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Micronutrients as Impurities of Inorganic Fertilizers Marketed in Saudi Arabia

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محتوى العناصر الصغرى المتواجدة كشوائب في الأسمدة المعدنية المسوقة في المملكة العربية السعودية

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خلاصة: تتلوث أسمدة المغذيات الكبرى المعدنية على الأرجح ببعض المغذيات الصغرى لذا فان محتوى الأسمدة المستخدمة في المملكة قد تم تحليلها لتقدير كميات الحديد و الزنك و المنجنيز و النحاس الكلية و الذائبة بها و هذه الأسمدة تمثل ثلاث مجموعات رئيسة هي الأسمدة الفوسفاتية، الأسمدة الصلبة متعددة العناصر، الأسمدة الذائبة في الماء متعددة العناصر. تبين أن أعلى محتوى للحديد الكلي في الأسمدة تحت الدراسة تتواجد في الإسمدة الفوسفاتية بينما أقل محتوى كلي من هذه العناصر يوجد في الأسمدة الذائبة في الماء متعددة العناصر و ظهر أن قدرا قليلا جداً من كمية الحديد الكلية ربما يكون ميسراً للنبات لذا فان الكمية الكلية من الحديد في تلك الأسمدة قد تثرى التربة بما يعادل ٢ جم فقط من الحديد لكل كيلوجرام من الأسمدة الفوسفاتية المضافة. أوضحت النتائج أن أعلى محتوى كلي من عنصر الزنك يتواجد في الأسمدة الفوسفاتية، وتقترح النتائج أن ما يقرب من ٠,٥ كجم من الزنك الكلي تتراكم في التربة إذا ما أضيفت كمية من الأسمدة تعادل ٥٠٠ كجم/ هكتار و تنخفض هذه القيمة بشدة إلى الربع إذا ما أخذ في الاعتبار القدر الميسر من الزنك فيها. أظهرت النتائج أن كلا من عنصري المنجنيز و النحاس في كافة الأسمدة تحت الدراسة منخفض نسبيا مقارنة بعنصري الحديد و الزنك، ودلت النتائج على أن الشوائب من عناصر المغذيات الصغرى و المتواجدة في الأسمدة المعدنية ربما لا يكون لها تأثير مباشر على تغذية النبات وذلك بسبب قلة ذوبانها وعليه فانه إذا ما اعتمد على تلك الشوائب في تغذية النبات لابد من التأكد أولا من مدى ملائمة المستويات الميسرة من تلك العناصر في التربة لنمو النبات.

ABSTRACT: Inorganic fertilizers with major nutrients are likely to be contaminated with some micronutrients. Fertilizers, utilized in Saudi Arabia, were analyzed for their total and water-soluble content of Fe, Zn, Mn and Cu. They represented three categories namely: phosphatic, solid multiple nutrient fertilizers (SMNF) and water-soluble multiple nutrient fertilizers (WSMF). Total iron content in examined fertilizers was higher in phosphatic fertilizers and lower in WSMF. Nevertheless, only a very small portion of the total iron content is likely to be available to plants. It was estimated, on the basis of total content, that almost 2 g of iron would be applied to soil for each added kg of phosphatic fertilizer. The highest total content of Zn was recorded for phosphatic fertilizers. The data suggested that less than half kg of Zn would be accumulated in soil if 500 kg of phosphatic fertilizers were applied in one year. This value however, fell dramatically, to one fourth of the value, when only the available forms of Zn were considered. Fertilizer content of manganese and copper were lower than both Fe and Zn. Micronutrient impurities present in inorganic fertilizers might not have an immediate influence on plant nutrition due to their lower solubility.

Keywords: fertilizer, inorganic, micronutrients, impurities, phosphates.

Application of micronutrient fertilizers to plants has become a common practice in the Kingdom of Saudi Arabia. This is because of the nature of the dominating soil, which is alkaline pH (7.4-8.8), and contains appreciable amounts of calcium carbonate (14-37.5 %; Bashour *et al.*, 1983). Nonetheless, in most cases, addition of micronutrient fertilizers is undertaken without appraising the actual need of soil itself. Moreover, other sources of micronutrients, rather than specific fertilizers, which may partially contribute in affording the growing plant with their needs have been ignored. In this connection, Senesi and Polemio (1981) emphasized that application of inorganic fertilizers frequently involves the addition of small quantities of trace elements that are commonly present in soils as traces. They added that in the case of mineral fertilizers these impurities are derived from parent rock materials. However, they may also be sourced from elsewhere. For example, equipment corrosion, catalysts and reagents, material added to commercial preparates such as filters, coaters and conditioners, etc. Liekam (1989) has indicated that because the quality of ores has declined over time, greater quantities of impurities are present in contemporary fertilizers when compared with

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those produced several decades ago. Kpomblekou and Tabatabai (1994) observed considerable amounts of trace metals in phosphate rocks. Charter *et al.* (1993) indicated that triple superphosphate and mono and diammonium phosphate (MAP and DAP) marketed in Iowa contained variable concentrations of many trace and non-trace metals. Some of these elements are even present in fluid fertilizers (Mortvedt and Giordano, 1977). Since the growers in the Kingdom of Saudi Arabia apply large amounts of macronutrient fertilizers, testing their contents for micronutrients would assess their role in enriching the soil with trace metals. Therefore, the objective of the present research was to determine the contents of Fe, Mn, Zn, and Cu present in macronutrient fertilizers marketed in the Kingdom and to estimate their contribution to soil fertility enrichment.

Materials and Methods

Fertilizer materials, either imported or locally produced, were obtained from various companies dealing with agrochemicals. These materials represented most of the fertilizers marketed in the Kingdom of Saudi Arabia. The fertilizer samples were grouped into three categories, namely; phosphatic, water-soluble multiple nutrient fertilizers (WSMF), and solid multiple nutrient fertilizers (SMNF).

The collected fertilizers were digested using the method of the Association of Official Agricultural Chemists (AOAC; Williams, 1984). Fe, Zn, Cu and Mn were detected in the digest by atomic absorption spectrophotometry (Perkin Elemer; Model 2380). N, P, and K contents were also examined in the selected fertilizers. Nitrogen was determined by the Kjeldahl method (Bremner, 1965), potassium was quantified by flame photometry (Page, 1982), while phosphorus was determined colorimetrically using the ascorbic-molybdate method.

For some fertilizers, water-soluble extractable micronutrients were examined. Fertilizer (10 g) was shaken in 50 ml distilled water for 30 min, filtered and the micronutrients examined as previously mentioned.

Results and Discussion

The micronutrients Fe, Mn, Zn, and Cu are notorious for creating nutritional disorders amongst crops. Since plants require only minute quantities of the other three elements, i.e. B, Mo and Cl, nutritional problems related to such elements are comparatively rare. Fe levels in the studied inorganic fertilizers ranged between 1554-2560 mg kg^{-1} in phosphatic fertilizers with a median of 2206.7 mg kg^{-1} (Table 1). In general, the different types of phosphatic fertilizer investigated had similar total content of iron, on average 2161.7 mg kg^{-1}. These results are almost 50% lower than those obtained by Arora *et al.* (1975) and Golly (1987) in their studies on Fe-content in superphosphate. However, present data was substantially lower than that reported by Charter *et al.* (1993) in their work on metal contents of inorganic fertilizers marketed in Iowa state, USA. They reported an average iron content of 10 g kg^{-1} for superphosphate and 12 g kg^{-1} for MAP. Iron levels of the SMNF examined herein varied between 4686.7 to 1029.2 mg kg^{-1} (Table 2). For WSMF, the median recorded value for Fe was only 317.5 mg kg^{-1} (Table 3). Therefore, it may be concluded that, on average, phosphatic fertilizers contained higher total iron content when compared against other fertilizer types.

TABLE 1

Nutrient content of phosphatic fertilizers.

No.	%			(mg kg^{-1})			
	N	P	K	Cu	Zn	Fe	Mn
1	18	46	0	28.20	312.00	1554.00	18.60
2	18	46	0	28.00	314.00	1554.20	18.40
3	11	52	0	42.20	454.00	2213.33	21.33
4	11	52	0	42.00	450.00	2200.00	21.00
5	11	52	0	43.73	448.67	2280.00	21.60
6	11	52	0	44.40	450.00	2300.00	21.60
7	18	46	0	36.47	364.67	2000.00	18.33
8	18	46	0	36.00	370.00	1980.00	18.00
9	18	46	0	36.27	368.00	2006.67	18.27
10	18	46	0	36.40	364.00	2000.00	17.80
11	18	46	0	40.20	392.67	2273.33	15.67
12	18	46	0	40.00	390.00	2200.00	15.40
13	18	46	0	38.13	356.00	2193.33	18.40
14	18	46	0	37.20	360.00	2200.00	18.00
15	0	46	0	41.80	367.33	2293.33	19.67
16	0	46	0	41.00	372.00	2320.00	20.60
17	0	46	0	42.00	363.20	2280.00	19.20
18	0	46	0	42.40	366.80	2280.00	19.20
19	11	52	0	43.07	447.87	2546.67	19.00
20	11	52	0	44.60	451.40	2560.00	19.00
Maximum				44.60	454.00	2560.00	21.60
Minimum				28.00	312.00	1554.00	15.40
Average				39.20	388.13	2161.74	18.95
Median				40.60	369.00	2206.67	18.80
SD				4.72	45.89	259.41	1.71

Testing water extractable iron of phosphatic fertilizers, which contain the highest total amounts of iron, indicated an average of 26 mg kg^{-1} for MAP and 243 mg kg^{-1} for DAP. Thereby indicating that most iron present as a contaminant of phosphatic fertilizers may not be available to plants. Noteworthy is that Fe compounds are generally poorly soluble; especially those containing ferric forms. Assuming that total iron content of phosphatic fertilizers would be eventually available in soil, the average Fe content of these

TABLE 2

Nutrient content of solid multiple nutrient fertilizers.

No.	%			(mg kg^{-1})			
	N	P	K	Cu	Zn	Fe	Mn
1	28	28	0	23.00	247.00	1446.67	16.73
2	14	38	10	29.47	300.00	1726.67	23.00
3	14	38	10	28.13	299.33	1806.67	22.00
4	11	29	19	23.20	211.33	1029.20	15.20
5	11	29	19	22.20	211.67	1037.47	15.80
6	28	28	0	21.87	225.13	1660.00	16.47
7	28	28	0	15.27	222.27	1320.00	12.67
8	16	20	0	18.60	242.20	1413.33	16.27
9	12	35	8	30.33	310.67	1980.00	20.47
10	18	18	5	3.07	435.33	4686.67	210.33
11	12	27	18	11.00	186.00	1100.00	14.00
12	23	23	0	22.60	108.73	2706.76	89.73
Maximum				30.33	435.33	4686.67	210.33
Minimum				3.07	108.73	1029.20	12.67
Average				20.73	249.97	1826.12	39.39
Median				22.40	233.67	1553.34	16.60
SD				7.88	80.59	1016.89	57.81

fertilizers (2161 mg kg^{-1}) would increase its content in by almost 2 g kg^{-1} of the added phosphatic fertilizer. This means that annual application of 500 kg ha^{-1} phosphatic fertilizer would dispatch about one kg of iron to the soil. This quantity would merely accentuate the available iron in soil by about 0.5 mg kg^{-1}. On the other hand, water soluble iron in such fertilizers would elevate soil iron levels by almost one tenth of the value *i.e.* 0.05 mg kg^{-1}. This approximation is based on the assumption that weight of the surface soil layer (0-30 cm) of one hectare is about 2 x 10^6 kg. Regarding available iron levels in soil of Saudi Arabia, Al Mustafa (1993) found that average extractable Fe of 46 different calcareous soils, representing the soils of Saudi Arabia, was 3.8 mg kg^{-1}. According to Lindsay and Norvell (1978) available iron in soils of Saudi Arabia is considered to be on the borderline (2.4-4.5 mg kg^{-1}) that might cause Fe deficiency. Recently, Modaihsh (1997) indicated that wheat grown on calcareous soil of Saudi Arabia responds to Fe application. As previous work carried out in the Kingdom revealed that native available iron in most soils is insufficient to meet plant requirements, one may consider available iron forms in these fertilizers of little significance. This viewpoint is not in a harmony with the data given by Singh *et al.* (1995). They related the increase in soil extractable Fe of some phosphate-treated plots to the contaminants being present in superphosphate fertilizer. However, it should be mentioned here that the phosphatic fertilizer which they applied, contained as much as double the amount of iron present in those from the current investigation. Moreover, the assessment of Singh *et al.* (1995) was executed after 11 years of continuous application of more than half-kg ha^{-1} of superphosphate.

TABLE 3

Nutrient content of water-soluble multi-nutrient fertilizers.

No.	%			(mg kg^{-1})			
	N	P	K	Cu	Zn	Fe	Mn
1	20	20	20	26.07	33.47	312.00	136.13
2	15	30	15	36.33	45.07	510.87	184.67
3	15	15	30	21.27	25.00	238.00	100.13
4	17	6	18	17.27	20.40	217.47	82.73
5	12	4	24	30.47	37.50	323.00	136.47
6	15	15	30	135.07	246.47	364.00	281.13
7	20	20	20	161.40	214.00	325.67	180.13
8	22	7	7	68.00	159.40	381.33	204.53
10	15	30	15	66.60	106.73	288.80	149.07
11	12	4	24	91.00	94.47	435.07	192.20
12	28	14	14	43.87	61.27	190.20	78.93
13	20	20	20	33.07	70.20	15.20	62.67
14	12	4	24	48.40	116.07	48.07	13.60
15	15	15	30	56.33	100.33	23.87	9.20
16	15	30	15	65.73	129.53	37.67	9.13
17	20\	20	20	104.20	197.00	433.53	157.53
18	21	7	7	90.93	148.07	384.87	253.27
19	15	30	15	96.00	212.80	416.87	173.07
20	15	30	15	864.67	297.33	890.87	889.33
21	13	3	43	41.33	79.60	61.27	67.47
22	16	40	6	22.33	276.00	1432.67	17.87
23	20	20	20	56.73	114.67	115.13	99.80
24	25	25	18	939.24	1563.00	529.33	1439.67
25	20	5	30	59.53	110.67	101.73	105.93
Maximum				939.24	1563.00	1432.67	1439.67
Minimum				17.27	20.40	15.20	9.13
Average				132.33	185.79	336.56	209.36
Median				58.13	112.67	317.50	136.30
SD				240.02	303.87	309.91	314.00

Total content of zinc in phosphatic fertilizers ranged between 312 to 454 mg kg^{-1} with a median of 369 mg kg^{-1}. MAP fertilizer contained higher levels of Zn when compared with DAP and TSP. But, zinc content was more or less similar (Table 1). These results are alike to those obtained by Golly (1987). She indicated that Zn content was 563 mg kg^{-1} in MAP and 475 in TSP. However, Arora *et al.* (1975) in a study on micro-element contents of fertilizers referred to lower Zn in TSP; averaging 165mg. Also the obtained values, in the current study, were higher than those given by Bear (1965) for global phosphate deposits (201 mg kg^{-1}). Zinc content of WSMF was much lower. Only one sample displayed a high value (1563-mg kg^{-1}). Detection of water-soluble Zn in some selected fertilizers used in the present study revealed that it represented almost one fourth of their total value (Table 4). Nonetheless, if the highest value of total Zn content in phosphatic fertilizers (454mg kg^{-1}) is considered as an

TABLE 4

Water soluble extractable micronutrients of some selected fertilizers derived from various sources in the Kingdom of Saudi Arabia.

No.	Fertilizer Grade/Type	Total Contents (($mg\ kg^{-1}$)				Water extractable ($mg\ kg^{-1}$)			
		Cu	Zn	Fe	Mn	Cu	Zn	Fe	Mn
1	12-27-18 (SMNF)	11	186	1100	14	2.45	17.15	5.00	1.05
2	23-23-0 (SMNF)	15	161	2666	20	1.25	6.20	5.00	3.20
3	11-52-0 (MAP)	45	451	2560	19	15.00	157.50	25.95	3.50
4	18-46-0 (DAP)	28	314	1554	18	5.00	112.00	167.50	0.75
5	20-5-30 (WSMF)	60	111	102	106	15.00	155.00	25.00	3.40
6	14-38-10 (SMNF)	29	300	1726	23	5.00	63.00	10.55	1.05
7	11-29-19 (SMNF)	23	211	1029	15	4.75	42.50	10.75	1.20
8	11-52-0 (MAP)	44	450	2300	22	15.00	159.00	25.90	3.40
9	18-46-0 (DAP)	36	370	1980	18	9.75	165.80	319.00	1.05
10	28-28-0 (SMNF)	22	225	1660	17	4.00	41.90	46.65	0.65

effective level, application of 0.5 Mg ha^{-1} YR^{-1} of P fertilizer would provide the soil with 454 g Zn ha^{-1}. Assuming that such Zn levels would be available to plants, then the amount of Zn available in soils might increase by only 0.23 mg kg^{-1}. This conclusion invalidates the assumption of Golly (1987) who suggested that application of phosphatic fertilizers provides the soil reserve with considerable amounts of zinc. It is of interest to note that under local conditions many workers (Mashhady, 1983; Al-Mustafa *et al.*, 1989; Modaihsh, 1997) have demonstrated that most Saudi Arabian soils are likely to contain insufficient levels of Zn; less than 1 mg kg^{-1}. Therefore, application of Zn has been given high profile by growers. However, from the data presented herein, inorganic fertilizers, especially phosphatic ones, would have a slight contribution to soil Zn levels.

Total content of Mn in the surveyed fertilizers centered around 16.60 mg kg^{-1} in SMNF fertilizers, 18.80 mg kg^{-1} in phosphatic fertilizers and 317.5 mg kg^{-1} in WSMF fertilizers. Similarly total Cu content was very low, with a median value of 22.4 mg kg^{-1} in SMNF fertilizers, 40.6 mg kg^{-1} in phosphatic fertilizers, and 58.13 mg kg^{-1} in WSMF fertilizers. The obtained values for Mn in phosphatic fertilizers resemble those given by Golly (1987) but were much less than those reported by others (*e.g.*, Arora 1975; Charter *et al.*, 1993). As for Cu, although values were comparatively low, they exceeded those reported by Charter *et al.* (1993) for phosphatic fertilizers marketed in Iowa (<1.5-13.0 mg kg^{-1}) but were similar to those found by Golly (1987). Water-soluble Mn and/or Cu of selected fertilizers comprised only a very small portion of total content (Table 4). The soils of Saudi Arabia mostly contain relatively high Mn content (Mashhady and Metwally 1979; Mashhady and El-Damaty, 1981), and the latter authors concurred that Mn application is of little significance for crop production. Therefore, under the prevailing conditions, enrichment of soil with Mn might be a luxury or even improper practice in terms of possible antagonistic interactions between elements. With regard to Cu, little work has been conducted using Saudi Arabian soils. Earlier investigations carried out by Mashhady (1983), using calcareous soils, showed that heavier textured Saudi Arabian soil in particular, might not induce Cu deficiency due to its inherently higher levels. The data discussed herein suggest that the impurities of inorganic fertilizers marketed in the Kingdom of Saudi Arabia contain reasonable amounts of both Fe and Zn but poor levels of Mn and Cu. The obtained results indicate that only very small portions of the total content of micronutrients, present as impurities, were water-soluble. In other words, these micronutrients might not have an immediate influence on plant nutrition but they may contribute at some future point in time; depending upon their solubility. Another aspect that should be considered in assessing the impact of these impurities is the labile pool of micronutrients in the soil itself. As the levels of both Fe and Zn in most Saudi Arabian soils are inadequate to meet plant requirements, direct fertilization with these two elements should be seriously considered.

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