When are Chelated Minerals Justified?

Robert J. Harmon

There is increased interest in micronutrient nutrition in modern dairy and beef operations. The primary reasons are the associations established with micronutrient status and immunity, disease resistance, and reproduction. Selenium, vitamin E, copper, and zinc, in particular, have been shown to play a role in some or all of these physiological functions (Harmon et al., 1994; Kellogg ,1990; Scaletti et al., 1999; Smith et al., 1985; Smith et al., 1984; Xin et al., 1991). Of course clinical deficiencies may be problematic for proper growth and production, but subclinical or marginal deficiencies are now widely recognized as a limiting factor for optimum immune function, disease resistance, and perhaps reproductive efficiency. An area of micronutrient nutrition that has received increased attention is the inclusion of organic trace minerals as a portion of the mineral supplement.

Why Organic?

The basic reason for the use of organic forms of trace minerals is the reported increased bioavailability of organic vs inorganic sources of the minerals. Although published reports have been quite variable when comparing organic and inorganic mineral availability, some evidence exists for advantages to supplementation with organic minerals. Clark et al. (1993) showed that beef cattle supplemented for 84 d with equal amounts of Cu in the form of Cu proteinate, Cu sulfate, or Cu oxide had liver Cu contents of 79.3, 56.8, and 34.3 mg/kg DM at the end of the supplementation period. These cattle had received Cu oxide previously, but still showed signs of Cu deficiency. Cao et al. (2000) evaluated eight commercially available organic zinc products for relative bioavailability in chicks or lambs. In lambs, bioavailability estimates relative to 100% for Zn sulfate were 130, 110, and 113 for one Zn proteinate product, Zn amino acid chelate, and one Zn methionine product, respectively.

In general, it appears that organic trace minerals are useful and provide some advantage in situations involving antagonistic minerals, e.g. high levels of Mo, S, Fe, or Zn interfering with the availability of Cu. Water quality must be considered when mineral antagonists are suspected. Organic minerals may be indicated in the following situations: 1) dry period of dairy cattle, 2) periparturient dairy cattle, 3) during stress (calving, transport, dramatic changes), and 4) in advance of breeding (30 to 60 d). Nockels et al. (1993) showed in stressed cattle that calves fed Cu lysine had 53% greater apparent Cu absorption and increased Cu retention compared with calves fed Cu sulfate. Numerous controlled studies or field trials have been run to evaluate the impact of organic minerals on somatic cell counts (SCC) in milk and udder health.

Organic Minerals, Mastitis, and Somatic Cell Counts

Studies at the University of Kentucky (Harmon et al., 1998) evaluated effects of Cu proteinate on copper status, udder infections of heifers at calving, and response to *E. coli* J-5 vaccination. Thirty-one primigravid Holstein heifers were maintained on a basal (6-7 ppm Cu; **-CU**) diet or diets supplemented (10 ppm) with either copper proteinate (**CUP**; Bioplex, Alltech, Inc.) or copper sulfate (**CUS**) beginning 120 d prepartum through about 60 d of lactation. All animals are vaccinated with *E. coli* J-5 bacterin at -60 d, -30 d, and at calving. Liver biopsies and blood samples were taken during the trial for liver and blood minerals and plasma ceruloplasmin (**Cp**). Serum was analyzed for titers to *E. coli* J-5. Table 1 shows mean liver Cu analyses throughout the trial. The CUP supplement showed an advantage over CUS at restoring Cu stores, particularly at the critical periparturient period. Liver Cu was higher (P<.07) in the CUP group than in the CUS group at calving. Interestingly, evaluation of overall mean liver and plasma Cu contents and plasma Cp activities tend to support the idea that organic Cu supplements have increased bioavailability over that of inorganic forms in periparturient heifers (Table 2). As expected, the overall mean liver Cu was about 2-fold higher in both CUP and CUS groups than that in -CU animals.

Table 1. Mean liver copper levels in heifers with no Cu supplementation (- CU) or supplemented with 10 ppm copper proteinate (CUP) or copper sulfate (CUS) from 120 d pre- to 60 d postpartum.

Days relative to parturition	**Dietary supplementation**		
	- CU	**CUP**	**CUS**
	------------------- ppm DM[1] -------------------		
- 120	68.4	59.1	62.2
- 90	77.2	116.7	130.3
- 60	87.7	164.3	184.8
- 30	103.8	236.9	209.4
Calving	99.3	291.3	225.3
30	132.5	307.3	247.5
60	93.3	280.1	306.9

[1] N; -CU=10, CUP=10, & CUS=11.

Table 2. **Overall mean (±SEM) liver and plasma Cu contents and plasma ceruloplasmin activities in heifers that received no copper (-CU), copper proteinate (CUP), or copper sulfate (CUS) supplementation 120 d prepartum to 60 d postpartum.**

Parameter	Dietary supplementation[1]		
	- CU	CUP	CUS
Liver Cu (ppm)[a]	81.4±7.6	169.6±14.9	173.6±13.4
Plasma Cu (?g/ml)[b]	.73±.01	.75±.01	.73±.01
Plasma Ceruloplasmin (IU/L)[a]	60.3±2.0	60.8±2.4	65.4±2.3

[a] Significant treatment effect, P<.01.

[b] Significant treatment effect, P<.02.

However, plasma Cu was highest (P<.07) in CUP animals, especially at calving (Table 3). This is in contrast to Cp activities which only responded to the CUS (Table 3).

Table 3. **Plasma Cu contents and plasma ceruloplasmin (Cp) activities in heifers that received no copper (-CU), copper proteinate (CUP), or copper sulfate (CUS) supplementation 120 d prepartum to 60 d postpartum.**

Days relative to calving	Plasma Cu (?g/ml)			Plasma Cp (IU/L)		
	-CU	CUP	CUS	- CU	CUP	CUS
-30	0.69	0.74	0.65	51.7	63.5	61.4
0	0.90	1.05	0.89	77.1	82.9	83.9
30	0.76	0.82	0.83	58.7	63.8	81.3
60	0.70	0.75	0.76	57.8	62.8	87.3

Cp is reported to be the major Cu transport protein produced in the liver. The blood Cu and Cp data suggest the CUP can affect plasma Cu levels without marked stimulation of Cp. The suggestion is that CUP may be taken up and/or transported via a different mechanism than inorganic forms of Cu.

Table 4 gives a summary of infection status at calving for all 31 heifers. A higher proportion of quarters were confirmed uninfected and fewer were infected with coagulase-negative staphylococci (considered a minor pathogen) in CUP (P<.01) compared with -CU and CUS groups. The higher percentage uninfected quarters in CUP-supplemented heifers compares with previous studies at Kentucky which showed similar results when 20 ppm copper sulfate was supplemented in the diets of prepartum heifers. Although CUP and CUS animals had higher (P<.05) percentage quarters infected with major pathogens than the -CU group, only 5, 5, and 1 infection were present in CUP, CUS, and -CU groups, respectively. Preliminary results of titers to *E. coli* J-5 do not suggest an obvious advantage among the dietary treatments.

Data addressing the specific mechanisms of Zn in resistance to mastitis are limited. Zn deficiency in ruminants has been postulated to weaken skin and other stratified epithelia (i.e. keratinocytes) as well as reducing the magnitude of increase of basal metabolic rate following infectious challenge (reviewed in Suttle and Jones, 1989). Because the mammary gland is essentially

a skin gland and the importance of the keratin lining of the streak canal in prevention of infection is known, speculation that Zn supplementation may enhance resistance to mastitis is tempting. Most studies in this area have focused on reduction of SCC during supplementation of organic forms of Zn. Kellogg (1990) summarized results of eight trials evaluating effects of Zn-methionine compared with equivalent amounts of Zn oxide and methionine. Overall, supplementation of Zn-methionine (180 or 360 mg Zn, 360 or 720 mg methionine) resulted in 22% decrease in SCC when feeding the lower level. Feeding the higher level of Zn-methionine lowered SCC by 50%. However, decreased SCC were not observed in another study of Zn-methionine supplementation.

Table 4. Quarter infection status (% quarters) of heifers at calving (d 1-3) that received no copper (-CU) supplement or supplementation with 10 ppm copper as proteinate (CUP) or sulfate (CUS) for 120 d prepartum.

Bacteriological results	Dietary supplementation[1]		
	- CU	CUP	CUS
Negative	47.5^{a}	67.5^{b}	45.5^{a}
CNS	27.5^{a}	7.5^{b}	31.8^{a}
Major pathogens	2.5^{c}	12.5^{d}	11.4^{d}
Other	0	5.0	2.3
Unclassified[2]	20.0^{c}	2.5^{d}	9.1^{e}
Mixed infection	2.5	7.5	4.5

CNS = coagulase-negative staphylococci.

Major pathogens = *S. aureus*, *Streptococcus* spp. and coliforms.

[1] - CU = 10 cows; CUP = 10 cows; CUS = 11 cows.

[2] Quarters from which duplicate milk samples yielded dissimilar culture results.

[ab] Values within a row with different superscripts differ, P<.01.

[cde] Values within a row with different superscripts differ, P<.05.

A limited number of studies have evaluated the effects of organic Zn on new mastitis cases. Galton (1990) saw no effect of Zn-methionine on rate of new infections resulting from experimental challenge with *Streptococcus agalactiae*, although SCC were significantly decreased in supplemented cows. In contrast, Spain (1993) reported beneficial effects of Zn proteinate (providing 50% of a total 800 mg Zn per cow per day as proteinate) on rate of new, naturally occurring intramammary infections. No effects of Zn proteinate supplementation on SCC or milk yield were observed compared with Zn oxide. However, numbers of new infections were doubled in the Zn oxide group compared to the proteinate supplemented animals (11 vs 5 new infections). The majority of isolates were environmental mastitis pathogens. Spain (1993) suggested that organic Zn is beneficial in enhancing resistance to mastitis pathogens because of the postulated role of Zn in maintaining skin integrity and the keratin lining of the streak canal.

Several studies have demonstrated a reduction in SCC in dairy cattle which were supplemented with combinations of mineral proteinates (Table 5). Harris (1995) reported results of a 90-day field trial in which one group of 70 cows received a TMR supplemented with 400 mg Zn per cow per day as Zn proteinate and the control group was fed the normal TMR. The mean SCC in the Zn proteinate group decreased 24% and the SCC in the control group increased 36%; SCC was 57% lower in the group supplemented with Zn proteinate at trial end. Adjustment for the lower SCC in the proteinate group at initiation of the trial would still show an estimated 30 to 40% lower SCC in the Zn proteinate cows. Boland et al. (1996) reported the results of three different trials in which a combination of mineral proteinates were supplemented to normal dairy cow diets; the control diet was the same as the proteinate-supplemented diet but without the mineral proteinates (Table 5). The mineral proteinates (Zn, Cu, and selenium yeast) provided the following supplemental minerals per cow per day in the diets during all three trials: Cu, 100 mg; Zn, 300 mg; Se, 2 mg). Blood mineral profiles were normal for both groups suggesting mineral status was adequate in both groups and unaffected by the supplements. In the groups receiving mineral proteinates in the three trials the SCC were reduced by 52%, 45%, and 35% over the duration of the trial. In the last trial SCC were reduced 52% during the final 4 weeks. Boland et al. (1996) indicated that these

Table 5. Influence of mineral proteinate (Bioplex) supplementation on somatic cell counts.

Form of proteinate supplemented	Mineral supplied daily as proteinate	% reduction in SCC	Reference
Zn	400 mg	57% (~ 40%; adjusted)	Harris, 1995 (n = 70 per group)
Cu Zn Se	100 mg 300 mg 2 mg	52%	Boland et al., 1996 (n = 7 per group)
Cu Zn Se	100 mg 300 mg 2 mg	45%	Boland et al., 1996 (n = 28 per group)
Cu Zn Se	100 mg 300 mg 2 mg	35%; wk 0 to 12 52%; wk 9 to 12	Boland et al., 1996 (n = 23 per group)

data showed a greater improvement in SCC the longer the treatment continued. Overall the results of these studies suggests a beneficial effect of organic mineral supplementation on SCC in the herd and, thus, on udder health.

Organic Minerals and Reproduction

Selenium and vitamin E have long been known to impact reproduction. A 1984 study (Harrison et al.) evaluated the effects of injections of 0.1 mg Se per kg BW at d 21 prepartum, dietary supplementation with 1000 IU vitamin E per cow per day for 21 days prepartum, both Se and vitamin E, or no treatment. Incidence of retained placenta was zero in cows receiving both Se and vitamin E compared with an average of 17.5% in the other groups. Incidence of metritis was 60% for cows receiving Se and 84% for those not receiving Se. Cystic ovaries were diagnosed in 19% of cows injected with Se and 47% for cows not treated with Se.

More recently the use of organic trace minerals has been evaluated for the impact on fertility. In a dairy study referred to previously, Boland et al. (1996) found that cows receiving organic trace minerals (Cu, Zn, and Mn proteinates and Se yeast) had a non-significant reduction in days to emergence of the first dominant follicle (7.8 vs 9.3), 5 fewer days to first ovulation, and 6 fewer days to first service. First service conception rate improved from 57.7% to 65.2%.

Fallon et al. (1993) showed that superovulated, cross-bred heifers receiving organic Cu, Zn, and Mn supplementation displayed a significant 8.5% increase in fertilization rate and a 36% increase in the numbers of fertilized embryos. Britt (1996) has suggested that supplementation of organic trace minerals in diets of superovulated cows resulted in increases in the number of transferable embryos per flush and a marked increase in the number of Grade I embryos collected. These observations coupled with positive observations in the field suggest that the use of organic trace minerals in dairy diets may play a beneficial role in reproductive performance.

Summary

It appears that organic trace minerals may have a place in dairy and beef diets when situations involving mineral antagonisms are encountered. In addition, organic mineral supplementation may be considered in the following situations: 1) dry period, 2) periparturient dairy cattle, 3) during stress (calving, transport, dramatic changes), and 4) in advance of breeding (30 to 60 d). A general recommendation is the inclusion of 25 to 30% of the supplemented mineral in an organic form, especially when proper supplementation with inorganic sources of trace mineral has not been effective.

References

Boland, M.P., G. O'Donnell, and D. O'Callaghan. 1996. The contribution of mineral proteinates to production and reproduction in dairy cattle. Page 95 in Biotechnology in the Feed Industry. T.P. Lyons and K. Jacques, ed. Nottingham University Press, Nottingham, UK.

Britt, J.S. 1996. Update on the effect of nutrition on embryo transfer results. Presented at 1996 AETA Meetings.

Cao, J., P.R. Henry, R. Guo, R.A. Holwerda, J.P. Toth, R.C. Littell, R.D. Miles, and C.B. Ammerman. 2000. Chemical characteristics and relative bioavailability of supplemental organic zinc sources for poultry and ruminants. J. Anim. Sci. 78:2039.

Clark, T.W., Z. Xin, Z. Du, and R.W. Hemken. 1993. A field trial comparing copper sulfate, copper proteinate, and copper oxide as copper sources for beef cattle. J. Dairy Sci. 76 (Suppl. 1):334.

Fallon, R.J., R. Matovani, J.F. Roche, and M.P. Boland. 1993. Effect of proteinated minerals and yeast culture on fertilization in superovulated heifers. Irish J. Agicul. Food Res. 32:111.

Galton, D. 1990. Effect of feeding Zinpro® to lactating dairy cows on udder health. Zinpro Technical Bulletin # D-8911.

Harmon, R.J., T.W. Clark, D.S. Trammell, B.A. Smith, K. Akers, P.M. Torre, B.E. Langlois, and R.W. Hemken. 1994. Copper status and mastitis in heifers with or without prepartum copper supplementation. J. Dairy Sci. 77(Suppl. 1):198.

Harmon, R.J., D.S. Trammell, B.A. Smith, and R.W. Scaletti. 1998. Effects of dietary copper insufficiency and sources of dietary copper on copper status and intramammary infections at calving. J. Dairy Sci. 81 (Suppl. 1):43.

Harris, B. 1995. The effect of feeding zinc proteinate to lactating dairy cows. Page 299 in Biotechnology in the Feed Industry. T.P. Lyons and K. Jacques, ed. Nottingham University Press, Nottingham, UK.

Harrison, J.H., D.D. Hancock, and H.R. Conrad. 1984. Vitamin E and selenium for reproduction of dairy cows. J. Dairy Sci. 67:123.

Kellogg, D.W. 1990. Zinc methionine affects performance of lactating cows. Feedstuffs 62:15.

Nockels, C.F., J. DeBonis, and J. Torrent. 1993. Stress induction affects copper and zinc balance in calves fed organic and inorganic copper and zinc sources. J. Anim. Sci. 71:2539.

Scaletti, R.W., D.S. Trammell, B.A. Smith, and Harmon, R.J. 1999. Role of dietary copper in enhancing resistance to coliform mastitis. J. Dairy Sci. 82 (Suppl. 1):35.

Smith, K.L., H. R. Conrad, B. A. Amiet, and D.A. Todhunter. 1985. Incidence of environmental mastitis as influenced by dietary vitamin E and selenium. Kieler Milchwirtschaftliche Forschungsberichte 37:482.

Smith, K.L., J.H. Harrison, D.D. Hancock, D.A. Todhunter, and H. R. Conrad. 1984. Effect of vitamin E and selenium supplementation on incidence of clinical mastitis and duration of clinical symptoms. J. Dairy Sci. 67:1293.

Spain, J. 1993. Tissue integrity: A key defense against mastitis infection: The role of zinc proteinates and a theory for mode of action. Page 53 in Biotechnology in the Feed Industry. T.P. Lyons, ed. Alltech Technical Publications, Nicholasville, KY.

Suttle, N.F. and D.G. Jones. 1989. Recent developments in trace element metabolism and function: Trace elements, disease resistance and immune responsiveness in ruminants. J. Nutr. 119:1055.

Xin, Z., R.W. Hemken, D.F. Waterman, and R.J. Harmon. 1991. Effects of copper status on neutrophil function, superoxide dismutase, and copper distribution in steers. J. Dairy Sci. 74:3078.