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IMPACT OF FOLIAR APPLICATION OF ZINC ON CURCUMIN AND MACRO AND MICRO ELEMENTS DISTRIBUTION IN CURCUMA LONGA

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Abstract

The present study was carried out to investigate the interaction of foliar applied zinc in the form of zinc hydroxy nitrate suspension with other elements in *Curcuma Longa* plants. The impact of the zinc application on the quality of turmeric was also estimated. The plant samples for our experiment were collected from Lam Dong province, Vietnam. Seven suspension solutions of nanosized zinc hydroxide nitrate whit different Zn concentration were used as Zn containing foliar fertiliser. Irrigation and fertilisation were the same for all variants. The Zn content and the content of selected micro (Cu and Fe) and macro (K, Ca, Mg, and P) elements in the plant's rhizome were determined by ICP Spectrometer "Prodigy 7" after digestion of the samples in the Mars 6 microwave system. Separation and quantification of curcuminoids were accomplished with liquid chromatography.

It was concluded that the content of Cu and Fe and macronutrients varies narrowly in the plant roots, with no significant impact of ZnHN fertilisation. The results for curcuminoids are too different, and their amount increases with the zinc content.

Keywords: zinc fertilisers, *Curcuma Longa*, micro and macro elements, curcuminoids.

INTRODUCTION

Zinc (Zn) is one of the eight microelements (along with manganese, copper, boron, iron, chlorine, molybdenum and nickel) that are essential for normal and healthy plants and plant reproduction. The mean Zn concentration in plant tissues is in the range of 15 - 80 $mg.kg^{-1}$ (Marschner, 1995). Its physiological role in plants is associated with its participation in many enzyme systems (superoxide dismutase, carbonic anhydrase, dehydrogenases and other), protein synthesis, the integration of cell membranes, etc. (Alloway, 2008). A Zn deficiency in plants causes many structural and functional disorders such as increased membrane permeability, a high concentration of active oxygen forms, a reduced photosynthetic rate, and growth restriction, etc. Correcting this deficiency can be achieved through soil or foliar fertilisation. One of the most promising nanosized foliar fertiliser is zinc hydroxy nitrate with the following composition: $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ (D. Vu, 2013)**.**

Turmeric isolated from the plant of *Curcuma longa* is the main source of curcuminoids, a yellow in color, having the specific flavour attributed from its volatile compounds, and has been used as a spice for the early time of human civilization. *Curcuma Longa* (*C. longa*) is a root crop belonging to the family *Euphorbiaceae* and is a small herb well known for its medical properties. It has been used widely in various traditional medicines to treat swelling, sores, jaundice, inflammatory diseases, kidney disorders, diabetes and viral hepatitis as bitter, astringent, stomachic, diuretic, febrifuge and antiseptic. Apart from the rhizome's richness in curcuminoid pigments and essential oils, it also contains carbohydrate, protein, mineral and other essential elements (Olojede et al., 2019). It grows in the tropical and subtropical climate over well-drained sandy-loam soils. The majority of soils in these regions are deficient in available zinc. The need for zinc fertilization triggered the necessity for studying the interaction effects of Zn with other plant nutrients in soils and plants. The object of our investigation was to investigate the interaction of foliar applied zinc in the form of zinc hydroxy nitrate (ZnHN) suspension with other elements in *Curcuma Longa* plants. The impact of the zinc application on the quality of turmeric was also estimated.

MATERIALS AND METHODS

Methods

The zinc hydroxide nitrate was prepared by pouring KOH solution into $Zn(NO_3)_2.6H_2O$ solution under vigorous stirring. The initial sodium hydroxide/Zn ratio was 1.6 and the time for precipitation - 30 minutes. The resulting white suspension contained 15.0% $Zn_5(OH)_8(NO_3)_2.2H_2O$ (7.9% Zn).

Zn content and the content of selected micro (Cu, Fe) and macro (K, Ca, Mg, and P) elements in the plant's rhizome after digestion of the samples in the Mars 6 microwave system were determined by ICP Spectrometer "Prodigy 7". Separation and quantification of curcuminoids were accomplished on ELITE LaChrome (Hitachi) Liquid Chromatograph with DAD. The method parameters are listed in Table 1. The calibration curve was linear, with a correlation of 0.9997.

Table 1. Instrument parameters for quantification of curcuminoids

Temperature	**30°C**
Injection amount	20µl
Detection	370nm
Flow rate	1,3 ml/min
Mobile phase	Acetonitrile: Methanol: Water (40:20:40)

Fig. 1 shows the separation of three curcuminoids in less than 11 minutes.

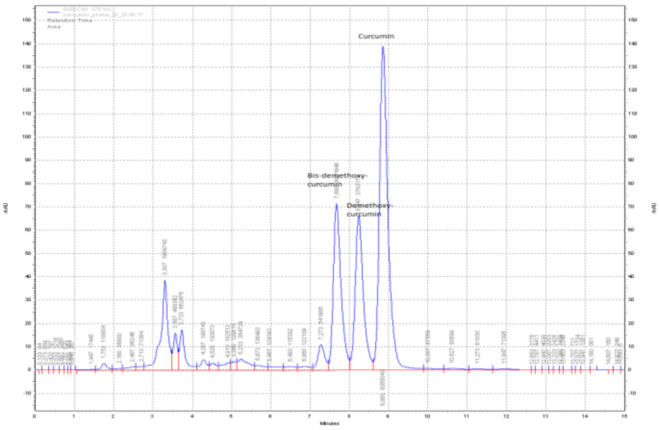

Fig. 1. Separation of curcuminoids in turmeric extract.

Field experiment

The field experiment was conducted in Lam Dong province, Vietnam. Before planting, surface soil samples (0-20 cm depth) from each harvesting plot were collected, air-dried, mixed and analysed for the selected physicochemical properties. The results are presented in Table 2.

The soil in this research area was with an acidic pH (5.87) and low content of organic matter. It is characterized by a low content of Ca, Cu, Mn, K and Zn and medium content of N, P and Fe. Since the soil is low in organic matter and nutrients in our experiment, we used a mixture of 4 parts of soil, 1 part of coco fibre and 0.5 parts of organic fertiliser.

Table 2. Soil composition.

Soil test parameter	Test level	Test rating
Soil pH (1:5)	5.87± 0,02	Acidic
Organic matter (%)	1.57	Low
(Nutrients mg kg^{-1})		
Total Nitrogen	894.0	Medium
Potassium (K_2O)	79.9 ± 2,4	Very Low
Phosphorous (P_2O_5)	1169 ± 24	Medium
Calcium	540.2±12,6	Very Low
Magnesium	422.5±17,4	Very Low
Copper	7.86 ± 0,38	Low
Manganese	160.2±3.24	Low
Iron	12346±270	Medium

Seven suspension solutions with different Zn concentrations were used. The scheme of the experiment is presented in Table 2. The foliar fertilizer was applied triple during the growth period – first, fourth and seventh week after germination. The size of the plots was 4.4 m^2 for all variants and the working solution for each spraying – 0.2 L plot^{-1}.

Table 2. Scheme of the experiment

Variant	$Zn_5(OH)_8(NO_3)_2$ suspension, g l^{-1}	$Zn_5(OH)_8(NO_3)_2$ suspension, g plot^{-1}
Control	-	-
1	6.6	1.32
2	10.7	2.14
3	14.8	2.96
4	18.9	3.78
5	23.0	4.60
6	27.0	5.40
7	32.8	6.56

After harvesting, random samples were collected. The rhizomes were washed, cleaned and air-dried at 40°C for 24 hours. All samples were milled, mixed, digested by a mixture of HNO_3 and H_2O_2 in a Microwave Digestion System MARS 6 - CEM Corporation and analysed for Zn, Cu, Fe, P, K, Ca and Mg.

The results were analysed statistically using IBM SPSS statistic software.

RESULTS AND DISCUSSION

A. Impact of foliar fertilisation on micro and macro elements content in the Curcuma Longa.

The most significant part of the total Zn in the soils is associated with Fe and Mn oxides. As a cation, Zn interacts with all plant nutrients present in the soil or absorbed by plants as anions, which include NO_3^- (nitrate), PO_4^{3-}, SO_4^{2-}, Cl^-, BO_3^{3-} and MoO_4^{2-} (R. X. Cao et al., 2003). Only phosphates can reduce the availability of Zn in soils. Besides, hydroxides and carbonates present in soil lead to adsorption of Zn on their surface or precipitation of Zn as Zn hydroxide or Zn carbonate, which reduce Zn availability to plants. Mechanisms responsible for positive or negative interactions between Zn and other nutrients in plants are not well understood. Leaf spraying with zinc-containing suspensions can avoid the problems with zinc blocking in the soil and unwanted interactions with other elements.

Figs 1 and 2 present the impact of Zn fertilisation on micronutrients (Cu and Fe) content in the rhizome of Curcuma Longa. Copper content ranged widely from 1.40 to 2.55 mg kg^{-1}, with the mean value for all variants 1.85 ± 0.30 mg kg^{-1} without a clear tendency. In many studies, antagonistic Cu and Zn interaction has been found, especially in contaminated soils with a high content of both elements (Kim, 2009). The data presented in Table. 1 show that the copper and zinc content of the soil used in our experiment is low, and a noticeable competitive interaction between the two elements cannot be expected.

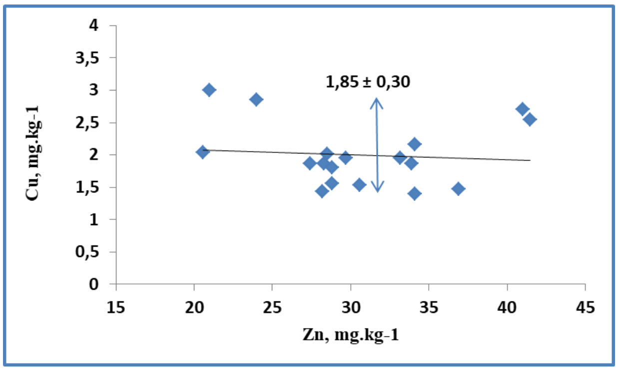

Fig. 2. Impact of Zn fertilisation on Cu content in the rhizome of *Curcuma Longa.*

The content of iron also varied within a wide range from 75.5 to 169.0 mg kg^{-1}, with the mean value for all variants 108.2 ± 30.0 mg kg^{-1} (Fig. 3). No clear tendency can be seen and in this case. According to some authors (Ambler et al.) Zn inhibited Fe translocation in some cases, which can lead to its accumulation in the roots. Probably in our case, the limiting factors in determining the content of micronutrient at the rhizome of Curcuma Longa are the soil properties.

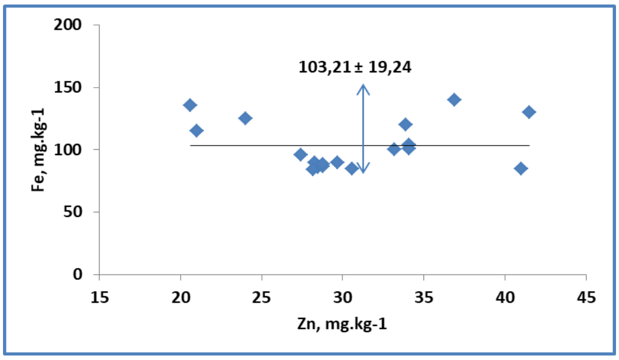

Fig. 3. Impact of Zn fertilisation on Fe content in the rhizome of *Curcuma Longa.*

Figs. 4-7 present the impact of Zn fertilisation on macronutrients (K, P, Ca and Mg) content in the rhizome of *Curcuma Longa*.

In general phosphorus and calcium react negatively with Zn and reduce its absorption by roots or/and its translocation to shoot in plants (Prasad et al., 2016). Zinc can get precipitated as Zn phosphate on addition of phosphate fertilisers (Lambert et al., 2007). Calcium in calcium carbonate can react with Zn in the soil solution to form calcium zincate ($CaZn_2(OH)_6.2H_2O$) (Jurinak et al., 1955), which may not be readily available to plants. Potassium and magnesium interact positively with Zn and increases its absorption and translocation in plants.

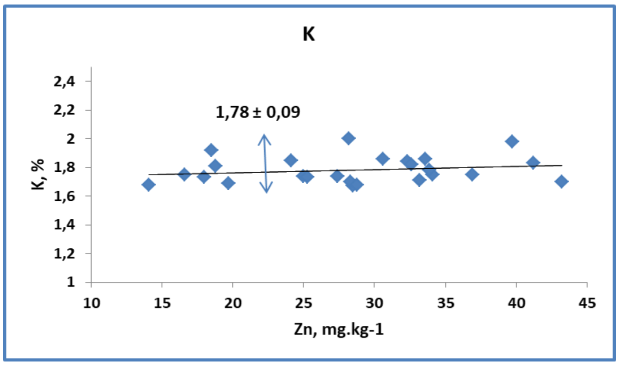

Fig. 4. Impact of Zn fertilisation on K content in the rhizome of *P. amarus.*

The results, presented in Figs 4 - 7 don't show any effect of foliar Zn fertilisation on P, K and Ca content in variants comparing with those of control plants. Their content varies in a very narrow range with averages of 1.78 ± 0.09% for K, 0.36 ± 0.02% for P and 0.16 ± 0.01 for Ca.

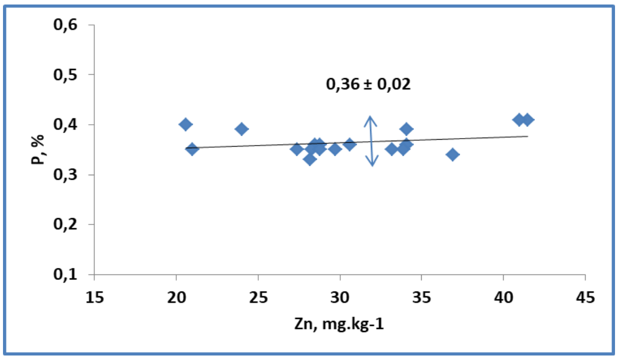

Fig. 5. Impact of Zn fertilization on P content in the rhizome of *Curcuma Longa.*

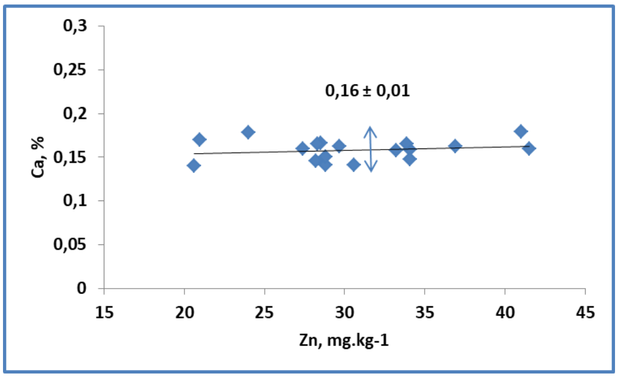

Fig. 6. Impact of Zn fertilization on Ca content in the rhizome of *Curcuma Longa.*

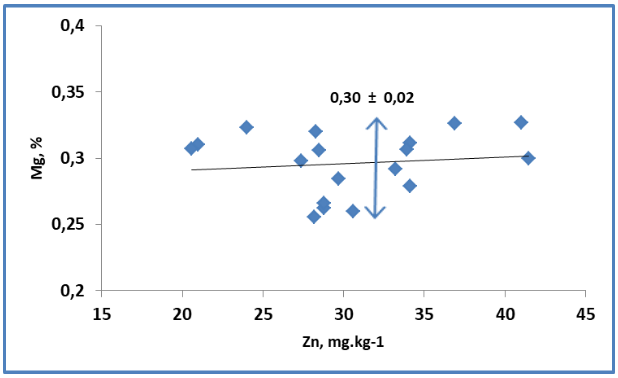

Fig. 7. Impact of Zn fertilization on Mg content in the rhizome of *Curcuma Longa.*

A little different is the result of magnesium. Its content varies within a wide range from 0.25 to 0.33% with the mean value for all variants 0.30 ± 0.02%. This substantial variation, however, does not allow for the conclusion of synergy or antagonism between the two elements.

These results show that the interaction of zinc with P, K, Ca and Mg depends not only on the type of plant but also on the mode of application of zinc. The interaction of zinc with macronutrients is much more pronounced in the soil solution and the roots of the plants than in their above-ground parts after using zinc-containing leaf fertilisers.

The summarized results for investigated micro and macroelement show that the foliar fertilization by Zn does not affect their content in the rhizome of *Curcuma Longa.* The positive effect can be sought in improving the plant physiological status and as a result, a change in the quality of turmeric. Such a positive impact was found by Nasiri et al. (2010) who have applied leaf fertilization with Cu and Zn to chamomile and have established considerably improving flower yield and essential oil content, especially in calcareous soils.

B. Impact of foliar fertilization on the quality of turmeric.

B.1 Impact of foliar fertilization on curcuminoids content in the rhizome of Curcuma Longa.

Curcumin is the most valuable ingredient of turmeric rhizomes. It has emerged as the most exploited phytoconstituents for its wide spectrum of biological activities. Mostly, it is available in the market as a mixture of three different constituents, commonly known as curcuminoids. These curcuminoids constitute majorly curcumin (up to 75%), followed by desmethoxycurcumin and bis-desmethoxycurcumin (Bansal et al., 2011). Figs 8 – 10 show our results for the impact of foliar fertilization by ZnHN suspension on the content of curcuminoids in the rhizomes of *Curcuma Longa.*

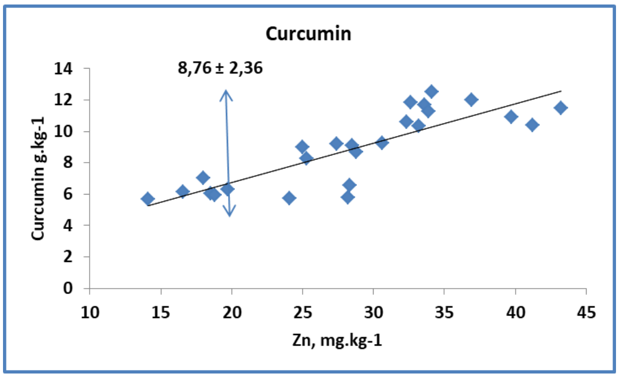

Fig. 8. Impact of Zn fertilization on curcumin content in the rhizome of *Curcuma Longa.*

The content of curcumin varied within a wide range from 5.66 to 12.53 g kg^{-1}, with the mean value for all variants 8.76 ± 2.36 g kg^{-1} (Fig. 3) with a clear tendency of increasing with the increase of Zn content.

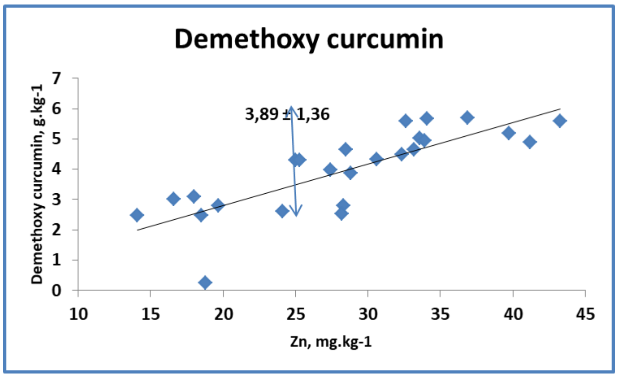

Fig. 9. Impact of Zn fertilisation on desmethoxy curcumin content in the rhizome of *Curcuma Longa.*

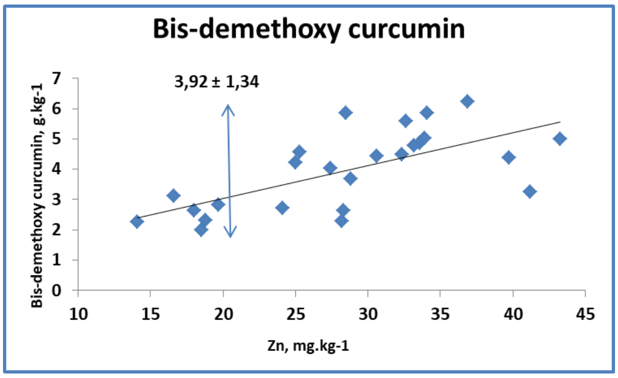

Fig. 10. Impact of Zn fertilisation on bis-desmethoxy curcumin content in the rhizome of *Curcuma Longa.*

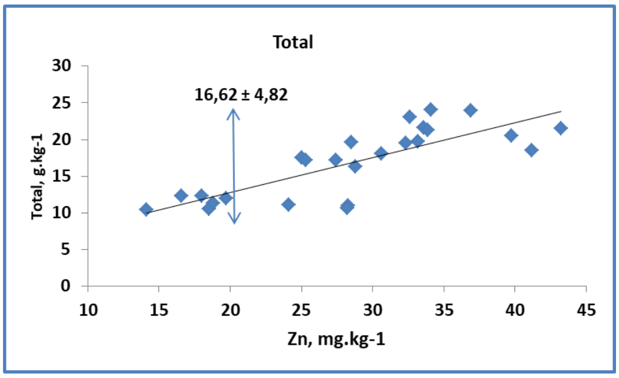

Fig. 11. Impact of Zn fertilisation on total curcuminoids content in the rhizome of *Curcuma Longa.*

The same trend is observed for desmethoxycurcumin and bisdesmethoxycurcumin, but their amount is significantly less than that of curcumin – respectively3.98 ± 1.36 and 3-92 ± 1.34 g kg^{-1}. Fig. 11 summarises the results for all curcuminoids. Their total content varies from 10.38 to 24.05 with a clear upward trend with the increasing zinc content.

B.2. Impact of foliar fertilisation on other main components of turmeric.

The results obtained (Table 3) show that the content of all components varied within a narrow range with no significant difference between the control sample and the variants ($p < 0.05$). It can be concluded that Zn foliar fertilisation has no impact on the investigated ingredients.

Table 3. Impact of foliar fertilisation on dry matter, protein, sugar, fats, vitamin C and ashes in turmeric.

Variant, №	Dry mather,%	Protein,%	Sugar,%	Fats,%	Vitamin C, mg kg^{-1}	Ashes,%
Control	***86,63±0.28***	***8,70±0.14***	***10,07±0.12***	***11,84±0,26***	***83.5±1.64***	***7.53±0.25***
1	87,28	8,82	9,99	11,85	77,3	7,12
2	86,13	8,13	10,12	12,71	83,6	7,30
3	87,41	7,49	12,65	12,30	82,4	6,94
4	86,40	7,74	11,61	12,46	72,9	6,86
5	86,63	7,62	8,84	12,45	83,1	7,78
6	86,42	8,24	12,80	13,15	72,9	7,49
7	87,25	7,93	8,34	12,01	77,4	6,53
8	86,89	7,97	11,54	12,47	82,9	7,00
Average for variants	**86.80±0,48**	**7.99±0,42**	**10.74 ±1,67**	**12.43±0,40**	**79.1±4,54**	**7.13±0,39**

CONCLUSIONS

A significant ($p < 0.05$) effect of foliar fertilisation by nanosized zinc hydroxy nitrate on curcuminoids in the rhizome of *Curcuma Longa* was found. The other ingredients forming the quality of turmeric remain unaffected.

The content of Cu, Fe and macronutrients varies narrowly with no significant impact of ZnHN fertilisation. The interaction of zinc with micro and macronutrients is much more pronounced in the soil solution and the roots of the plants than in their above-ground parts after using zinc-containing leaf fertilisers. The positive effect can be sought in improving the plant physiological status and as a result, a change in the quality of turmeric.

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