

## CHANGES IN DTPA-EXTRACTABLE Zn, Cu, Fe AND Mn IN TWO ALKALINE CALCAREOUS SOILS FOLLOWING N FERTILIZATION

F. HUSSAIN and A. RASHID,

*Soil Science Division, Nuclear Institute for Agriculture and Biology, Faisalabad*

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**Abstract.** Changes in DTPA-extractable zinc, copper, iron, and manganese in two alkaline calcareous soils following fertilization from Thikriwala and Kamalia in the Faisalabad district were studied. The results of the present study reveal that the effect of acidifying N fertilizers on micronutrient status may not always be favourable as substantial decrease in Zn and Mn solubilities was recorded with N application to these alkaline calcareous soils. DTPA-extractable micronutrients as influenced by various levels of urea and zinc in two soils incubated for 13 days at  $30 \pm 1^\circ$  and 17% field capacity was also studied.

### Introduction

Micronutrient disorders have been increasingly observed in various crops grown on alkaline calcareous soils of Pakistan.<sup>1</sup> However, Zn disorders have been found to be more common and thus more research effort has been placed on Zn fertilization than on all other micronutrient problems.<sup>1,3</sup> Micronutrient deficiencies have generally been attributed to their low availability from soils and several soil conditions have been reported to promote their deficiencies in plants.<sup>4</sup> In view of frequent incidences of micronutrient disorders, their solubilities in soils is becoming a subject of increasing importance.

The solubility of heavy metals in soils greatly depends upon soil pH.<sup>5</sup> The pH of our soils is alkaline and this seems to be an important factor interfering with the solubilities of heavy metals in soils. Any farm practice which depresses soil pH may enhance their solubilities in soils. For example, the acidic properties of  $(\text{NH}_4)_2\text{SO}_4$  corrected Fe deficiency in petunias.<sup>4</sup> Lauer<sup>6</sup> examined the possibility of increasing Zn solubility by the inclusion of Zn with  $(\text{NH}_4)_2\text{SO}_4$  fertilizer. He observed that the formation of soluble Zn-NH<sub>3</sub> complex increased Zn solubility in soils.

Our farmers are making liberal applications of N fertilizers. It would, therefore, be of great interest to learn about the effect of these fertilizers on the solubilities of heavy metal ions in our soils which are mostly alkaline and calcareous. The present paper reports this information on two upland soils.

### Materials and Methods

Two soil samples (0-15 cm) differing in texture were collected from Thikriwala and Kamalia towns of the Faisalabad district. The soils were air-dried and crushed to a fineness of 2 mm. Physico-chemical characteristics of the soils have been detailed else-

where.<sup>7</sup> Twenty five g portions of the soils for each treatment were taken in flat-bottomed plastic vessels. The treatments in triplicate consisted of 0, 2.5, 5.0 and 10.0 ppm Zn as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and 0, 37.5, 75.0 and 150.0 ppm N as  $\text{CO}(\text{NH}_2)_2$  (urea). Zn and N sources were applied as their aqueous solutions by adjusting the moisture level of the soil in each vessel to 75% of its field capacity. The soils maintained at this moisture level were incubated at  $30 \pm 1^\circ$  for 13 days, a period found sufficient for maximum fixation of Zn (data not shown). At the end of the incubation period, the soil samples were extracted with 0.005 M DTPA (diethylenetriamine-pentaacetic acid) and the concentrations of Zn, Cu, Fe and Mn in the soil extracts were determined by atomic absorption spectrophotometry.<sup>8</sup> The data were processed by standard statistical procedures.

### Results and Discussion

*Effect of N on DTPA-extractable Zn (native plus applied).* Irrespective of the N levels, DTPM-extractable Zn of both soils progressively increased with an increase in Zn rate ( $P < 0.01$ , Table 1); this was expected. N application on the other hand produced significant reduction in extractable Zn of both soils ( $P < 0.01$  for both the soils). Although this decrease was not so pronounced, yet it strongly conflicted with the earlier reports showing N to enhance micronutrient solubility by soil pH depression and thus their uptake by upland plants.<sup>9</sup> Such an effect did not appear to operate in the present study. The depression in Zn solubility by N application also suggested that probably the mechanism of soluble Zn-NH<sub>3</sub> complex formation resulting from N application in upland soils<sup>6</sup> was also not operative in these soils. Urea is an acidifying N carrier but the decreased solubility of Zn by its application was quite surprising. The mechanism is, however, obscure.

TABLE 1. DTPA-EXTRACTABLE MICRONUTRIENTS AS INFLUENCED BY VARIOUS LEVELS OF UREA AND ZINC IN TWO SOIL INCUBATED FOR 13 DAYS AT  $30 \pm 1^\circ$  AND 75% FIELD CAPACITY

Applied		0.005 M DTPA-extractable micronutrients							
Zn	Urea	Thikriwala soil				Kamalia soil			
		Zn	Cu	Fe	Mn	Zn	Cu	Fe	Mn
ppm		ppm							
0	0	0.27	0.45	1.38	3.35	0.64	1.64	6.97	3.74
	37.5	0.24	0.47	1.38	3.16	0.61	1.75	7.12	3.52
	75.0	0.24	0.45	1.45	3.14	0.58	1.64	6.97	3.17
	150.0	0.23	0.46	1.30	2.93	0.56	1.71	7.57	3.12
2.5	0	1.83	0.49	1.53	3.54	2.19	1.61	7.12	3.86
	37.5	1.72	0.47	1.53	3.29	2.13	1.71	6.83	3.49
	75.0	1.74	0.49	1.23	3.38	1.91	1.71	7.42	3.34
	150.0	1.74	0.46	1.09	3.29	1.93	1.78	7.57	3.21
5.0	0	3.40	0.47	1.38	3.83	3.61	1.71	6.83	3.89
	37.5	3.28	0.50	1.38	3.29	3.52	1.68	6.97	3.52
	75.0	3.19	0.50	1.53	3.26	3.43	1.71	7.42	3.43
	150.0	3.19	0.52	1.59	3.53	3.34	1.71	7.72	3.11
10.0	0	6.49	0.48	1.53	3.46	6.77	1.68	6.97	3.90
	37.5	6.34	0.50	1.53	3.35	6.51	1.68	7.86	3.65
	75.0	6.30	0.50	1.60	3.35	6.47	1.71	7.42	3.43
	150.0	6.30	0.52	1.53	3.37	6.25	1.71	7.87	3.09
LSD (0.05)									
(Urea means)	0.05	NS	NS	0.21	0.09	0.04	0.36	0.12	
LSD (0.05)									
(Zn means)	0.05	0.03	0.09	0.21	0.09	NS	NS	NS	
LSD (0.05)									
(Urea $\times$ Zn means)	NS	NS	6.20	NS	NS	NS	NS	NS	NS

*Effect of N DTPA-extractable Mn (native).* Like Zn, extractable Mn of Thikriwala and Kamalia soils decreased with N application ( $P < 0.05$  and  $0.01$  respectively). In the case of the Thikriwala soil, the lowest level of N produced a significant reduction in Mn solubility but no further decrease occurred with increasing N rate. However, in the case of the Kamalia soil, the decrease in Mn solubility by N application was progressive. The reduction in extractable Mn by acidifying N carrier like urea also contradicted the earlier reports showing N as enhancing micronutrient solubility by soil pH depression.<sup>9</sup> A remarkable decrease in Mn solubility by urea application was, therefore, surprising. The reason is not known.

*Effect of N on DTPA-extractable Cu and Fe (native).* Extractable Cu and Fe of the Thikriwala soil, a light-textured soil, remained unaffected by N application. However, extractable Cu and Fe increased significantly with N application to a heavy-textured Kamalia soil ( $P < 0.05$  and  $0.01$  respectively). This was also interesting because increased solubility of these metal ions by the application of acidifying N

fertilizer would have been more on sandy soil than that of a clayey soil having high buffering capacity against soil pH changes.<sup>10</sup>

#### General Discussion

The results of the present study reveal that the effect of acidifying N fertilizers on micronutrient status of the soils may not always be favourable as substantial decrease in Zn and Mn solubilities was recorded with N application to these alkaline calcareous soils. Earlier reports stated that N fertilizers sometimes may also induce or accentuate Zn deficiency in plants. According to these reports, N fertilizers achieve this effect in several ways: by stimulating plant growth,<sup>11</sup> by increasing soil pH<sup>12</sup> and perhaps also by increasing the retention of absorbed Zn in the roots as protein complexes and thus preventing its movement to the tops.<sup>13</sup> From the results of the present study it appears probable that even N carriers with acidic soil reaction may also induce or accentuate Zn deficiency in upland plants by decreasing Zn solubility in alkaline calcareous soils.

Mn deficiencies in these soils are not so severe and widespread at present. Keeping in view the present data, it seems probable that N application to these soils may not prove hazardous as far as Mn status of these soils is concerned.

Extractable Cu and Fe remained unaffected in sandy soil but increased in clayey soil with N application. Such results could not be explained merely on the basis of pH shift by the application of N fertilizers because these soils contained large quantities of  $\text{CaCO}_3$ .<sup>7</sup> Stanton and Burger<sup>14</sup> reported that N application resulted in a lowering of pH only in the absence of  $\text{CaCO}_3$ . They observed that in the presence of  $\text{CaCO}_3$ , such an effect was not manifested. Moreover, under upland conditions, pH shift has been observed mainly on light textured soils receiving liberal N application.<sup>10</sup> Therefore, a reasonable conclusion could hardly be drawn.

Our farmers mostly use urea and  $(\text{NH}_4)_2\text{SO}_4$  as N fertilizers which have acidic soil reaction. The present results serve to emphasize that further studies on a wider range of soils, are warranted to test the present findings and to know definitely the possible role played by these N fertilizers in the solubilities of these heavy metal ions in alkaline calcareous soils.

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