

MICRO-NUTRIENT FORMULATIONS FOR AGRICULTURE

Part-II. Copper, Zinc, Manganese and Chromium Preparation

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Micro-nutrient formulations for agriculture purposes have been produced mounting copper, zinc, manganese and chromium on five different fritted compositions. Release of elements was monitored by extracting the metals with ammonium citrate solution and estimating them by means of an atomic absorption spectrophotometer. The results show that release of copper can be controlled at a level of 1.4 to 4 ppm, that of zinc at 1.7 to 5.2 ppm, manganese at 1.8 to 8.6 ppm, while that of chromium at 0.02 to 0.3 ppm, by leachings, spread over a period of one hour to 10 days.

Key words: Micro-nutrients, Agriculture, Slow release nutrients.

Introduction

In spite of several attempts to improve the yield per hectare, Pakistan has not been able to achieve the target commonly attained by advanced countries. The main reason for the failure to achieve a breakthrough is the deficiency in supply of the major agricultural inputs like water, fertilizers and pesticides. Both macro and micro-nutrients are essential to get a proper yield of crops. The amount of zinc, copper, manganese, chromium etc., the major micro-nutrients which are taken up by the crops, seems insignificant when compared with macro-nutrients, yet a deficiency of just one of these trace elements can have such a devastating effect on crops as may be experienced by the deficiency of a macro-nutrient. According to surveys, 85% of the soil samples collected from the four provinces of the country are either at a marginal level or are deficient in zinc and copper [1-3]. According to Sillanpää [4] a widespread deficiency of Zn and B in the soils of Pakistan is indicated and low availabilities of Cu and Mn are reported in various locations. Khattak and Perveen [5] have also reported a deficiency of Cu, Zn, Fe and B in different places of the country. This, in the absence of extensive surveys, suggests that the soils might also have only marginal quantities of other trace elements like manganese and chromium, if at all it is not deficient in them.

The availability of elements from the soil to the crops remains variable perhaps because of the large number of interacting constraints. To do away with problems of this kind some such formulations should be available which by applying in only a few hundred gram quantities could contribute desired elements to make up for need of the soil and plants. In an earlier paper, six different methods for preparation of micro-nutrient formulations were reported placing individual elements in different lattice and environment [4].

It is known, however, that a single element cannot be suggested to compensate for the deficiency of one crop or crops of different nature. The practice, therefore, is to either broadcast in the soil a single formulation containing a mix of needed elements or to use a number of formulations, each representing a different element. Both preparations have their advantages and disadvantages. The advantages of the mixed formulation are that too many preparations are avoided and the same material, if unused, can provide the elements over and over again. The disadvantage of such preparations is that a certain element though not needed is also available and taken up by the plant under environmental constraints. This may prove detrimental to its growth.

It is already known [6-13] that rice crops respond to Zn; citrus plants to Zn, Cu and B; maize, sorghum, cotton, sunflower and sugar-beet to Zn and B while potatoes respond to Mn, Fe in different parts of the country. For these reasons it is believed that sustained release of elements should be the criterion and not their number. It, perhaps, is not important to have the same element in a large quantity because it could limit the growth of crops. A number of elements in small quantities on the other hand could be beneficial if they are within the range of stimulating the growth.

In the previous paper [14] the preparation of frits and non fritted compositions containing Cu and Cr was reported. The mounting media were frits; red clay, plaster of paris, cement sand mixture and plaster of paris - sand mixture. The main reason for the choice of silicate frits was that they are the least soluble. It was concluded from the study that raw, non-fritted or non-sintered compositions releasing higher quantities may be used in single crops requiring high concentration while the fired and fritted compositions should be suitable for crops/plants requiring low but regular amount of micro-nutrients in

the micro-environment. Having optimised conditions for preparation of the frits, it is intended to report the production of compositions containing four metals viz, Cu, Cr, Zn and Mn mounted on different proportions of red clay and soda ash and to study their release characteristics, assuming that the mix of elements would stimulate the growth of plants.

Experimental

Five micro-nutrient formulations were prepared using mounting carriers mentioned in Table 1. The ingredients such as soda ash and red clay were ground to pass through a 100 mesh sieve. Mixture 'A' containing metal oxides in fixed proportion of 29.949 g ZnO, 23.790 g MnO₂, 1.5034 g CuO and 1.757 g Cr₂O₃ was added to mixture 'B' containing red

clay and soda ash in varying proportions as mentioned in Table 1.

One gram each of different fritted compositions was taken in separate plastic bottles containing 20 ml of 1.0 N ammonium citrate solution. The contents of the bottles were kept stirring during entire experimentation. The solutions were filtered at designated time intervals ranging from one hour to 10 days. The release of metals viz, Cu, Zn, Cr and Mn in all compositions was determined with the help of a computerised Atomic Absorption Spectrophotometer.

Results and Discussion

The data compiled in Table 2 and depicted in Figs. 1-4 suggest that the frits start releasing the metal ions with the commencement of leaching process. The release of all metal ions is low ranging from a minimum of 0.18 to a maximum of 8.65 ppm in 240 hrs. The maximum is noted for Mn. This bears out the earlier conclusion that metals are placed in a firm lattice. The variations in release characteristics are likely to occur with a change in the amount of soda ash.

The release of Cu (Fig. 1) ion for formulations III, IV and V increases only slowly from first to the 24th hr and, thereafter, it is slightly more marked. At the end of the 3rd hr. the release among five compositions decreases in the following order: II > I > III > IV > V; at the end of the 24th hr, it changes to II > I > III > IV > V, whereafter the release from III and IV is

TABLE 1. RAW MATERIAL COMPOSITION FOR PREPARATION OF FRITS

Mixture No.	Composition of					
	A				B	
	ZnO (g)	MnO ₂ (g)	Cr ₂ O ₃ (g)	CuO (g)	Red clay (g)	Soda ash (g)
I	29.949	23.790	1.757	1.5034	180	20
II	29.949	23.790	1.757	1.5034	170	30
III	29.949	23.790	1.757	1.5034	165	35
IV	29.949	23.790	1.757	1.5034	160	40
V	29.949	23.790	1.757	1.5034	150	50

TABLE 2.

Composition No.	Metal released	1hrs ppm	2hrs ppm	3hrs ppm	4hrs ppm	6hrs ppm	12hrs ppm	24hrs ppm	36hrs ppm	48hrs ppm	72hrs ppm	168hrs ppm	240hrs ppm
I	Cu	1.5	1.4	1.4	1.4	1.4	1.5	1.7	2.3	3.2	3.0	3.5	3.8
	Zn	4.6	4.9	4.7	4.9	4.9	4.9	5.2	2.9	2.9	2.9	2.9	2.9
	Mn	3.1	3.2	3.2	3.8	3.4	3.5	3.8	5.64	6.42	6.67	6.94	8.112
	Cr	0.02	0.08	0.08	0.1	0.14	0.15	0.16	0.16	0.165	0.17	0.17	0.18
II	Cu	0.5	1.90	2.2	2.4	2.2	2.2	2.4	4.0	4.4	4.5	4.6	4.7
	Zn	3.8	3.8	4.0	4.3	4.6	4.1	4.0	3.2	3.21	3.2	3.1	3.0
	Mn	1.8	2.5	2.8	2.7	2.8	2.7	2.9	4.82	5.46	5.81	6.62	7.744
	Cr	0.14	0.14	0.15	0.15	0.16	0.165	0.167	0.168	0.175	0.21	0.23	0.25
III	Cu	0.6	0.6	0.7	0.7	0.8	0.8	0.9	1.4	1.6	1.6	1.7	2.8
	Zn	3.4	3.4	3.5	3.6	3.7	3.8	4.6	3.3	2.9	2.9	2.9	2.6
	Mn	2.0	2.0	2.1	2.2	2.4	2.4	2.6	4.50	4.81	4.71	5.51	7.105
	Cr	0.08	0.09	0.09	0.11	0.11	0.12	0.125	0.13	0.13	0.16	0.18	0.2-3
IV	Cu	0.5	0.5	0.6	0.6	0.6	0.7	0.9	1.3	1.4	1.4	1.5	1.7
	Zn	3.9	3.0	3.8	3.9	4.1	4.6	4.6	3.1	3.1	3.1	3.1	3.1
	Mn	2.2	2.2	2.6	2.4	2.6	3.0	3.0	5.59	5.51	5.53	6.49	7.93
	Cr	0.12	0.12	0.12	0.12	0.15	0.16	0.24	0.24	0.26	0.29	0.30	0.30
V	Cu	0.5	0.5	0.5	0.5	0.6	0.7	0.8	1.1	1.2	1.4	1.5	1.4
	Zn	4.3	4.3	4.3	4.5	4.6	4.9	5.0	3.1	3.1	2.7	2.7	2.7
	Mn	2.1	2.5	2.6	2.7	2.6	2.8	3.2	3.90	5.94	6.40	8.10	8.65
	Cr	0.08	0.09	0.1	0.14	0.15	0.15	0.16	0.21	0.25	0.29	0.29	0.31

Note: The values given in this table are cumulative.

the same but in others, slight increase is noticeable at the end of the 240th hr. Apparently the diminution in concentration in the leaching is due to the increase in alkalinity contributed by increasing proportion of soda ash in the frits.

The maximum release of Zn (Fig. 2) from each of the five compositions is observed in the first 24 hrs of extraction, whereafter there is a sharp decline. At the 3rd hr of leaching, the order to release is as follows: I > V > II > III > ; after the 24th hr it was to I > V > III > IV > II > and at the 240th hr it is IV > II > I > V > III >. The differences among the values at the 24th hr for III, IV and II and for all compositions at the 240th hr leaching, are not very significant. However, Fig. 2 does reveal some characteristic variations: the maximum for I, III and V is attained in 24th hr while for II and IV it is attained in 12 hrs. The sharp decline from the maximum is noted at the 36th hr. and levelling off of these values thereafter. Solubility behaviour of trace fertilizer elements as studied by Katyal and tandhawa [6] shows that solubility of Zn, Cr, Cu and Mn decreases with increase in pH. This phenomenon is very marked above pH 6

for Cu, Cr and Mn and below pH 6, these three are very freely soluble while for Zn decrease in solubility with the increase of pH occurs even below pH6. This is why Zn release curves (Fig. 2) show abrupt decrease in solubility after 24th hr due to increase in pH to approximately 5.5. The starting pH in all cases in release experiments for Cu, Cr, Mn and Zn was 5.

The maximum release of Mn (Fig. 3) in the first 24 hrs is noted to be 3.8 ppm from composition I; in all other cases it lies between 2.6 to 3.2 ppm. The rise in concentration is small in the first 24 hrs as may be seen from Fig. 3, where a flattening of the curve is noted for this period. In contrast with zinc a sharp rise is noted in each case hereafter. At the 3rd hr the release is in the following order: I > II > IV > V > III; at the 24th hr it changes to I > V > IV > II > III and at the 240th hr to V > I > IV > III > II. However, the differences as noted from Fig. 3 suggest that the release from I is rather anomalous otherwise the values obtained are in accord with the alkalinity of micro-environment of the metal.

The release of Cr (Fig. 4) is very small in each case as was expected of frits or sinters with some soda ash reported earlier [14]. The maximum release of 0.14 ppm is noted in case of composition II in the first hour but the maximum does not go beyond 0.31 ppm for V in 240 hrs. The sharp rise or fall in

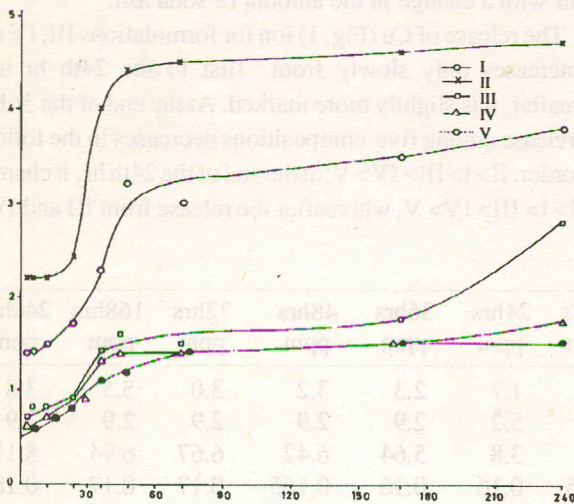


Fig. 1. Release of Cu.

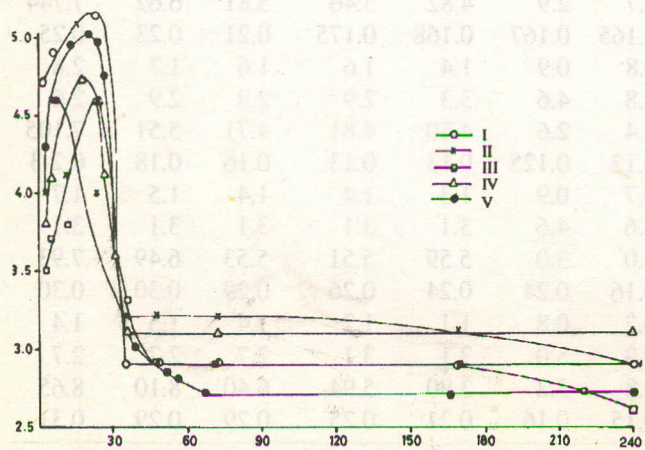


Fig. 2. Release of Zn.

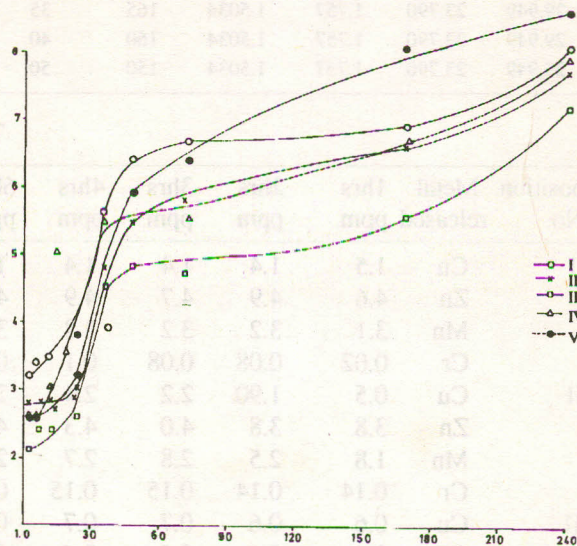


Fig. 3. Release of Mn.

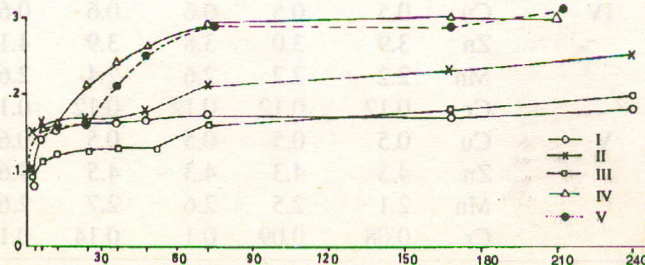


Fig. 4. Release of Cr.

release as noted in other ions after the 24th hr is spread over 72 hrs in this case. At the 3rd hour the release recorded is in the following order: II>IV>V>III>I which changes to IV>II>V>I>III at the end of 24 hrs and to V>IV>III>II>I at the end of 240 hrs which is the descending order of alkalinity. This supports the previous conclusion that metal is encased in firm lattice. Higher alkalinity in micro-environment, introduced apparently by increasing quantity of soda ash in the mix makes the metal more accessible to the solvent action of ammonium citrate.

It may be seen from the descending order in concentration of metal ions in the leachings that the release of Cu depends on alkalinity of composition, the higher alkalinity, the lower the release. Similar is also the case with zinc where the concentration of ion rises in first 24th hours but decreases thereafter, and at the 240th hr it is almost the same in all leachings. Further investigations seem necessary in this area to know the reasons for constancy of concentration but buffer of the medium seems to be mainly responsible for this observation. Mn concentration in leachings increases with time in each composition and at the end of 240th hr the descending order suggests higher efficiency of composition V followed by I and the remaining three lower only in degree.

The release of metals in a mixed frits composition release very small quantities which according to reported data are within critical as well as toxic limits. For example, Katyal and Randhawa [6] have found that 20 ppm Zn can limit the yields of wheat, cotton, rice and maize, while concentrations higher than 150 ppm can prove toxic. Similarly, 181 ppm of Mn and 9 ppm of Cu are the normal values for maximum wheat output. The range of critical values for this crop is: 20 ppm Zn, 27-216 ppm Mn and 8-20 ppm Cu; for rice the range is 21-50 ppm Zn and 25-200 ppm Mn while for maize, the range is 21-70 ppm Zn, 18-54 ppm Mn and 5-30 ppm Cu. The essentiality of Cu was reported by Sommer [7] and was, later on, confirmed by Arnon [8]. Excess Cu in water culture solutions, sand culture or even in the field, commonly induces iron-chlorosis symptoms in plants [9] but the range for normal growth in most plants usually falls between 5 and 20 ppm.

Chromium is not one of the essential micro-nutrients, but as described earlier, it has a definite role in nitrogen fixation. Further more it has been supported that Cr at 5-10 ppm. in nutrient solution produced iron chlorosis in oat plants and it has also been found that with 16 ppm of Cr in cationic form reduced the growth by 10%, 50-70%, 70-90% of the control plants of tomato, oats and kale respectively [10]. Schropp [11] found a stimulation of growth of corn seedlings in solution cultures using upto 0.5 ppm of chromic ion, toxicity at 5 ppm and very little growth at 50 ppm. Saunder [12] found that 5 ppm of chromium ion in sand culture was decidedly

toxic to tobacco and its 10 ppm concentration to corn in sand culture soils.

These observations, therefore, suggest that the quantity of metals released is far below their toxic limits and critical values. The experimental observations also suggest that there is a definite correlation between the alkalinity of frits and the release characteristics. The release of copper and chromium is directly proportional to the amount of soda ash in the composition prepared for obtaining frits.

Conclusion

Frits, prepared with a mixture of red clay, metal oxides and soda ash in increasing quantities, have been evaluated for their leachability under field conditions. It is observed that their extraction is rapid in first 24 hrs and levels off thereafter. All the frits have a firm lattice except possibly III whose Cr extraction is similar to that noted for the chromium sinter using red clay and 10% of soda ash and was attributed to the presence of a firm lattice. The presence of a number of elements does not seem to constrain the release of metals which are solubilized in a uniform manner, characteristic of individual frits. This indicates that it is more important to prepare a melt which can effectively disperse and dissolve the metal oxide to form a homogeneous mass and assure a firm lattice. In case the lattice is not homogenous erratic release may be observed.

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