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MICROELEMENTS AND THEIR CHELATE FORMS IN NUTRITION OF MONOGASTRIC ANIMALS: A REVIEW

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Abstract

The aim of this work was to analyze the available data concerning the characteristics and effects of micro elements and their chelate forms in swine and poultry nutrition on production parameters and cholesterol content in the tissues of broiler chickens. Usage of copper chelate forms in piglets nutrition led to increased feed consumption by 4% and daily gain weight of 4.2%. The same trend was observed in fattening pigs fed diets supplemented with 200 ppm of copper, with increased daily gain by 14.3%. The research, which aimed was to explore the possibility of significantly lower inclusion levels of minerals, the introduction of organically bound forms in broilers have not any significant differences, indicating that the much lower levels of minerals in organic form had positive impact on production parameters of broiler chickens, and improved production results of hens and parents of heavy line hybrids. The inclusion of molybdenum and sulfur in feed with high levels of copper, 100 and 200 ppm had a positive effect on the broilers growth intensity. Adding 50 ppm of molybdenum and 50 ppm of sulfur in the mixture with 100 ppm of copper, at the end of the experimental period, increased the body weight of chickens for 8.35% compared to the control group, while in the second fattening period, the group with addition of 100 ppm of copper was most effective. Also it is observed a significantly lower concentration of copper (P< 0.01) in the liver in the presence of molybdenum, with and without the presence of sulfur, compared to groups that contained only copper in feed. The use of chelate forms of minerals in monogastric nutrition is a newer trend that is still not fully accepted in practical production and further research in this area is needed. In deciding whether to use a more efficient, but also more expensive mineral chelate forms, environmental requirements must be taken into account.

Key words: *chelates, nutrition, poultry, swine.*

INTRODUCTION

Chelates are a special group of complex compounds known to researchers for more than eight decades (Stanacev et al., 2004). These are heterocyclic compounds in which the metal ion is bound to two or more atoms spatially oriented functional groups on the same ligand, constructing chele. The most stable structure of the complexes has five and six member rings, and the stability of the chelate in comparison to the analogous dithiocarbamate ligands, known as the chelate effect. The biological activity of the metal is determined by the physical and chemical properties, and their position in the periodic table of elements. The elements of the fourth period are biologically active, and the presence of *d*-electrons gives them a strong preference towards the formation of biologically active complexes-chelates. Chelate formation is carried in the digestive tract during digestion, between transition metals (Fe, Zn, Cu, Mn, Co, Mo) and organic substances in the structure are electron donor atoms N, O and S. Complex formation is carried out by hybrid-dization of electrons from both electronic sources (metal and ligand) in *s, p* and *d* orbitals, resulting in a new hybridized orbitals. Relation between sulfur and metals in contrast to nitrogen and oxygen can be very firm, while the ionization potential of the chelate is very small. Such compounds are ineffective in diet, and in some cases toxicosis accumulate in tissues. Protein digestion and their products are good chelators, such as amino acids, which are building with metal chelates with the structure of typical five-member rings. From the chelating groups, especially the characteristic copper salts of amino acids, blue in color and beautifully crystallized are often used for the separation and identification of amino acids (Kessler et al., 2001; Ferketi et al., 2009; Huang et al., 2009). Feeds that are used bean in the diet, containing sufficient amounts of chelators, regardless to the specific added products. Such substances such as proteins, amino acids, peptides, starch and cellulose, citric and oxalic acids and other organic compounds of EDTA, a chelating properties and affect the metabolism of microelements. The key role of these compounds is to form soluble complexes and prevent insolubility of metals in weakly alkaline digestive tract (Donghua et al., 1995; Du et al., 1996; Hemken, 1997; Adamovic et al., 1997; Pupavac et al., 1999). Chelates are the most useful forms of metal and ligand interactions of the organism. In chelates, metal activity is increased by 10^5 to 10^7 in relation to the ionic state (Chernavina, 1970; Georgievski et al., 1982). Chelates benefits consist of greater physical stability, which reduces the separation of trace elements and vitamins in feed oxidation and increases there adoption. Transition of metal complexes are octahedral with the exception of Cu^{++} to form a twisted octahedron and with that achieves maximum stability.

MATERIALS AND METHODS

SIGNIFICANCE AND MINERALS RESORPTION

The content of microelements in feed often does not match animal needs for several reasons:

- Changing the genetic potential of animals in the direction of bigger and more meat animal productivity
- Reduced levels of microelements in feed.
- Nutrition knowledge on the importance of microelements in metabolism, reproduction, health maintenance and animal production.

Therefore, in conditions of intensive animal production it is essential to provide addition of minerals to the complete feed mixtures. The importance of microelements in addition to animal feed was observed last sixty years. Initially knowledge was limited to the application of inorganic mineral sources, and low utilization of minerals to address the increasing concentration in the diet, which are often resulted in an overdose, or waste of minerals (Manang et al., 2010; Guo et al., 2001). Today, as feed additives is used mineral chelates in a form of proteinates, minerals and amino compounds, or oligopeptides that are linked to better utilization of minerals in animals compared to inorganic sources and higher production. Normative needs of animals in microelements were determined as for most nutrients, according to the conducted experiments. In determining the need for such basic criteria are taken animal age, gender, body weight, intensity of production, type of diet, the possibility of diet consumption (Dibner, 2005; Dibner et al., 2007). But in the world today there are great differences in recommendations for individual nutrients. Review of certain recommendations by the regulations of complete feed mixtures in Serbia is given in Table 1. Recommended amounts of microelements differ according to literature sources. Deviations occur as a result of different amounts of microelements in the soil, and thus in plants.

Table 1. Microelements recommendation for complete feed mixtures, mg/kg

Microelement	Monogastric animals		
	Poultry	**Pigs**	**Horses**
Copper	6-8	20	10-19
Manganese	50-80	20-30	27-38
Zinc	30-60	100	38-43
Iron	30-40	100-120	48-62
Cobalt	-	-	0.1
Selenium	0.15	0.1	0.1
Iodine	0.5-0.8	0.5	0.1-0.5

(Ordinance on the quality and other requirements for feed, 2000).

In addition to provide minerals to animals, it is necessary to implement appropriate production technology of mineral premix that is added in the diet (Adamovic et al., 1997). This is particularly important, because of insufficient amounts of microelements, in the long run cause the deficit, and thus a negative impact on the reproductive potential animal health. Then, large amounts of certain microelements in relation to the optimal needs may have a variety of negative consequences, and ultimately fatal toxic end. This is especially related to heavy metals (lead, cadmium, and mercury). The problem to determine the optimal concentration of microelement is their interactions with each other due to an increase in one of microelements which may cause deficit of another. Natural fertilizers are the best way to supply microelements to the animals. They are in plants in organic form, which in comparison to other sources has the highest utilization. Important microelement content in the feedstuffs is shown in Table 2.

Table 2. Concentration of microelements in feedstuffs, mg/kg

Nutrient	Copper	Manganese	Zinc	Iron	Cobalt	Selenium
Corn, grain	2.2	7.2	12.4	43.0	0.8	0.02
Wheat, grain	11.0	32.0	31.0	50.0	4.3	0.06
Barley, grain	6.0	20.0	30.0	66.0	5.4	0.35
Soybean, grain	78.0	15.0	29.0	220.0	16.0	0.13
Soybean meal	14.6	35.3	31.0	290.0	1.4	0.13
Sunflower meal	27.6	39.0	61.0	289.2	0.8	0.08
Rapeseed meal	25.0	68.0	59.0	240.0	1.2	1.0
Alfalfa hay	8.2	31.5	21.5	420.0	1.4	0.5

Adamovic et al., 1997.

Far more important is the target mineral proteinates impact on specific functions of enzyme systems in the body, because they are absorbed intact. The absorption of minerals depends on the fate of the amino acid or peptide that is bound. Since different tissues and enzyme systems have different requirements for amino acids, mineral binding to specific amino acid or peptide with synthetic chelates increases the chance that adequate micronutrient be shipped to a specific tissue or enzyme system (Table 3), according to Du et al. (1996), Pupavac et al. (1999), and Stanacev et al. (1999).

Table 3. Target tissue of some copper chelates

Microelement	Amino acid	Tissue
Copper	Tryptophan	Muscle
	Lysine	Bone
	Histidine	Liver

SYNTHETIC CHELATES

Findings have contributed to microelements in the form of inorganic compounds bean gradually suppressed from the animal diet and bean replaced with chelates, which are already on the market or as a special type of EDTA chelates, which are added to diet. The efficiency depends on the chelate stability constants (Kratzer et al., 1959; Georgievski et al., 1982; Brown and Zeringue, 1994). If the stability constant of the complex is higher than the constant of the complex formed between microelements and diet components and lower, than the constants of complexes in animal tissues chelate will be effective. This area is well known in the animal feed industry for almost 40 years, and the products obtained during this period were distinguished by their characteristics. The original chelates had very high stability constants were practically useless. Newer versions are copies of natural compounds chelate that occur in the body, and their synthesis is used as a ligand proteins, peptides and amino acids. Synthetic chelates must be compatible with the body how they could be absorbed, and their stability is maintained at a certain pH level (Reddy et al., 1992; Brown and Zeringue, 1994; Huang et al., 2009; Manang et al., 2010). The research, which aimed to explore the possibility of including significantly lower levels of minerals, the introduction of organically bound forms in broilers diet had no any significant differences, indicating that much lower levels of minerals in organic form have positive impact on production performance of broiler chickens (Table 4). Today, the most commonly used chelates are Fe, Zn, Cu, Mn and Co, and the experimental results confirm the hypothesis that the chelates in the diet increases the absorption for adoption of microelements, which reflects the increase in growth, reproductive efficiency of animals and meat quality.

In addition to chicken nutrition, organic minerals found application in the diet of laying hens and parent flocks with significant improvement of production results (Table 5 and 6).

Table 4. Influence of organic and inorganic minerals on broiler chickens performance of 42 day age

Mineral form	Body weight, kg	Feed conversion
Inorganic (Cu+Fe+Zn+Mn+Se), 75.3 ppm	2.053	1.89
Organic (Cu+Fe+Zn+Mn+Se), 25.1 ppm	2.068	1.90

Alltech Yu d.o.o (2008)

Table 5. Influence of microelements on egg shell quality and layers persistence

Production parameters	Control group	Microelements*
Egg weight, g	62.25	62.75
Shell weight, g	5.71	5.90
Shell thickness, mm	0.361	0.366
Cracked eggs,%	3.56	2.98
Persistence,%	80.13	82.10
Egg firmness, N	29.45	29.99

Alltech Yu d.o.o (2008), *-Bioplex (Cu, Mn, Zn)

Table 6. Bioplex influence on productive performance of heavy hybrid broilers parents line

Production parameters	Control group	Bioplex
Total egg production/hen	109.05	110.96
Egg for incubation/hen	98.33	101.27
Consumption (kg/hen)	24.76	25.10
Egg fertility,%	86.80	87.39
Chickens/hen	85.35	88.50

Alltech Yu d.o.o (2007)

Based on these results it can be concluded that the use of organic minerals improves the performance have a significant economic impact throughout the growing season.

RESULTS AND DISCUSSIONS

EFFECT OF COPPER, IRON AND SELENIUM CHELATES IN PIGLETS AND FATTENIG SWINE PRODUCTION

The efficiency of the chelate is manifested in several ways, primarily through better absorption, higher mineral levels in serum, increased retention of minerals and higher levels of the enzyme. The use of these compounds in animal nutrition increasing production, improving product quality and reduce production costs (Stanacev et al., 1999). Coffey et al. (1994) performed a series of experiments with piglets for a period of 28-35 days in order to determine the efficiency of Cu-lysine compared to $CuSO_4$. In all experiments it was noted the improvement of physical indicators of production. Feed consumption increased by 4%, daily gain by 4.2% and feed conversion ratio for 10.6%. That same year, Zhou et al. (1994) compared the efficacy of copper from $CuSO_4$ and Cu-lysine in weaned piglets under conditions of *ad libitum* feeding. Piglets fed with a mixture of Cu-lysine consumed more feed by 29% and achieved a higher daily weight gain by 19%. The same trend was found in fattening pig nutrition. Stimulatory effect of 200 ppm Cu from different sources ($CuSO_4$ and Cu-lysine) was studied by Apgar and Kornegay (1996). The results of these studies show positive effects of Cu-lysine. Daily weight gain with the same feed intake was higher for 14.3%. Research Close (1998) show a better effect on piglets production in the period of 10-30 kg of body weight (Table 7). Piglets on treatment with 160 ppm Cu, 60 ppm which comes from $CuSO_4$ and Bioplex 100 ppm of Cu showed a 5.5% increase in feed consumption, improved daily gain by 10.8% and the efficient use of feed for 5.1% compared to the control group with copper sulphate.

Table 7. Effect of copper source in piglets and fattening swine production

Author	Animal category	Cu source	Weight gain*	Feed conversion*	Feed consumption*
Coffey et al., 1994.	Piglets	Cu-lysine	104.2	99.4	104.0
Zhov et al., 1994.	Piglets	Cu-lysine	119.0	-	129.0
Apgar and Kornegay, 1996.	Fattening swine	Cu-lysine	114.3	-	100.0
Close, 1998.	Piglets	$CuSO_4$ 60ppm Bioplex 100 ppm	110.8	94.8	105.5

-compared to $CuSO_4$

Addition of iron chelate forms in the form of Bioplex Fe in the diet of sows, 30 days before partus, leads to a significant increase in the concentration of iron in the blood serum and colostrum. In newborn piglets, there is no significant increase in the number of red blood cells and hemoglobin, because there was a significant increase in the concentration of iron in the blood serum and liver (Table 8).

With the increasing number of sows in gestation, there is an increasing loss of selenium, and it was found that the concentration of selenium in sows at the end of the third gestation is decreased by 10-20% compared with the approximate age of the animals, which are not farrowed, if they are fed with mixture of standard quality.

Table 8. Influence of chelated bonded iron (Bioplex Fe) in gravid sows in piglets anemia prevention

	Control	Bioplex Fe
Sows on a partus day		
Erythrocytes number x 10^{12}	5.99	5.65
Hemoglobin concentration, g/l	114.3	111.7
Fe concentration in blood serum, μmol/l	53.3	61.1
Fe concentration in colostrum, μmol/l	1.17	1.44
Piglets on a partus day		
Erythrocytes number x 10^{12}	3.97	3.97
Hemoglobin concentration, g/l	81.2	81.4
Fe concentration in blood serum, μmol/l	44.3	48.4
Fe concentration in colostrum, μmol/l	315.4	445.1

Kessler et al. (2001).

The biggest mobilization occurs during lactation when the metabolic needs are largest. Selenium plays an important role in the transfer of immunity in piglets, and therefore the maintenance of general health. From the research results of Janyk (1998), shown in Table 9, it can be seen that the piglets from sows fed with Sel-Plex had higher body weight and daily gain during the lactation period in contrast to the pigs on diet treatment with inorganic selenium.

Table 9. Influence of organic and inorganic selenium form on piglets performance

	Control	Inorganic Se (Na-Selenite)	Organic Se (Sel-Plex)
Born piglets	11.7	12.0	11.6
Live-born piglets	9.90	10.28	9.8
Mortality after weaning,%	15.49	13.08	10.54
Weaned piglets	8.37	8.94	8.77
Body weight after birth, kg	1.48	1.43	1.53
Daly bod weight gain, g	212.0	213.5	221.4

EFFECT OF ANTAGONISM BETWEEN MOLYBDENUM, SULFUR AND COPPER ON BROILER CHICKENS PERFORMANCE

Biogenic elements are chemically very active substance, so that their absorption and metabolism depend largely on the interactions that take place in the feed, the digestive tract, cells and tissues (Stanacev and Kovcin, 1998). Just a few years after establishment of stimulatory effect caused by high doses of copper, Pflander and Ellis (1960) finds that the molybdenum showed the same effect. The stimulatory effect of this element is attributed to microflora, since the component bacterial dehydrogenase molybdenum. Together copper and molybdenum may act in two ways, depending on their concentration, and the presence of mutual relations in the form of inorganic sulfate sulfur (Stanacev et al., 2001). Since these are two essential nutrients, very active chemically, absorption and metabolism of them depend heavily on the interactions that take place in the feed, the digestive tract, cells and tissues. Antagonistic elements have mutual interrelationships according to many researchers. Some of the interactions occurring at digestive tract, while the others run into the metabolism. With rough violation of element nutritional balance it can be expected heavy toll on health, due to the lack of enzymes which of they are activators (xanthine oxidase and ceruloplasmine). This violation occurs only when one of its elements exceeds the minimum toxic level of tolerance. Toxic surplus molybdenum deficiency causes secondary copper or copper-enzymes, and the consequences are anemia and depression of growth. These changes can be restored to normal physiological state supplementation with inorganic sulfur in the sulfate form, apart from increasing the copper content in the liver. To the level of copper in the liver were held constant, molybdenum and sulfur must be continually introduced into the body. In doing so, it builds insoluble molybdenum sulphide that is not absorbed and does not prevent the absorption of copper, and it is excreted from the body. Stanacev et al. (2001 and 2001a) in their investigation aimed to establish the effect of antagonism between copper, molybdenum and sulfur from sulfate on the production parameters of broiler chickens and copper accumulation in the liver (Table 10). The introduction of molybdenum and sulfur in diet with high levels of copper, 100 and 200 ppm had a positive effect on the growth intensity of broilers. Adding 50 ppm molybdenum and 50 ppm of sulfur in the mixture with 100 ppm of copper, at the end of the trial period, increased the body weight of chickens for 8.35% compared to the control group, while in the second fattening period, the group with addition of 100 ppm copper was most effective. From the results of Stanacev et al. (2001 and 2001a), it can be concluded that the microelements copper, molybdenum and sulfur from sulphate exhibit antagonism in the digestive tract of broilers, which is manifested by interference of copper absorption and synthesis of heavy soluble coppermolybdate, which reflects the accumulation of copper in the liver (Table 10).

Table 10. Copper concentration in chicken liver, ppm

Group	T1	T2	T3	T4	T5	T6
Cu	**0**	**100**	**100**	**100**	**200**	**200**
Mo	**0**	**0**	**50**	**50**	**0**	**50**
S	**0**	**0**	**0**	**50**	**0**	**50**
Initial day	52.51	52.51	52.51	52.51	52.51	52.51
6. day	37.03	44.15	24.10	26.05	69.77	39.93
13. day	40.63	54.75	30.35	32.75	83.90	51.30
20. day	34.88	41.68	16.55	17.73	59.60	26.30
49. day	22.48	28.60	15.10	16.20	30.75	24.08

Looking at the results shown in Table 10 is observed much lower concentration of copper in the liver in the presence of molybdenum, with and without the presence of sulfur, compared to groups that contained only copper in diet. This difference was statistically significant ($P < 0.01$).

CONCLUSIONS

Based on the presented data it can be concluded that the use of chelate mineral forms in pig and poultry is recent trend with increasing tendency due to the prohibition of the usage of antibiotics. Ban on antibiotics usage in animal nutrition led to the finding of different nutritional additives that can improve performance, animal health and meat quality intended for human consumption. Findings on the use of minerals chelated forms in animal nutrition is still limited, given the wide range of their activities, there is a need for further research in this area. Decision should be made whether to use more efficient, but more expensive mineral chelate forms taking into account the increasingly stringent demands of ecology and environmental protection.

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