



DEPOSITION OF ORGANIC TRACE METAL COMPLEXES AS FEED ADDITIVES IN FARM ANIMALS

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Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

Keywords: Copper, zinc, iron, manganese; metal complexes, feed additives, deposition

Trace elements are essential for maintenance and production of farm animals, but most of the feeding stuffs do not contain adequate amount of most of them, therefore to supplement them in complete feed with trace elements is necessary. However, the rate of absorption and tissue deposition of trace elements from different complexes is also different which may have food safety aspects because of the maximum level of some trace minerals. The present review, based on scientifically proved results, discussions about the rate of absorption and deposition of different metal (Cu, Zn, Fe and Mn) proteinates, amino acid chelates (e.g. lysine, methionine, methyl-hydroxy-methionine) and humic acid complexes of trace elements. The results showed that metal proteinates have higher rate of tissue accumulation as compared to inorganic salts, and additionally some metal-proteinates (e.g. copper-proteinate) also improves the tissue deposition of manganese. Metal propionates, as possible new trace element supplements have positive effects on the rate of absorption which was proved by the higher blood serum levels. In the case of humic acid chelates there are some results about their positive effects on bioavailability of trace minerals but those were not scientifically proved. In conclusion it can be stated that organic metal complexes have better bioavailability than their inorganic counterparts, in particular modern farm animal genotypes with higher requirement level and also in stress conditions.

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iron may be deposited in the heart and kidneys.⁶ Generally, livestock do not accumulate extremely high levels of manganese in their tissues when excess manganese is fed.⁶ Manganese concentrations in edible tissues linked with the dietary manganese intake.

Introduction

Trace elements are essential elements for maintenance and production of farm animals, because they are constituents of hundreds of proteins involved in intermediary metabolism, hormone secretion pathways, and immune defense systems.¹ However, most of the feeding stuffs do not contain adequate amount of most of the trace minerals,^{2,3,4} therefore supplementation of complete feeds with trace elements is necessary. However, the bioavailability and tissue deposition of trace elements is different from different sources, which may have food safety aspects because of the maximum level of some trace minerals. Knowledge on typical concentrations and accumulation in edible tissues and products of the element is an important tool for risk assessment and consumer protection.

For instance copper concentrations are highest in most of farm animals in the liver, and are related to the dietary intake, whereas muscle concentrations are more conserved.⁵ Normal liver copper concentrations are higher in ruminants than in pigs and chickens, and also found that relatively small amounts of dietary copper greatly increase liver copper concentrations in ruminants. Excess intake of zinc leads to an higher deposition in the liver, pancreas, kidney, and bone. Concentrations in milk and skeletal muscle of various species are more conserved.⁶ Zinc concentrations in edible tissues linked with dietary intake of various zinc compounds and doses.⁷ When animals are exposed to excessive amounts of iron, it is preferentially deposited in the liver, spleen, and bone marrow. With very high doses,

Inorganic trace mineral supplementation of the diets of farm animals result in a high level of mineral excretion. Obviously, this is not only wasteful but also harmful to the environment. For example, poultry manure, applied on a nitrogen basis, contains Zn and Cu approximately 66 and 56%, respectively, above the level of crop requirements.⁸ As compared to Cu, Mn, and Zn, Fe increased linearly with increasing intakes of these trace minerals, as was found in a poultry experiments.⁹ However, a noticeable reduction in Zn and Cu (but not Mn or Fe), excretion could only be achieved by dietary manipulation.^{10,11} There are contradictory results in respect of trace mineral excretion, as in a trial with broiler chicken the replacement of inorganic copper or iron with amino acid chelates decreased by 34% and 5-21% of Cu and Fe respectively, in the excreta,¹² but in another one a partial or complete replacement of inorganic with amino acid chelates of iron, copper, zinc and manganese at the rate of 25, 50, 75 and 100% in the diets but did not find consistency in decreasing values of the above mentioned trace element content of the excreta. However, the reduction was significant in laying hens.¹³

Inorganic salts of trace elements usually have poor bioavailability, primarily because of the numerous nutrient and ingredient antagonisms that impair absorption.¹⁴ In contrary organic metal complexes with small peptides (refer as proteinates), lysine, methionine or methyl-hydroxy-methionine chelates,¹⁵ propionates¹⁶ and humic acid chelates¹⁷ have higher bioavailability.¹⁸ The higher bioavailability in the case of chelates probably based on the ring structure of such chelates which protects trace minerals from chemical reactions in the gastrointestinal tract, and

keeps its stability even at low pH. Additionally, chelates carry negative charge therefore they are more effectively pass through the intestinal wall, and by different other routes, mainly by the amino acid transport system than inorganic compounds. The rate of passive diffusion is higher because of the less interaction between the mineral and other nutrients. This alternative pathway for absorption is leading to a reduction in the excretion. However, in the case of propionates two postulations are available about their absorption. The first is that metal-propionates absorb as complex, and the other one is that before absorption the complex hydrolyse and absorb independently the metal ion and propionate.¹⁸ Higher rate of relative bioavailability of the so-called organic forms of trace minerals has been proven, among others, in the case of copper, zinc, manganese and iron.¹⁷ Chelated zinc increased by 35% more broiler chicken tibia mineral content, manganese chelate bioavailability is about 1.2 times of its sulphate; iron has a bioavailability of 1.3-1.85 times of its inorganic form.²¹

Copper complexes

Relative bioavailability of different copper compounds in poultry as compared to CuSO_4 in poultry was Cu-Lys: 114%; Cu-Met: 92%; Cu-proteinate: 108%,¹⁹ in piglets CuCl_2 : 118%; Cu-Met: 85% and Cu-Lys: 105%²⁰ and in ruminants (sheep and cattle) Cu-Lys: 104%.¹⁹

In a mineral balance study with pigs²³ the diet was supplemented with 0, 50, or 100 mg kg^{-1} copper as Cu-proteinate, or 250 mg kg^{-1} as CuSO_4 . There were linear increases ($P < 0.001$) in Cu absorption, retention, and excretion with increasing Cu-proteinate. Pigs fed 100 mg kg^{-1} copper as Cu-proteinate absorbed and retained more and excreted less Cu than pigs fed 250 mg kg^{-1} copper as CuSO_4 . Blood plasma copper concentrations increased linearly with increasing Cu-proteinate. However, 50 or 100 mg kg^{-1} copper as Cu-proteinate increased Cu absorption and retention, and decreased Cu excretion with 77 and 61%, respectively, as compared to 250 mg kg^{-1} copper as CuSO_4 .

In broiler chicken the most sensitive indicator is the tibia which is showed a linear increase of its copper content with the dose, but the rate of increase depends on the Cu salt or complex. Organic complexes, such as Cu-proteinates showed higher rate of accumulation as compared to in-organic salt (CuSO_4). The results also indicated that organically-complexed copper demand the actual requirement at lower dose than inorganic salt²⁴. However, in other trial¹³ partial or complete replacement of inorganic Cu with amino acid chelate at the rate of 25, 50, 75 and 100% in the diets did not increase significantly the tibia copper content.

Zinc complexes

Relative bioavailability of different zinc compounds in poultry as compared to ZnSO_4 and based on the tibia Zn content was ZnO: 85 %; Zn-Met: 133 %; Zn-proteinate: 120 % and Zn-propionate: 126 %, ^{19,25,28} in piglets ZnO: 55-87 %; Zn-Lys: 83%; Zn-Met: 99 % and Zn-proteinate: 100 %^{19,26} and in ruminants (sheep and cattle) Zn-Lys:102 %; Zn-Met: 109 % and Zn-proteinate: 112%.¹⁹

The bioavailability of zinc from different sources also depends on the composition of the diet. For instance higher phytate and fibre content reduce the bioavailability of zinc from sulfate, whereas zinc in the form of Zn-Met was protected from their negative effect²⁸.

Humic acid complexes of zinc did not increase the zinc accumulation in muscle, kidney, liver and blood plasma, which means that humic acid do not have positive effect on bioavailability of zinc as compared to ZnSO_4 .²⁹ That negative result is contrary to a few previous findings where it was found that humic acid has high bivalent cation binding capacity in the order of $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$ and improves their absorption. However, it also has been found that the interaction of humic acid with metal ions in solution increases with pH and humic acid concentration³⁰ whereas decreases with metal ion concentration.

In weaned piglet nutrition zinc-oxide used as antibacterial compound against gastrointestinal diseases at high dose (2000 mg kg^{-1} feed as zinc)³¹ but it resulted high rate of zinc excretion through feces, while zinc-methionine at the dose of 200 mg kg^{-1} feed as zinc reduce the occurrence of diarrhea at the same rate.³²

In broiler chicken the Zn content of tibia showed a linear increase with the dose of Zn-proteinate but even at the highest dose did not lead to a higher concentration as in the case of inorganic salt. However, zinc concentration reached a plateau at a lower concentration level. This probably due to a smaller exchangeable pool of zinc from organic complexes, which mobilize more efficiently during the high growth phase of fattening period than from inorganic source.²⁵ In contrary another trial¹⁴ partial or complete replacement of inorganic Zn with amino acid chelate at the rate of 25, 50, 75 and 100 % in the diet did not increase significantly the tibia zinc content.

Zinc as zinc propionate was more effective than inorganic zinc salts or zinc-acetate, for the induction of moulting. Additionally zinc propionate resulted quick recovery, and more yields after the moulting period. It suggested that zinc propionate is more effective, and less toxic, zinc source for moulting induction than inorganic or even some organic compounds.³³

There are few reports available about the effect of different zinc complexes in ruminants. Zinc-methionine chelate increased significantly the activity of Cu/Zn superoxide-dismutase activity in dairy cows as compared to the same dose of ZnSO_4 . Higher rates of incorporation of zinc to metallo-enzymes, such as superoxide-dismutase, probably due to the higher by-pass rate of Zn-Met through rumen passage.³⁴ This higher rate of incorporation of Zn-Met into zinc metallo-enzymes would be the cause, that this Zn-chelate improves the reproductive traits (fewer days to conception after calving) of high lactating dairy cows.³³ Zinc propionate also recommended using as zinc complex for dairy cows because of its significantly higher rate of absorption, as determined by blood plasma zinc level after bolus intake, than other zinc sources.³⁴

Iron complexes

Relative bioavailabilities of different iron compounds in piglets, as compared to ZnSO₄, are as follows: Fe-fumarate: 95-100 %; Fe-proteinate: 110-122 % and Fe-Met: 177-184%.²²

In broiler chicken the Fe content of tibia did not show increase with the dose of Fe-proteinate, and iron excretion increased with the dose, but it was lower, but not dose-dependent manner and significantly than using inorganic salt. Which means iron has no exchangeable pool of iron in tibia, or that iron content of the basal diet was higher than the actual requirement which resulted dose-dependent rate of excretion.^{13,25}

In laying hens replacement of inorganic iron with 75 or 100 % iron amino acid chelate in the diet significantly decreased the iron content of the liver.¹³

Manganese complexes

Relative bioavailability of different manganese compounds in broiler chickens based on tibia deposition as compared to MnSO₄ as follows: MnO: 127 %; Mn-Met: 110 %; Mn-Met-hydroxy analogue: 114 %.³⁵ Similar tendency was found based on an ileal absorption study with broiler chicken³⁶ and on the basis of tibia manganese content in piglets MnO: 85 % and Mn-Met: 120 %, respectively.²² However, it should be noted that in the above mentioned studies the Mn content of the diets was higher than the maximum permitted level in the EU countries legislation.

Bioavailability of Mn from Mn-proteinate seems to affect by, among other factor, some adverse situations, such as; it was found that the bioavailability of Mn-proteinate showed much higher values (125-140%) as compared to MnSO₄ in heat-stressed broiler chickens.²²

Tibia content is generally accepted as a suitable indicator of manganese levels of animals. In contrary to that some trials showed that partial or complete replacement of inorganic Mn with amino acid chelates at the rate of 25, 50, 75 and 100% in the diets did not increase the tibia manganese content¹³. Additionally a novel manganese chelate, Mn-methionine hydroxyl analogue also did not result in significant higher tissue concentration than MnSO₄ at the same dietary levels³⁶. The same tendency was found using tibia manganese content in laying hens and piglets and excretion in milk as indicator³⁷.

Conclusions

In conclusion, based on scientifically proved data, it may be assumed that organic metal complexes usually have better bioavailability than their inorganic counterparts in most of farm animal species. This is important for better demand for the requirement of trace minerals of modern farm animal genotypes in particular in adverse conditions, and also important for decreasing the environmental load with manure.

Acknowledgements:

The publication is supported by the TÁMOP-4.2.2.B-10/1-2010-0011 and TÁMOP-4.2.1.B-11/2/KMR-2011-0003 projects. The projects are co-financed by the European Union and the European Social Fund.

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Received: 29.10.2012.

Accepted: 07.11.2012

