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Micronutrient Sources And Agronomic Responses

Ray B. Diamond

Micronutrient fertilization has been recognized as an important part of crop production in some locations for several years. As crop production is intensified and more concentrated primary nutrient fertilizers are used, micronutrient fertilizers will become a more important consideration for efficient crop production. This paper lists several important sources of the micronutrients, discusses factors affecting their availability to plants, and gives examples of the relative agronomic effectiveness of several sources.

Properties and Reactions: Properties of micronutrient sources vary considerably. Sources may be completely water soluble or very slightly soluble. Inorganic sources may be supplied as relatively pure compounds, mixtures of compounds containing one or more micronutrients, or mixtures with non-micronutrient compounds. Organic sources are available as synthetic chelates or natural organic complexes of metal ions. Inorganic salts are also incorporated into a glass-like matrix (frits) to delay their release. Therefore, one classification of micronutrient sources is: (1) Inorganic salts, (2) Synthetic chelates, (3) Natural organic complexes, and (4) Fritted micronutrients.

Inorganic Salts: Sulfates of Cu, Fe, Mn, and Zn and borates and molybdates are the most common sources of micronutrients. In general, these forms are more soluble than others in the inorganic class. Several common inorganic salts used as micronutrient fertilizers are listed in table 1. The concentration of element in a source varies because of the degree of hydration of a compound or the relative purity.

Boron sources used most are sodium tetraborates with various levels of hydration which result in B concentrations of 11 to 20 percent. These materials are relatively water soluble but highly soluble boric acid or sodium octaborate (Solubor) are often used as foliar sprays. Calcium borate is the least soluble of the B materials listed. Incorporation of sodium tetraborates into conventional granular fertilizers does not affect the water solubility of the B (1, 2) although the hydrated borates react with superphosphate and release water which causes problems in granulation (3). Anhydrous sodium tetraborate is suitable for granulation with superphosphate. The sodium borates are soluble in fluid N and mixed fertilizers and may be applied in this way. Due to the narrow range between deficiency and toxicity of B, it must be uniformly mixed with macronutrient fertilizer when applied this way to prevent locally high concentrations in the soil.

Table 1. Inorganic Sources of Micronutrients.

Common or Trade Name	Percent of Element
Boron:	
Borax	11
Borate-46, Agribor, Tronabor	14
Borate-65	20
Boric acid	17
Solubor	21
Calcium borate	10
Copper:	
Copper sulfate	25-40
Basic copper sulfate	53
Copper oxide	60-86
Copper carbonate	52
Iron:	
Ferrous sulfate	20-37
Ferric sulfate	20-28
Ferrous ammonium sulfate	16
Nu-Iron (oxalate)*	30
Maganese:	
Manganous sulfate	22-35
Manganous oxide	30-65
Manganous-manganic oxide	69
Manganous carbonate	27-46
Basic manganous sulfate	53
Manganous chloride	43
Molybdenum:	
Sodium molybdate	39-46
Ammonium molybdate	56
Molybdic oxide	47-66
Zinc:	
Zinc sulfate	22-36
Zinc oxide	60-80
Zinc carbonate	56
Zinc oxysulfate	52
Zinc chloride	50
Zinc nitrate (fluid)	15
Zinc manganese ammonium sulfate	15
Zinc ammonium sulfate	10

*The metallic salt of an organic acid is commonly classified as inorganic.

Ammonium and sodium molybdate are the primary sources of Mo. They are water soluble while molybdic oxide is slightly soluble. Molybdenum is applied with seed, as foliar spray, or mixed with fertilizer, lime, or gypsum.

Sulfates of heavy metal micronutrients can be granulated for blending with macronutrient fertilizers. Water insoluble forms are not suitable sources in granular form because of the small surface area exposed for reaction in soil. Several of the relatively insoluble sources are applied as powders alone to the soil, incorporated in fluid or granular macronutrient fertilizers, and coated on granular fertilizers. Methods of incorporating micronutrients in fertilizers were discussed by Young (4).

Inorganic sources of Mn and Zn form insoluble reaction products when applied with macronutrient fertilizers having a saturated salt solution of relatively high pH (5, 6). Acid-forming fertilizers are better carriers of Mn and Zn than non-acid-forming fertilizers. Ammoniation during production decreases the solubility of Zn (7, 8). Reaction products of Zn with triammonium pyrophosphate (a major component of ammonium polyphosphate fertilizers) are more soluble than with ammonium orthophosphate (5) while the opposite is true with Mn (6). Copper is used as the sulfate and oxide. The effects upon solubility of mixing Cu sources with macronutrients have been studied very little, but it is likely that behavior in many situations would be like Zn. Soil applications of inorganic Fe sources are generally ineffective for crops because Fe is easily changed in unavailable forms in soil. Recent work has shown some promise in maintaining ferrous and ferric sulfates in an available form in soil when applied with fluid ammonium polyphosphate fertilizers (9).

Synthetic Chelates: A chelating agent is a compound (usually organic) which can combine with a metal ion in such a way that a ring structure is formed between a portion of the chelating agent molecule and the metal. This combination prevents the metal ion from reacting with other substances to form insoluble compounds. A chelate is the compound formed by the combination of chelating agent and metal. Commercially available synthetic chelating agents and the concentration of micronutrient in chelates of each are shown in table 2. The general stability sequence of these chelates of micronutrients and Ca decreases as follows: Fe^{+++} - Cu^{++} - Zn^{++} — Fe^{++} — Mn^{++} — Ca^{++}.

However, factors other than relative stability of metal chelates determine the relative quantities present in a given set of conditions. The relative stability of ferric chelates decreases in the order of EDDHA > DTPA > EDTA > HEEDTA > NTA while the stability of these chelates of the other ions listed above decrease as follows: DTAP > EDTA HEEDTA > NTA > EDDHA (10). In other words, EDDHA chelation of Fe is greatly favored over the other micronutrients.

Generally, the stability of metal chelates is greater near neutral than at low or high pH. This is an important consideration in incorporation of metal chelates into macronutrient fertilizers. Mixing ZnEDTA with phosphoric acid prior to ammoniation resulted in a breakdown of the chelate but adding ZnEDTA with the ammoniating solution left a stable chelate (11).

According to Wallace (10), the important reactions of metal chelates in soils are: release of the metal, fixation on clay, and metal substitution. Resistance to microbial breakdown and mobility on many soils make them useful sources of micronutrients.

Natural Organic Complexes: Many naturally occurring organic compounds contain chemically reactive groups similar to synthetic chelating agents. Those used commercially to complex micronutrients usually are prepared from byproducts of wood pulp industries. Metal chelates of these compounds have relatively lower stablity than the common synthetic chelates. Also, these chelates are more readily broken down by microorganisms in soil. The natural organic complexes of micronutrients are lower in cost than synthetic chelates and can be economically used in many situations. Most are suitable for foliar sprays and mixing with fluid fertilizers. Some common natural organic complexes of micronutrients are shown in table 3.

Fritted Trace Elements: Frits are micronutrient fertilizers prepared by fusing inorganic micronutrient compounds into a silicate matrix. The materials are slowly soluble in soil, but the rate of dissolution is controlled to some degree by varying the particle size and the composition of the matrix. A wide range in micronutrient concentration may be produced, and more than one micronutrient may be included in a fritted material. Fritted materials may be incorporated in granular fertilizer or applied separately.

Plant Availability: Crop uptake of applied micronutrients depends upon the source and physical state of the micronutrient, type of carrier, method of inclusion with the carrier, method of application, nature of the soil, and characteristics of the crop. Probably the most important property of a micronutrient source is water solubility. Water-soluble sources are agronomically effective when applied in the granular state while insoluble materials are not. Several relatively insoluble sources are solubilized in soil and thus are available to plants when applied in powdered form. The method of application of micronutrients which are relatively mobile in soil is not critical while less mobile micronutrients are more available when distributed in the rooting zone. Soil characteristics influence micronutrient availability through their effects upon solubility and mobility of the nutrient. The crop may influence the apparent availability of micronutrients because of its rooting pattern, nutrient requirement, and specific ability to take up the nutrient.

In the remainder of the paper, the above principles for various sources of micronutrients will be illustrated. However, because of limited research data on source comparisons of some micronutrients and the lack of published agronomic data on most of the natural organic complexes, these areas are necessarily incomplete Also, much data on source comparisons is of limited usefulness because criteria necessary for evaluation of sources were not met in the experiments. To determine the relative effectiveness of fertilizer sources (macronutrient or micronutrient), the following conditions must be met: (1) A positive response to the nutrient in question must be obtained. (2) Growth-limiting

Table 2. Synthetic Chelates.

Chelating Agent	Micronutrient Content, Percent Element			
	Cu	Fe	Mn	Zn
EDTA	7-13	5-14	5-12	6-14
HEEDTA	4-9	5-9	5-9	9
NTA	-	8	-	13
DTPA	-	10	-	-
EDDHA	-	6	-	-

Table 3. Common Natural Organic Complexes Commercially Available.

Company	Trade Name	Micronutrient*				
		Cu	Fe	Mn	Zn	Multiple
Brandt Chemical Company	Claw-El	X	X	X	X	X
Davies Nitrate Company	Danitra	X	X	X	X	X
Georgia Pacific	Ke-Min		X		X	X
Kaiser Agricultural Chemical	Key-El	X		X	X	X
MacAndrews and Forbes Company	Silviplex	X	X	X	X	X
Rayonier, Inc.	Rayplex	X	X	X	X	X
West Virginia Pulp and Paper Company	Reax	X	X	X	X	

*Range of elemental concentration—4.5 to 14.5 percent.

Table 4. Response of Corn to Zinc Sources, Physical State, and Placement in Greenhouse Experiments.

Applied Zn		Relative Yield1			
Physical State	Source	Zn at 1.6 Mg./Pot		Zn at 6.4 Mg./Pot	
		Mixed	Placed	Mixed	Placed
	None	29	29	29	29
Solution	$ZnSO_4$	91	40	100	46
Solution	Zn-Rayplex	89	50	92	61
Solution	ZnEDTA	96	86	89	96
Powder	$ZnNH_4PO_4$	92	26	87	27
Granular	$ZnSO_4$	54	34	43	32
Granular	Zn-Rayplex	37	26	46	39
Granular	ZnEDTA	107	80	96	94
Granular	$ZnNH_4PO_4$	29	21	44	20

1. $ZnSO_4$ solution at rate of 6.4 mg./pot = 100.

Soil Sci. Soc. Amer. Proc. 30:86-89. 1966.

Table 5. Relative Agronomic Effectiveness of Granular Macronutrient Fertilizers as Carriers of Zinc From Zinc Oxide and Zinc Sulfate.

Macronutrient Fertilizer	Agronomic Effectiveness for Forage Yield[1] $ZnSO_4$	ZnO
Ammonium nitrate	59	8
Urea	40	12
Ammonium polyphosphate	78	70
Monoammonium phosphate	75	24
Concentrated superphosphate	93	91
Diammonium phosphate	20	15
Ammoniated superphosphate	17	13
Ammonium phosphate nitrate	19	12
Nitric phosphate	11	7
Urea-ammonium phosphate	8	8
Ammoniated N-P-K (0 percent)[2]	48	-
Ammoniated N-P-K (10 percent)[2]	49	-
Ammoniated N-P-K (30 percent)[2]	40	-
Ammoniated N-P-K (40 percent)[2]	18	-
Ammoniated N-P-K (50 percent)[2]	6	-
Ammoniated N-P-K (100 percent)[2]	2	-

1. Relative to finely divided $ZnSO_4$ or ZnO which equals 100.
2. Formulated from ammonium sulfate, ordinary and concentrated superphosphates, potassium chloride, and zinc sulfate. Numeral in parentheses is degree ammoniation of superphosphates.

J. Agr. Food Chem 17·1,2, 2-1,275. 1969.

factors other than the nutrient in question must be minimized. (3) One treatment must be a zero rate of the nutrient in question. (4) More than one nonzero rate of the nutrient from each source must be included; one of these rates should be less than that needed to obtain optimum response.

Obviously, the data must show a response to the nutrient and the applied rate must be low enough to permit possible differences to be expressed. Unfortunately, these points are often forgotten.

Boron: Boron in soluble forms can be leached from sandy soil when rainfall is relatively high. Under these conditions, it may be necessary to make repeated applications of soluble sources of B or use a slowly soluble source. Winsor (12) reported leaching and toxicity problems with borax. Borax at the lowest rate of application gave a slight increase in yield but higher rates were quite toxic. Boron deficiency symptoms with borax treatments occurred as the season progressed. Calcium borate was less toxic than borax but was solubilized too readily to supply B throughout the season without reaching toxic levels in midseason. Borosilicate was less toxic than either of the other sources and supplied adequate levels of B when applied at a rate equivalent to about 3 pounds of B per acre.

On soils where leaching is less of a problem, maximum yields during the year of application may be obtained with a single application of borax. This was illustrated by Ovellette (13). Also, he showed that alfalfa response was good to residual B from frit of fine particle size 3 years after it was applied to soil. There was no response where borax had been applied 3 years earlier. Calcium borate was intermediate in effectiveness for supplying residual B.

Boron is incorporated in several commercial fertilizers. Mortvedt (1, 2) has shown that incorporation of sodium tetraborate in granules of nitric phosphate and concetrated superphosphates does not appreciably change the solubility of B. Similar responses of alfalfa and corn to borax alone and incorporated in concentrated superphosphate were shown (2).

The sodium tetraborates cost from 50 cents to 80 cents per pound of B.[1]

Copper: Copper sulfate and oxide are applied separately and in combination with macronutrient fertilizers. Crop responses were good to these sources applied separately or in combination with fertilizers on organic soils where Cu deficiency occurs most often (14). There appears to be little agronomic data on responses to Cu chelates, and it is questionable whether there is an agronomic need for organic sources of Cu. However, chelates or complexes may be desirable to incorporate adequate levels in fluid fertilizers. Current prices of Cu from $CuSO_4$, CuO, and CuEDTA are about $1, 70 cents, and $5 per pound of Cu, respectively.

1. Approx. costs supplied by Dr. John Mortvedt, TVA, Muscle Shoals.

Iron: Inorganic sources of Fe generally are agronomically ineffective as soil applications. Crop response to the sulfates are sometimes obtained at extremely high rates. Mortvedt and Giordano (9) recently have shown responses of greenhouse-grown sorghum to ferric and ferrous sulfates when applied in fluid ammonium polyphosphate fertilizers. The data illustrates the lack of response to the inorganic sources applied alone and that these sources incorporated in fluid ammonium polyphosphate fertilizers are about 50 percent as effective as FeEDDHA (the most effective of the soil-applied Fe sources). Field trials are being conducted in Kansas, Nebraska, and Oklahoma to determine the practical significance of these findings. The relative effectiveness of 3 common Fe chelates was shown by Boxma and DeGroot (15). The results appear to be typical of those in many reports showing that FeEDDHA is the most effective source of soil-applied Fe in calcareous soils. However, FeEDTA is effective on acid soils and FEHEEDTA on slightly alkaline soils. One pound of Fe costs about $40 in FeEDDHA, about $15 in FeDTPA, $5 in FeEDTA, and about 25 and 30 cents in $FeSO_4$ and $Fe_2(SO\ )_3$.

Manganese: The inorganic Mn sources except MnO_2 are agronomically effective. Shepherd et al. (16), obtained no difference among sulfate, oxide, carbonate, and frit sources tested for onions on a muck soil. MnEDTA generally appears to be no more effective than inorganic sources of Mn; on organic soils it is sometimes less effective. Apparently, the ineffectiveness of MnEDTA is due to rapid substitution of Fe for Mn in the chelating agent and subsequent fixation of Mn by soil organic matter (17). Recent greenhouse work indicates that MnDTPA may be more effective than MnEDTA (15). Leaching experiments showed that considerably more Mn was maintained in a soluble form when MnDTPA was applied rather than when MnEDTA was applied. The relative prices of MnO, $MnSO_4$, and MnEDTA are 15 cents, 30 cents, and $5 per pound of Mn, respectively.

Molybdenum: Mo deficiencies occur most often in legume crops grown on

acid soils In many instances, Mo fertilization is a substitute for liming since neutralizing soil acidity increases the availability of soil Mo. This substitution is probably justified in some cropping situations, for example, in clover pasture where rough terrain makes it almost impossible to apply lime and in a rice-soybean rotation if it is undesirable to raise the soil pH. Ammonium and sodium molybdate, as well as molybdic oxide, are effective sources of Mo when applied as seed treatment, foliar sprays, separately, or with macronutrient fertilizers. These sources must be uniformly applied to prevent toxicity. Toxicity to animals eating forage of high Mo concentration is the greatest problem, although toxicities to plants have been observed. Recommended rates of Mo is around 1 ounce per acre. The cost is about $2.25 to $2 50 per pound of Mo.

Zinc: More research effort has been placed on Zn fertilization than on all other micronutrient problems. Likely, this results from the widespread occurrences of Zn deficiencies and the many sources of Zn available on the market. Since Zn is relatively immobile in soil, factors which affect solubility and distribution within soil greatly affect availability to crops. Some of these factors are solubility and particle size of materials applied, method of application, and reaction products formed in soil. The relative mobility of the classes of Zn sources were shown by Sorensen et al. (18) by leaching studies in soil columns. ZnEDTA was maintained in a water-soluble form and leached through the soil columns by excessive water, while Zn-Rayplex and $ZnSO_4$ moved about 4 inches into the soil; ZnO remained in the upper 1 inch of soil. Movement of other relatively insoluble materials such as Zn frits and $ZnNH_4PO_4$ would be similar to that of ZnO. This effect of mobility on availablity to plants was shown by Brown and Krantz (19). Table 4 was equally effective when applied in solution or granular form and mixed or spot placed. The other sources were equal to ZnEDTA when solutions or powders were mixed with soil but less effective when applied in granular form or spot placed.

Concentration of Zn in granules also influences distribution within soil and agronomic effectiveness of the source. Mortvedt and Giordano (11) calculated that 1,040, 26, and 2 granules of -8+9 mesh size per square foot containing 0.05, 2.0, and 36 percent Zn, respectively, will provide 1 pound of Zn per acre. They also calculated from Zn movement studies that granules containing 0.5, 2.0, and 8.0 percent Zn in concentrated superphosphate influenced Zn levels in 5.0, 1.2, and 0.3 percent of the soil in pots when Zn was applied at a rate of 1 ppm.

Soil pH has a great effect upon the solubility of Zn. Terman et al. (20), showed yield and Zn uptake decreased with rising soil pH and that the effectiveness of several P sources as carriers of Zn was related to their influence on soil pH.

TVA researchers have completed a considerable amount of work comparing macronutrient fertilizers as carriers of several sources of Zn. In general, the effectiveness of Zn both applied alone and in carriers is related to its water solubility, particularly when granulated and/or spot or band placed in soil. The relative effectiveness of several combination of carriers and sources are shown in table 5. The relative effectiveness of some P carriers of ZnEDTA, Zn Rayplex, fritted Zn, and a finely ground Zn alloy were studied by Mortvedt and Giordano (21). The carrier had no effect on the availablity of ZnEDTA which was an effective source of Zn. Other sources were less effective although ammonium polyphosphate and concentrated superphosphate appeared to be satisfactory carriers of Zn-Rayplex and Zn frit.

Approximate costs of ZnO, $ZnSO_4$, and ZnEDTA are 15 cents, 35 cents, and $3 per pound of Zn, respectively.

Summary: The agronomic efffectiveness of micronutrient fertilizer sources is dependent largely upon the interrlationships of product solubility, particle size, and placement or distribution in soil Generally, limiting distribution in soil through increasing particle size, increasing concentration in granules, or band application reduces the effectiveness of relatively immobile forms of micronutrients as compared to greater contact with soil. Limiting distribution of the more mobile chelated forms of micronutrients has little effect upon the availability to crops. In selecting sources of micronutrients to use, one should consider cost per pound of element, the adaptability of sources to the desired cropping and fertilization system, and the relative quantity of element required from various sources for the application system chosen.

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for TVA's nation- of fertilizer introduction and education programs. He received the B. S. degree in agronomy from Ohio State University and the M. S and Ph.D. degrees in soils from the University of Florida. He joined TVA in 1963 and since 1964, has given guidance in planning, evaluating, and reporting of projects for evaluating new fertilizers and determining crop response to macro-, secondary, and micronutrients. He has worked closely with cooperating land-grant universities in the evaluation of ammonium polyphosphates and micronutrient sources and carriers Currently, his work includes coordinating the evaluation of a new controlled-release nitrogen fertilizer, sulfur-coated urea

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