USE OF BASIC SALTS OF IRON AND ZINC AS PLANT AMENDMENTS IN SOILS

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ABSTRACT: In a greenhouse experiment, the effects of adding zinc (Zn) and iron (Fe) as either their basic salts or as commercial chelates were compared for the production of lettuce. The basic salts were found to be as effective as the chelates in providing Zn and Fe as well as being more environmentally safe.

INTRODUCTION

Calcareous soils frequently supply insufficient quantities of Zn and Fe for normal plant growth. Therefore, a common practice is to apply chelates of Zn and Fe to such soils to satisfy the crop requirement (Wallace and Lunt, 1956; Wallace, 1983; Wallace and Wallace, 1983a). However, the synthetic chelating agents are frequently too expensive to be used in general field agriculture and are difficult to supply at the correct concentration. This has led to the search for alternative sources of these micronutrients (Mortvedt, 1986; Wempati and Loeppert, 1986; Parpian and Anderson, 1988). Chelating agents can be toxic to plants when used in excess and have been found to inhibit the uptake of other cations by plant roots (Wallace, 1983; Wallace and Wallace, 1983b). In adition, these heavy metals must not be applied in excess since they can have deleterious environmental effects, such as the depression of the nitrogen-fixing microbial populations in soils (McGrath et al., 1988).

Basic salts of many of the heavy metals are intermediately soluble between those of the simple salts and those of the hydroxides, so they could be considered as 'slow release' when added to soils as an alternative source of plant micronutrients. Unlike the chelates, basic salts are not stable in solution, so they cannot promote the movement of cations and other heavy metals down the soil profile. Basic salts are crystalline, easy to handle, and do not introduce any foreign component into the environment. Thus, they could be considered as being environmentally safe.

In a previous paper (Galvez et al., 1987), it was shown that addition of the basic salts of Zn, copper (Cu), and cobalt (Co) to a sandy soil resulted in values for their 'capacity factor' (I/Q) (Mattingly, 1965) lower than those for their simple salts but higher than for their corresponding hydroxides.

In this paper, the basic salts of Fe [$Fe_4(OH)_{11}NO_3 \cdot 2H_2O$] and Zn [$Zn_5(OH)_8Cl_2 \cdot H_2O$] were used in a greenhouse experiment to evaluate the effect of their addition to a sand and to a calcareous sandy soil on the weight and nutritional status of lettuce (*Lactuca sativa* L.) plants. The results were compared with those obtained by using the commercially available chelates of Fe and Zn as soil amendments.

The basic salt of Fe, $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$, referred to as bFe, has recently being synthetized (Lopez-Delgado et al., 1988) and has been used as a plant nutrient for the first time in this experiment. The use of the basic salt of Zn, $Zn_5(OH)_8Cl_2 \cdot H_2O$, referred to as bZn, to correct deficiencies of this element in plants, animals, and human beings is protected by a patent (P9300705).

MATERIALS AND METHODS

The experiment was carried out in a greenhouse using ca. 0.15/m^3-capacity containers fulled with either sand or a calcareous sandy soil (from now on soil). Some characteristics of the sand and soil are shown in Table 1. Four lettuce plants were planted in each container, three to be sampled after 40, 70, or 100 days, respectively, leaving the fourth to be sampled at the flower stage.

A factorial experiment with five different treatments was set up to compare the effects of the addition to the soil of the basic salts, bFe and bZn, with those of two commercial chelates (Sandofer R, 6% Fe as EDDHA; Bundolin Corrector Zn-14 R, 14% Zn as EDTA, referred to as chFe and chZn, respectively). In two of these, mixtures of the basic salts and the commercial chelates were applied: treatment bZnchFe (the basic salt of Zn plus chelate of Fe) and treatment chZnbFe

TABLE 1. Some Characteristics of the Sand and the Calcareous Sandy Soil Used.

	pH (H_2O)	$CaCO_3$	Mechanical Analysis: Coarse Sand	Fine Sand	Silt	Clay
		- - - - - - %	- - - - - - - - -			
Soil	8.5	8.6	87.4	2.5	2.5	7.6
Sand	6.3	0.0	98.3	1.2	0.4	0.1

	DTPA-Extracted Micronutrients, μg/g: Fe	Cu	Mn	Zn
Soil	3.6	0.2	1.2	0.5
Sand	1.4	0.06	0.3	0.12

(the chelate of Zn plus the basic salt of Fe). In the third treatment, there was no addition of either Zn or Fe (treatment zero). The other two treatments were chelates alone, chZnchFe and basic salts alone, bZnbFe. Each treatment was replicated three times. The applications of Zn and Fe corresponded to normal agricultural practice, *i.e.* the corresponding weights of chelates and basic salts, equivalent to 7 Zn kg/ha and 3 Fe kg/ha, respectively. Another experiment was conducted to compare normal (bZnbFe), half (1/2bZnl/2bFe) and double (2bZn2bFe) doses of basic salts.

In all experiments, each container received a NPK fertilization equivalent to 50, 30, and 200 kg/ha of N (3.4 g as NH_4NO_3 A.R. per container), P_2O_5 (1.3 g as $Ca(H_2PO_4)_2{\cdot}H_2O$ A.R. per container), and K_2O (3.8 g as KCl A.R. per container). The containers were periodically watered with a basal nutrient solution in deionised water which contained all the essential macro- and micro-nutrients, except Zn and Fe.

Aerial parts of plants were taken at three stages of growth as mentioned above, weighed, and prepared for analysis. Leaves were washed several times with deionised water, dried at 60°C for 24 h, and ground. For the P, K, Ca, Mg, Na, Fe, Cu, Mn, and Zn determinations, the dried leaf subsamples were ashed and treated with concentrated HCl on a hot plate (Pinta, 1973; Pinta et al., 1973). The P in solution was analysed by the method of Murphy and Riley (1962), Na and K by flame emission spectrophotometry, and the remaining elements by atomic absorption spectrophotometry. Nitrogen was determined after Kjeldahl digestion (Pinta et al., 1973). The analytical measurements were checked against a known plant standard (*Olea europaean*, CRM062).

Data analysis were carried out using the STATIGRAFICS package. Monofactorial ANOVAs were used to test treatment effect on measured variables: When a significant effect was detected, TUCKEY's test was used to compare means. A significance level of $P<0.05$ was used throughout the study.

RESULTS AND DISCUSSION

Mean values of the weight of plants and the concentrations of N, P, K, Ca, Mg, and Na in leaves at the three stages of growth for the lettuce grown in sand are given in Table 2. In general, no significant differences between the weights and the nutritional status of the plants for the five treatments were found at any stage of growth. Although some differences were observed between the mean values of N, P, K, Ca, Mg, and Na contents of the lettuce leaves from plants receiving different treatments, the mean values were always within the ranges considered as normal (Geralson et al., 1973; Wolnik et al., 1983) regardless of the form in which both Zn and Fe were applied. Similar results were found for lettuce grown in soil with no significant differences between treatments. All of these results indicate that the basic salts are as good as the chelates for supplying both Zn and Fe.

However when the content of micronutrients in the lettuce leaves was calculated, some differences appeared (Table 3). Using sand as the substrate, the chelates (chZnchFe treatment) supplied significantly more Fe to the lettuce plant. In contrast in calcareous soil, the basic salts and chelates did not differ significantly for supplying Fe due possibly to the effect of the active carbonate present. For Zn ,the chelate was more effective than the basic salt in providing Zn to the lettuce plant, whether the substrate is either soil or sand. The Mn and Cu contents did not reflect any cause or effect relationship with treatment, but the

TABLE 2. Weight and Nutritional Status of Plants of *Lactuca sativa* L. at Different Stages of Growth in Sand (Mean values of three replicates in g or % dry weight).

Element	Stage of Growth	Treatment Applied				
		zero	bZnbFe	chZnchFe	bZnchFe	chZnbFe
Weight, g	1	70.4a	84.3a	64.7a	67.7a	55.8a
	2	218.9a	208.4a	216.8a	172.6a	204.1a
	3	275.8a	284.9a	226.8a	228.5a	240.1a
N, %	1	3.45a	2.70a	3.31a	3.39a	3.29a
	2	2.66a	2.59a	2.55a	2.47a	2.66a
	3	2.68ab	2.57a	2.53a	2.62a	2.99b
P, %	1	0.41a	0.34a	0.37a	0.33a	0.36a
	2	0.34a	0.35a	0.31a	0.31a	0.38a
	3	0.30a	0.30a	0.26a	0.27a	0.41a
K, %	1	4.97c	4.30a	4.77bc	4.20a	4.50ab
	2	4.33a	3.97a	4.10a	4.13a	4.23a
	3	4.71a	5.04a	4.88a	5.18a	4.84a
Ca, %	1	1.12a	1.14a	1.41a	1.23a	1.10a
	2	1.08a	1.05a	1.00a	1.16a	0.94a
	3	1.85ab	1.56ab	1.90b	1.57ab	1.21a
Mg, %	1	0.26a	0.25a	0.29a	0.26a	0.28a
	2	0.21a	0.20a	0.23a	0.23a	0.20a
	3	0.32a	0.27a	0.32a	0.26a	0.24a
Na, %	1	0.67a	0.71a	0.66a	0.72a	0.66a
	2	0.55a	0.51a	0.58a	0.58a	0.51a
	3	0.60a	0.68a	0.73a	0.66a	0.57a

Values followed by the same letter in the same row, do not differ significantly ($P < 0.05$).

absence of the chelate was clearly reflected in an increase in Mn content in the leaves for lettuce grown in soil (zero treatment). Leaf Cu contents for lettuce plants grown in sand (not shown) were very high (ca. 35 ppm) and similar for all treatments and stages of growth, reflecting contamination by a Cu-containing fungicide which had to be applied several times on the plants.

TABLE 3. Micronutrient Composition of Plants of *Lactuca sativa* L.at Different Stages of Growth. (Mean value of three replicates in µg/g dry weight).

Element	Substrate Used	Stage of Growth	Treatment Applied			
			zero	chZnchFe	bZnchFe	chZnbFe
Fe, µg/g	Soil	1	47a	43a	44a	34a
		2	50a	52a	58a	55a
		3	63a	77a	78a	82a
	Sand	1	131a	154a	138a	136a
		2	67a	117c	73ab	100bc
		3	148ab	235c	139ab	160b
Zn, µg/g	Soil	1	15a	31b	15a	37b
		2	15a	30b	14a	54c
		3	23a	44b	21a	68b
	Sand	1	25a	52c	26a	36b
		2	33a	43c	27a	40bc
		3	48a	73b	48a	61b
Mn, µg/g	Soil	1	25a	7a	14c	10b
		2	22ab	6a	14ab	37b
		3	57c	43b	21a	44b
	Sand	1	80a	128b	94a	83a
		2	157a	123a	143a	116a
		3	231c	219b	197ab	122a
Cu, µg/g	Soil	1	6a	5a	4a	9a
		2	5a	6a	5a	4a
		3	7a	10b	9b	14c

Values followed by the same letter in the same row do not differ significantly ($P < 0.05$).

TABLE 4. Cationic Balance of Plants of *Lactuca sativa* L. at Different Stages of Growth in Sand (Mean values of three replicates in millequivalents).

Treat	Stage of Growth	Macronutrients x 10^3 K	Ca	Mg	Na	Total	Micronutrients x 10^5 Cu	Mn	Fe	Zn	Total
bZnbFe	1	6.3	3.3	1.2	0.9	11.7	0.4	1.9	3.5	0.5	6.2
	2	14.1	7.2	2.3	1.5	25.1	1.3	7.3	5.1	1.4	15.2
	3	24.4	14.6	4.2	2.8	45.9	2.3	14.8	11.1	2.6	30.8
						82.8					52.2
chZnchFe	1	5.3	3.0	1.0	0.6	9.9	0.3	2.0	3.5	0.7	6.5
	2	15.1	7.2	2.7	1.9	26.8	2.3	6.4	8.9	1.9	19.5
	3	16.7	12.4	3.6	2.1	34.8	3.1	10.9	17.3	3.5	34.7
						71.5					60.7

The total cationic content for both the macro- and micro-nutrients in the leaves of lettuce plants grown in sand and treated with chelates (chZnchFe treatment) or with basic salts (bZnbFe treatment) are given in Table 4. In this comparison, the possible influence of the soil or of either the chelates and basic salts (chZnbFe and bZnchFe treatments) are avoided. In Table 4, it can be seen that the accumulation is more regular through the different stages of growth and the final total content of the macronutrients was greater for the basic salts as compared to the chelates. Also it is evident that the lettuce plants were able to take up more micronutrients from the chelate form than that from the basic salts, expect for Mn. It is possible that free chelating anions depress the availability of the macronutrients and Mn (Halvorson and Lindsay, 1977; Wallace and Wallace, 1983b).

The Fe/Mn ratio will increase if there is an interference between Fe and Mn (Knezek and Greinert, 1971). As is shown in Table 5, applying the chelates (chZnchFe treatment) to lettuce plants grown in soil, the Fe/Mn ratios are higher than that for the basic salts (chZnbFe treatment), at least in the early stages of growth. For lettuce grown in sand, this effect does not appear.

Increasing the application rate of the Fe basic salt (bZn2bFe treatment), will increase the Fe/Mn ratio in lettuce leaves grown in sand as shown in Table 6.

TABLE 5. Effect of the Chelates of Fe on the Fe/Mn Ratio of Plants of *Lactuca sativa* L. at Different Stages of Growth (Mean values of three replicates).

	Ratio Fe/Mn					
Stage of Growth	**1**		**2**		**3**	
Treatment	**soil**	**sand**	**soil**	**sand**	**soil**	**sand**
chZnbFe	3.52	1.60	1.49	0.88	1.86	1.32
chZnchFe	6.17	1.32	8.18	0.93	1.79	1.07

TABLE 6. The Fe/Mn Ratio of Plants of *Lactuca sativa* L. Given Increasing Quantities of the Basic Salt of Fe at Different Stages of Growth in Sand (Mean values of three replicates).

	Ratio Fe/Mn		
Stage of Growth	**1**	**2**	**3**
Treatment			
bZn1/2bFe	0.83	0.96	1.23
bZnbFe	1.65	1.02	1.51
bZn2bFe	1.79	2.27	5.75

These results seem to show that the presence of chelating anions is enhanced by the Fe-insolubilizing capacity of soils, which can induce a reduction of the Mn content in lettuce leaves, shown by the higher Fe/Mn ratios. The Fe-basic salt does not produce this effect when applied at the commercially recommended dose. Although no chlorotic symptoms were observed and there was no induction of nutrient imbalance, it is possible that there is increased competition for metabolic

TABLE 7. Effect of the Chelates of Zn on the P Content of Plants of *Lactuca sativa* L. at Different Stages of Growth (Mean values of three replicates).

	Ratio P/Zn					
Stage of Growth	1		2		3	
	soil	sand	soil	sand	soil	sand
Treatment						
chZnchFe	34.5	72.5	26.7	80.0	16.6	41.3
bZnchFe	76.7	122.2	55.0	155.0	39.5	59.2

positions (Mengel and Kirkby, 1982; Olsen, 1972) with increased applications of the Fe-basic salt. This is in accord with the increasing values of the Fe/Mn ratio during the later stages of growth (Table 6).

When a soil is well provided with P, interferences in the transport of Zn into the plant can occur (Stukenholtz et al., 1966). The interference is shown through the appearance of high initial values for the P/Zn ratio, which decreases to normal values in between P/Zn = 75 and P/Zn = 300 when larger doses of Zn are applied (Olsen, 1972). As shown in Table 7, when Zn chelate is added (chZnchFe treatment), the lettuce grown in sand and in soil show very low values for the P/Zn ratio. This can be interpreted as the chelate giving excess Zn to the plant. The P/Zn ratios given in Table 7 are near normal for lettuce grown in sand. When Zn is added as basic salt (bZnchFe treatment), the P/Zn ratio is normal or near normal. This is especially so when lettuce is grown in sand, because the depressing effect of the presence of active calcium carbonate which affects the availability of P and Zn is absent (Udo et al., 1990). When the application rates are half or double than that commercially recommended are used as the basic salt (1/2bZnbFe and 2bZnbFe treatment), the values of the P/Zn ratio on lettuce grown on sand are normal and do not change, or change little, showing the ability of the basic salt to regulate the availability of the micronutrient (Table 8). The same can be deduced for the Zn-Fe interaction. Rosell and Ulrich (1964) showed that plant leaves

TABLE 8. The P/Zn Ratio of Plants of *Lactuca sativa* L. Given Increassing Quantities of the Basic Salt of Zn at Different Stages of Growth in Sand (Mean values of three replicates).

	Ratio P/Zn		
Stage of Growth	1	2	3
Treatment			
1/2bZnbFe	113.8	114.8	209.9
bZnbFe	131.5	128.3	275.0
2bZnbFe	144.4	127.5	248.8

TABLE 9. Effect of Increasing Quantities of the Zn Basic Salt on the Fe Content of Plants of *Lactuca sativa* L. Grown in Sand at Different Stages of Growth (Mean values of three replicates).

	Fe, µg/g		
Stage of Growth	1	2	3
Treatment			
1/2bZnbFe	76.3	89.0	121.7
bZnbFe	78.3	99.0	135.5
2bZnbFe	71.7	98.7	213.3
1/2bZn1/2bFe	73.0	94.7	113.3
1/2bZn2bFe	70.2	92.7	317.7

compensate for Zn deficiency with Fe concentrations higher than normal. As shown in Table 9, lettuce grown in sand to which half or double the Zn commercial doses are added (1/2bZnbFe and 2bZnbFe treatments), have normal Fe values, below 350 ppm Fe, and that the same happens when double doses of Fe are applied to lettuce which receive half doses of Zn (1/2bZn2Fe treatment).

CONCLUSION

The basic salts of Zn or Fe can supply these elements to lettuce in a safe and convenient way. These basic salts do not interfere with the uptake of other elements, such as P or Mn, and produce plants with adequate weight and correct nutritional status.

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