (Zn) (mg)	3 007	1 507	–
Zinc (chelate) (Zn) (mg)	–	1 500	3 000
Manganese (sulphate) (Mn) (mg)	2 002	1 000	–
Manganese (chelate) (Mn) (mg)	–	1 000	2 000
Iron (Fe) (mg)	602	601	598
Cobalt (Co) (mg)	10	10	10
Selenium (Se) (mg)	5.1	5.1	5.1
Iodine (I) (mg)	30.2	30	30
Vitamin A (I.U.)	600 000	600 000	600 000
Vitamin D_3 (I.U.)	120 000	120 000	120 000
Vitamin E (mg)	1 800	1 800	1 800
Vitamin B_1 (mg)	9.8	9.8	9.8
Vitamin B_2 (mg)	2.4	2.4	2.4
Vitamin B_6 (mg)	6.9	6.9	6.9
Pantothenic acid (mg)	200	200	200
Nicotinic acid (mg)	507	507	507
Yeasts (mg)	21	7.2	–
Antioxidant (mg)	1 000	1 000	1 000

dards (Table 1). In feed samples, after previous wet mineralization (with a mixture of nitric, sulphuric and perchloric acid) with the use of TH-3 mineraliser (DHN PAN) the content of minerals (Ca, Mg, Na, Zn, Cu and Mn) using an atomic absorption spectrophotometer (AAS-3 EA-30 Carl Zeiss) was determined. Phosphorus was estimated as a complex using the vanadomolybdate method and Specol-11 Carl Zeiss (AOAC, 2005). The amount and source of macro- and microelements in daily rations for cows during lactation are presented in Tables 3 and 4.

Two weeks before calving dry cows were transferred into calving pens, and 7 days after calving the cows returned onto their stalls in branch. Immediately after calving the first colostrum was milked and dry matter, total protein, total fat, lactose and fat-free dry matter were determined by instrumental methods and MilcoScan 133B apparatus.

The apparatus was calibrated once per month with the application of suitable standards as well as with the use of standard milk sample. In samples of colostrum the contents of minerals (Ca, P, Mg, Zn and Cu) were also determined. Moreover, milk samples were taken from 8 cows from each group in the 1st, 2nd and 3rd month after calving and Ca, P, Mg, Zn and Cu were determined. From those cows samples of blood were also taken from the belly vein, and the glucose level as well as the content of urea and minerals – calcium, phosphorus, magnesium in the blood serum were estimated by chemotests POCH Gliwice. The samples of blood serum, after previous wet mineralization, were examined for zinc, copper and manganese using an atomic absorption spectrophotometer (AOAC, 2005).

All results were statistically analyzed by one-way analysis of variance and multiple-range Duncan's test using the software StatSoft (2001).

Table 3. Quantity and source of macro- and microelements in diets fed to dairy cows (daily milk yield = 25 to 30 kg)

Mineral	Forages	Concentrate	Mineral mixture	Total	Per 1 kg of DM
Macroelements		(g/day/head)			(g/kg)
Calcium (Ca)	79.2	40.1	23.4	142.7	6.6
Phosphorus (P)	45.0	32.3	30.0	107.3	4.9
Magnesium (Mg)	34.4	12.3	15.0	61.7	2.8
Sodium (Na)	15.1	10.9	11.0	37.0	1.7
Microelements		(mg/day/head)			(mg/kg)
Copper (Cu)	119.8	60.1	120.0	299.9	13.8
Zinc (Zn)	504.8	587.5	601.4	1 693.7	78.0
Manganese (Mn)	637.8	411.7	400.4	1 449.9	66.7

Table 4. Microelement derivates from mineral concentrate and its percentage proportion in relation to the intake from diets fed to dairy cows

Microelements		Experimental groups					
		(mg/day/head)			percentage of intake		
		group I	group II	group III	group I	group II	group III
Copper	inorganic	120	60	0	40.0	20.0	0.0
	organic	0	60	120	0.0	20.0	40.0
Zinc	inorganic	601	301	0	35.5	17.8	0.0
	organic	0	300	600	0.0	17.7	35.5
Manganese	inorganic	400	200	0	27.6	13.8	0.0
	organic	0	200	400	0.0	13.8	27.6

RESULTS AND DISCUSSION

The content of macroelements Ca, P, Mg and Na per 1 kg of dry matter of fodders was similar to the recommendation from INRA'88 standards. The bulky feed provided 40–50% of these macroelements. The bulky feed provided only 30–40% of microelements (Zn, Cu and Mn) and the remaining part was provided from concentrate and mineral mixtures. According to the methodical assumption of the experiment 20 and 30% of the requirement of these elements should be covered by organic forms of zinc, copper and manganese. Because of different contents of these elements in bulky feed some differences from assumptions occurred, the requirement for Zn in organic form was covered at 17.7 and 35.5%, for Mn at 13.8 and 27.6% and for Cu at 20 and 40%.

The content of basic nutrients and minerals in colostrum is presented in Table 5. The application of organic forms of trace elements (Zn – 300 and 600 mg; Mn – 200 and 400 mg; Cu – 60 and 120 mg) to dry cows from group II and III had a positive effect on the colostrum composition. A significant ($P \leq 0.01$) increase in dry matter from 20.90 to 23.35% was observed as well as in its concentration of protein and fat. At the same time a slight decrease in immunoglobulin level and a visible decrease ($P \leq 0.01$) in lactose level were observed. Changes in the colostrum composition could be important for calf rearing in relation to the better immunoglobulin absorption (Szulc et al., 1991; Chudoba-Drozdowska, 1996; Szulc and Zachwieja, 1998).

The application of bioplexes of Zn, Cu and Mn had a positive influence on an increase in the minerals level in colostrum. A significant ($P \leq 0.01$) increase was observed in Ca, P, Zn and Cu contents in the colostrum of cows from group III, who received 30% of the requirement of Zn, Cu and Mn for trace elements as bioplexes. Moreover, in the colostrum of cows from group II (20% of the requirement of Zn, Cu and Mn covered as bioplexes) the content of Ca, P, Zn and Cu significantly ($P \leq 0.01$) increased in comparison with the mineral composition of colostrum of cows from the control

Table 5. Content of nutrients and minerals in the colostrum of cows

	Experimental group		
	I	II (20%)	III (30%)
Nutrient			
Dry matter (%)	20.90^{Aa}	22.36^{ABb}	23.35^{Bb}
Crude protein (%)	11.70^{A}	12.15^{ABa}	13.01^{Bb}
Crude fat (%)	4.57^{A}	6.23^{B}	6.18^{B}
Lactose (%)	3.13^{Aa}	2.85^{ABb}	2.66^{Bb}
Fat-free dry matter (%)	16.33	16.13	17.17
Immunoglobulins (G/l)	103.47	98.59	99.56
Minerals			
Calcium (g)	1.59^{Aa}	1.68^{ABa}	1.80^{Bb}
Phosphorus (g)	1.52^{A}	1.52^{A}	1.82^{B}
Magnesium (g)	0.27^{a}	0.29^{ab}	0.31^{b}
Zinc (mg)	9.41^{Aa}	10.26^{ABb}	11.79^{Bc}
Copper (mg)	2.03^{a}	2.26^{b}	2.27^{b}

^{A,B}values in the rows with different letters differ significantly ($P \le 0.01$)
^{a,b}values in the rows with different letters differ significantly ($P \le 0.05$)

group (Table 5). Szulc et al. (1991), emphasized that the proper nutrition of cows in a prenatal period could have a significant influence on the composition and biological value of colostrum.

The bioplexes of Zn, Cu and Mn had a positive influence on the mineral management of cows in the first period of lactation. In the first month of lactation milk from cows of group III (30%) contained a significantly ($P \le 0.05$) higher level of calcium and zinc (Table 6). The levels of phosphorus, magnesium and copper were also higher but differences were insignificant in comparison with milk from cows of the control group. The data could document a better absorption of these elements from organic forms. It is in agreement with experiments conducted by Iwańska et al. (1999) and Strusińska

Table 6. Content of basal nutrients in milk during the first three months of lactation

Milk component	Month of lactation	Experimental group		
		I	II (20%)	III (30%)
Calcium (g/kg)	1	1.06^{a}	1.08^{a}	1.18^{b}
	2	1.15	1.12	1.12
	3	1.20	1.17	1.12
Phosphorus (g/kg)	1	0.95	1.05	1.01
	2	1.00	0.98	0.98
	3	0.98	1.00	1.00
Magnesium (g/kg)	1	0.11	0.11	0.12
	2	0.12	0.12	0.11
	3	0.13	0.12	0.12
Zinc (mg/kg)	1	3.76^{a}	3.69^{a}	4.20^{b}
	2	4.32	4.09	4.23
	3	4.45	4.37	4.98
Copper (mg/kg)	1	1.49	1.53	1.55
	2	1.64	1.63	1.67
	3	1.63	1.61	1.73

^{a,b}values in the rows with different letters differ significantly ($P \le 0.05$)

Table 7. Content of selected biochemical indicators and minerals in the serum of cows (during 3 months *post partum*)

Component	Month of lactation	Experimental group		
		I	II (20%)	III (30%)
Glucose (mmol/l)	1	2.22	2.23	2.18
	2	2.03	2.16	2.07
	3	2.20	2.09	2.14
Urea (mmol/l)	1	4.23	4.33	3.83
	2	4.31	4.85	4.36
	3	3.99	3.69	4.57
Minerals				
Calcium (g/kg)	1	1.96^{a}	1.90^{a}	2.14^{b}
	2	1.98^{a}	2.16^{b}	2.13^{b}
	3	2.22	2.30	2.33
Phosphorus (g/kg)	1	1.85^{a}	1.86^{a}	2.07^{b}
	2	1.57^{A}	1.93^{B}	2.16^{BC}
	3	1.85^{A}	2.04	2.42^{BC}
Magnesium (g/kg)	1	1.20	1.20	1.24
	2	1.30	1.23	1.14
	3	1.20	1.25	1.23
Zinc (µmol/l)	1	16.54	16.83	17.01
	2	17.47	17.55	17.54
	3	17.79	18.25	18.83
Copper (µmol/l)	1	11.33^{a}	13.38^{b}	13.22^{b}
	2	11.64	11.49	12.13
	3	11.22	13.24	13.40

^{A,B}values in the rows with different letters differ significantly ($P \leq 0.01$)
^{a,b}values in the rows with different letters differ significantly ($P \leq 0.05$)

et al. (2003), who administered amino acid chelates to cows.

In the 2nd and 3rd month after calving no differences in mineral contents in milk were noted.

Kinal et al. (2005) stated that the dietary application of chelates of Zn, Cu and Mn to cows with average milk yield of 6 500 kg had no influence on the content of calcium, phosphorus, magnesium and sodium in milk. On the other hand, these authors reported a higher ($P \leq 0.05$) content of zinc and copper in milk of these cows in comparison with milk of cows from the control group receiving trace elements in sulphate forms.

The levels of glucose and urea in blood (Table 7) were similar for all groups and similar to the reference values given by Winnicka (2004).

The contents of macro- and microelements in the blood serum especially of cows from group III receiving bioplexes of Zn, Cu and Mn in amounts 30% of the requirement (Table 7) indicate the positive effect of this form on the mineral management of cows. It is confirmed by a significantly ($P \leq 0.05$) higher level of calcium in the 1st and 2nd month of lactation. In the 3rd month of lactation differences were statistically insignificant. The level of phosphorus in the blood serum of cows receiving a mineral mixture of zinc, copper and manganese in organic forms was ($P \leq 0.05$) higher in the 1st month and significantly ($P \leq 0.01$) higher in the 2nd and 3rd month of lactation. There were no statistically differences in the content of magnesium and zinc in the blood serum of all cows in the first trimester of lactation. In the first month after calving the level of copper was significantly ($P \leq 0.05$) higher in the blood serum of cows receiving 20 and 30% of the requirement for this element as bioplex (group II and III).

In experiments of Kinal et al. (2005) on cows with average milk yield of 6 500 kg milk, who received Zn, Mn and Cu in organic forms, a significant increase in zinc and copper in blood serum was determined. The data confirm the results reported by Peterson et al. (1987), Iwańska et al. (1999) and Strusińska et al. (2003), who indicated that the application of trace elements as chelates or yeast enriched with these microelements increased their bioavailability to rumen microorganisms and at the same time the possibility of better transfer of trace elements to the tissues, including blood. Other authors also pointed out this effect of the application of various forms of zinc and copper (Spears, 1996; Olson et al., 1999; Huert et al., 2002).

Experimental data indicated that the application of bioplexes of zinc, copper and manganese in the nutrition of cows with average milk yield of 9 500 kg milk for lactation had a positive effect on the level of minerals in colostrum, milk and blood of cows. These differences were significant in cows receiving 30% of the requirement for these elements as bioplexes whereas the covering of cows' requirement by 20% of trace elements from bioplexes was less effective.

REFERENCES

AOAC (2005): Official Methods of Analysis. 17th ed. Association of Official Analytical Chemists., Arlington, USA.

Chudoba-Drozdowska B. (1996): Zoohygienic conditions for healthy calves in various breeding systems. Zesz. Nauk AR Wrocław, 54, 1–58. (in Polish)

Huert M., Kincaid R.L., Cronrath J.D., Busboom J., Johnson A.B., Swenson C.K. (2002): Interaction of dietary zinc and growth implants on weight gain, carcass traits and zinc in tissues of growing beef steers and heifers. Anim. Feed Sci. Technol., 95, 15–32.

Iwańska S., Strusińska D., Zalewski W. (1999): The use of *Saccharomyces cerevisiae* 1026 used alone or with tannin-mineral premix on biochemical parameters of blood and milk in dairy cows. Acta Vet. Hung., 47, 53–63.

Kinal S., Korniewicz A., Jamroz D., Ziemiński R., Słupczyńska M. (2005): Dietary effects of zinc, copper and manganese chelates and sulphates on dairy cows. J. Food Agric. Environ., 3, 168–172.

Olson P.A., Brink D.R., Hickok, D.T., Carlson M.P., Schneider N.R., Deutscher G.M., Adams D.C., Colburn D.J., Johnson A.B. (1999): Effects of supplementation of organic and inorganic combinations of copper, cobalt, manganese and zinc above nutrient requirement levels on *postpartum* two-year-old cows. J. Anim. Sci., 77, 522–532.

Peterson M.K., Streeter C., Clark C.K. (1987): Mineral availability with lambs fed yeast culture. Nutr. Rep. Int., 36, 521–528.

Spears J.W. (1996): Organic trace minerals in ruminant nutrition. Anim. Feed Sci. Technol., 58, 151–163.

StatSoft (2001): Statistica – Data Analysis Software System. Version 6. Available at: www. Statsoft.com

Strusińska D., Iwańska S., Mierzejewska J., Skok A. (2003): Effects of mineral-vitamin and yeast supplements on concentrations of some biochemical parameters in the blood serum of cows. Med. Wet., 59, 323–326. (in Polish)

Szulc T., Zachwieja A. (1998): Colostrum Sucklings' Elixir of Life. Wyd. AR Wrocław, 327, 56–57. (in Polish)

Szulc T., Janeczek W., Chudoba-Drozdowska B., Małyszko W. (1991): Influence of feed additives used for cows during periparturient period on milk performance and calves rearing. Zesz. Nauk. AR Wrocław, 206, 33–41. (in Polish)

Winnicka A. (2004): The Reference Values of the Basal Laboratory Examinations in Veterinary Medicine. SGGW, Warszawa, 37–70. (in Polish)

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