

Micro Nutrients Accumulation in Effluent Irrigated Soils of the Korangi Industrial Area, Karachi-Sindh

MIDRAR-UL-HAQ, HAJI KHAN PUNO, RIAZ A. KHATTAK[†], M. SALEEM SAIF AND KAZI SULEMAN MEMON

Department of Soil Science, Sindh Agriculture University, Tando Jam - Pakistan

[†]*Department of Soil and Environmental Sciences, NWFP Agricultural University, Peshawar - Pakistan*

Corresponding author's e-mail: midrarulhaq59@yahoo.com

ABSTRACT

To assess the micronutrients accumulation in effluent irrigated soils of the Korangi Industrial Area, Karachi (Sindh), this study was conducted during the years 2000 and 2001. The soil samples were collected from two depths 0-20 and 20-40 cm. A total of 88 soil samples were collected including 80 samples (40 samples from each depth) from soils irrigated with effluents and eight samples (four samples from each depth) from soil irrigated with tubewell waters, considered as 'background soil'. All the soil samples were analyzed for chemical properties and micronutrients concentrations. The soil samples were found alkaline in reaction, non-saline, moderately to highly calcareous in nature and low to adequate in organic matter content. The average values of Zn, Cu, Fe and Mn were 4.35, 4.89, 17.83 and 13.02 mg kg⁻¹, respectively in effluent irrigated soils at surface 0-20 cm soil depth while these values decreased in sub-soils and were recorded as 3.32, 3.29, 13.60 and 10.88 mg kg⁻¹, respectively. The average values of Zn, Cu, Fe, and Mn in tubewell irrigated soils were 1.80, 3.10, 5.39, and 5.29 mg kg⁻¹ at 0-20 cm and 1.53, 2.53, 4.62, and 3.43 mg kg⁻¹ at 20-40 cm soil depth, respectively. The micronutrients levels in effluents irrigated soils were significantly ($P < 0.05$) higher than those in tubewell irrigated soils.

Key Words: Nutrients; Irrigated Soil; Korangi; Karachi

INTRODUCTION

Micronutrients are involved in many key metabolic processes such as respiration, photosynthesis and fixation of some major nutrients (Mengal & Kirbay, 1987). In general, plants are much more resistant to an increased concentration than to an insufficient level of a given element (Kabata-Pendias & Pendias, 1984). Micronutrients enter into the soil system via different pathways including agricultural additives such as lime, fertilizer, manure, herbicides, fungicides and irrigation waters as well as via potentially deleterious materials such as sewage sludge, municipal composts, industrial and mine wastes, dredged materials and atmospheric deposits (Berrow, 1986). In the soil, micronutrients are adsorbed and retained by the organic and inorganic soil colloids (Bride, 1986) and then supplied to the plants for essential metabolic processes and enzymatic reactions (Adrian, 1986). The micronutrients Zinc (Zn) and copper (Cu) are adsorbed by soil colloids and soil organic matter and known to exist as exchangeable ions. Although they do form insoluble compounds, their availability in soils is not generally controlled by precipitation. However, Iron (Fe) and Manganese (Mn) chemistry in soils is largely governed by precipitation reactions. Soils pH and oxidation-reduction status exert a major influence on the availability of Fe and Mn (Bernard *et al.*, 1980).

This paper presents results of the micronutrients (Zn, Cu, Fe & Mn) in effluent and tubewell irrigated soils of Karachi, Sindh, Pakistan. The build up of these elements with time period is also investigated and discussed.

MATERIALS AND METHODS

The soil samples were collected from agricultural fields in the Korangi Industrial Area and Memon Goth (Malir Area), Karachi. All the fields were grown with seasonal vegetables, which receive industrial effluents and tubewell water for irrigation in the Korangi Industrial Area and Memon Goth, respectively. The composite soil samples were collected in polythene bags from two depths (0-20 & 20-40 cm) with the help of stainless steel auger. The criteria for selection of the sampling sites were based on the possible contamination due to irrigation with industrial wastes waters. A total of 88 soil samples were collected from Karachi, Sindh including 80 samples (40 samples from each depth) from Korangi Industrial Area soils irrigated with effluents and eight samples (four samples from each depth) from Memon Goth soils irrigated with tubewell waters considered as 'background samples'.

The samples were collected from the same locations both in summer and winter seasons of the years 2000 and 2001. The soil samples brought to the laboratory were air dried, sieved (< 2 mm) and then analyzed for pH and EC by 1:5 soil water suspension method (Mc Lean, 1982; Rhoades, 1982), Lime by acid neutralization method (Richards, 1954), organic matter by Walkely and Black Method (Nelson & Sommer, 1982), soil texture by Bouyoucos hydrometer method (Gee & Bander, 1986), while micro nutrients (Zn, Cu, Fe & Mn) were extracted with AB-DTPA (Havlin & Soltanpour, 1981) and then analyzed by atomic absorption spectrophotometer (Perkin Elmer, Model No. 2380). The significance of results was tested by t-test ($P < 0.05$) as described by Steel and Torrie (1980).

RESULTS AND DISCUSSION

To evaluate the effect of year, season and sampling depth, analysis of variance using 2³ factorial RCBD was applied on the data for the concentrations of micronutrients (Zn, Cu, Fe & Mn) in soil samples collected from Korangi Industrial Area, Karachi during summer and winter seasons of the years 2000 and 2001. Table I provides the summary of the statistical analysis with given level of probability. The ANOVA showed significant variations within the given sites of sampling as evident from the level of probability and co-efficient of variations, which ranged from 20.25 – 52.23%. This observation is understandable as soil samples were collected from diverse locations.

Table II shows data for the concentration of Zn, Cu, Fe and Mn in soil samples collected during summer and winter seasons of the years 2000 and 2001. The comparison of the mean values of micronutrients in effluent irrigated soil samples (n = 40), with the concentration in tube well irrigated soil samples (n = 4), based on t-test is provided in Table III. Table IV indicates the relationship of micronutrients with soil pH and organic matter content. The data regarding soil chemical properties is presented in Table V.

AB-DTPA Extractable Micronutrient Concentration.

Zinc. The concentrations of Zn [Zn], varied between 0.30 to 5.63 mg kg⁻¹ in surface soils (0-20 cm) and from 0.22 to 5.06 mg kg⁻¹ in subsurface (20-40 cm) with the mean values of 3.71 and 2.97 mg kg⁻¹, respectively in summer 2000 (Table II). During the winter 2000, [Zn] ranged from 0.57 to 6.97 in surface and 1.81 to 5.97 mg kg⁻¹ in sub-surface soil samples having mean values of 4.19 and 3.61 mg kg⁻¹, respectively.

Similarly, in summer 2001, [Zn] ranged from 2.44 to 8.22 with the mean value of 4.98 mg kg⁻¹ in surface soils while 1.28 to 5.18 with the mean value of 3.17 mg kg⁻¹ in sub-soils. The [Zn], during winter 2001, varied between 2.00 to 8.10 and 1.48 to 6.11 with the average values of 4.87 and 3.67 mg kg⁻¹ in surface and sub-surface soil samples, respectively. The overall mean value of Zn in effluent irrigated soil samples was 4.35 mg kg⁻¹ against the background value of 1.80 mg kg⁻¹ for 0 - 20 cm soil depth while 3.32 mg kg⁻¹ against 1.53 mg kg⁻¹ for 20-40 cm soil depth (Table III).

The analysis of variance showed that [Zn] in the year 2001 was significantly higher than that in the year 2000 and similarly, significantly higher in the surface soils compared to sub-surface soils (Table I). According to t-test comparison, [Zn] in effluent irrigated soil samples was significantly higher than that in tube well irrigated soil samples (Table III). Such a significant variation can be ascribed to effluents application in irrigation water.

The average values of Zn observed in this study are higher than those reported by Sillanpaa (1985), Bozdar (1991) and Tunio (2001) for various sites of Sindh. They reported low level of Zn in these soils ranging from 0.20-

1.39 mg kg⁻¹ because tubewell and canal waters rather than industrial effluents were used for irrigation.

Copper. The concentration of copper [Cu] in summer 2000 ranged from 2.79 to 6.71 and 1.93 to 5.58 with the average values of 5.59 and 3.68 mg kg⁻¹ at 0 - 20 and 20 - 40 cm soil depths, respectively. The range of [Cu] observed during winter 2000 for surface and sub-surface soil samples was 1.46 to 5.88 and 0.93 to 3.86 with the mean values of 3.92 and 2.75 mg kg⁻¹, respectively (Table II).

Similarly, the observed range of Cu during summer 2001 was 3.34 to 7.46 with the average value of 5.87 mg kg⁻¹ for 0-20 cm and 1.78 to 5.06 with the average value of 3.83 mg kg⁻¹ for 20-40 cm soil depth. During the winter 2001, the [Cu] ranged from 2.11 to 7.10 with the mean concentration of 4.17 mg kg⁻¹ and from 1.52 to 5.13 with the average value of 3.12 mg kg⁻¹ in surface and sub-surface soil samples, respectively (Table II). The overall mean concentration of Cu in effluent irrigated soil samples were 4.89 and 3.29 mg kg⁻¹ in surface and sub-surface soil samples, respectively. While, the mean value of Cu in

Table I. Summary of ANOVA showing the effect of year, season and sampling depth on the concentrations of micro nutrients (Zn, Cu, Fe, Mn) at the given level of probability

Sources of variations	Micro nutrients in effluent irrigated soils (n=80)			
	Zn	Cu	Fe	Mn
Year	0.004	>0.15	0.121	>0.15
Season	0.086	<0.0001	<0.0001	0.0001
Depth	<0.0001	<0.0001	<0.0001	0.069

Table II. Concentration of micronutrients (mg kg⁻¹) in effluent irrigated soil samples collected from various sites of Korangi Industrial Area, Karachi, Sindh, during summer and winter seasons of the years 2000 and 2001

Soil Depth (cm)	Micronutrient	Values	Year 2000		Year 2001	
			Summer	Winter	Summer	Winter
0-20	Zn	Min	0.30	0.57	2.44	2.00
		Max	5.63	6.97	8.22	8.10
		Mean	3.71	4.19	4.98	4.87
	Cu	Min	2.79	1.46	3.34	2.11
		Max	6.71	5.88	7.46	7.10
		Mean	5.59	3.92	5.87	4.17
	Fe	Min	3.34	3.30	5.44	5.78
		Max	33.34	23.96	36.6	24.12
		Mean	18.85	13.60	22.06	15.66
	Mn	Min	4.31	6.27	9.16	7.02
		Max	47.20	16.11	34.86	17.08
		Mean	15.87	8.98	17.07	11.57
20-40	Zn	Min	0.22	1.81	1.28	1.48
		Max	5.06	5.97	5.18	6.11
		Mean	2.97	3.61	3.17	3.67
	Cu	Min	1.93	0.93	1.78	1.52
		Max	5.58	3.86	5.06	5.13
		Mean	3.68	2.75	3.83	3.12
	Fe	Min	2.58	8.14	3.12	4.02
		Max	28.66	20.48	28.32	20.32
		Mean	14.94	12.23	15.10	12.35
	Mn	Min	2.63	5.13	5.22	4.66
		Max	41.85	19.13	24.26	15.46
		Mean	14.14	7.62	12.68	8.66

Min= Minimum; Max= Maximum.

Table III. Comparison of the average values (mg kg⁻¹) of micronutrients in effluent and tube well irrigated (background) soil samples collected from various sites of Karachi, Sindh Province

Micronutrients	Soil Depth (cm)	Effluent irrigated soil mean values (n=40)	Tube well irrigated soil mean values (n=4)	t-value
Zn	0-20	4.35	1.80	9.26**
	20-40	3.32	1.53	8.90**
Cu	0-20	4.89	3.10	2.92
	20-40	3.29	2.53	3.73*
Fe	0-20	17.83	5.39	8.10**
	20-40	13.66	4.62	12.81**
Mn	0-20	13.02	5.29	5.83*
	20-40	10.88	3.43	4.98*

*,** Tube well irrigated soil values are significantly lower than the mean values of effluent irrigated soils at P < 0.05 and 0.01, respectively

tubewell irrigated soil samples were 3.10 and 2.53 mg kg⁻¹ for the given respective soil surfaces (Table III).

The analysis of variance showed that [Cu], is significantly higher in summer compared to winter season and similarly, significantly higher in surface soils than that in sub-surface soils (Table I). The t-test comparison showed that [Cu] in effluent irrigated soils was significantly higher than that in tube well irrigated soils. This difference might be due to industrial effluents containing Cu from various industries.

According to Lindsay and Norvell (1978) the DTPA - Cu concentration above 0.2 mg kg⁻¹ is considered adequate while Havlin and Sultanpour (1981) observed that AB-DTPA - Cu concentration above 0.5 mg kg⁻¹ could be considered adequate. Tunio (2001) reported Cu concentration range of 2.16-2.75 mg kg⁻¹ in tubewell irrigated soils of Latif Experimental Farm, Sindh Agriculture University (SAU) Tandojam. The observed mean values of Cu given in Table II showed that the soils of Korangi Industrial Area, Karachi contained an adequate amount of Cu required for crops growth and are higher than the values observed by Tunio (2001) for Sindh soils, which were tubewell irrigated.

Iron. The iron concentrations [Fe], varied from 3.34 to 33.34 in surface soils and from 2.58 to 28.66 mg kg⁻¹ in sub-surface with the mean values of 18.85 and 14.94 mg kg⁻¹, respectively during summer 2000 (Table II). While in winter 2000, [Fe] ranged from 3.30 to 23.96 in surface and 8.14 to 20.48 mg kg⁻¹ in sub-surface soil samples having mean values of 13.60 and 12.23 mg kg⁻¹, respectively.

Table IV. Relationship of pH and soil organic matter (O.M) with micronutrient

IV	Soil depth (cm)	Zn		Cu		Fe		Mn	
		R	t	r	t	r	t	r	t
pH	0-20	-0.62	4.84***	-0.35	2.32*	-0.45	3.12**	-0.19	1.20
	20-40	-0.41	2.75**	-0.22	1.42	-0.44	3.06*	-0.63	5.01***
O.M	0-20	0.85	10.1***	0.46	3.22**	0.64	5.19**	0.12	0.74
	20-40	0.68	5.68***	0.41	2.76**	0.51	3.63***	0.20	1.28

*, **, *** Significant at P < 0.05, 0.01 and 0.001, respectively; IV= Independent variable

Similarly, in summer 2001, [Fe] ranged from 5.44 to 36.60 with the mean concentration of 22.06 mg kg⁻¹ in surface soils while 3.12 to 28.32 with the mean concentration of 15.10 mg kg⁻¹ in sub-soils. During winter 2001, [Fe] declined and ranged from 5.78 to 24.12 and 4.02 to 20.32 with the average of 15.66 and 12.35 mg kg⁻¹ in surface and sub-surface soil samples, respectively (Table II). The data showed that [Fe] was lower in winter than that in summer and similarly, was lower in sub-surface soils than that in surface soils. The overall mean [Fe] in effluent irrigated soil samples was 17.83 mg kg⁻¹ against the background value of 5.39 mg kg⁻¹ in surface soils while 13.66 mg kg⁻¹ against 4.62 mg kg⁻¹ in sub-surface soils (Table III).

The analysis of variance showed that [Fe] is significantly (P < 0.0001) higher in summer season compared to winter and similarly, significantly higher in surface soils than that in sub-surface soils (Table I). The t-test comparison showed that [Fe] in effluent irrigated soils was significantly (P < 0.05) higher than that in tube well irrigated soils (Table I). Such a significant variation can be associated with effluent irrigation and higher organic matter content.

According to Havlin and Soltanpour (1981), the AB-DTPA - [Fe] above 4.0 mg kg⁻¹ could be considered adequate. The observed mean values of [Fe] in Table II showed an adequate amount of [Fe] in soils of Korangi Industrial Area, Karachi. Memon (1985) reported similar results about the adequate amount of [Fe] in soils of Hyderabad. This adequacy was not due to effluent irrigation but due to heavy application of commercial fertilizers as well as farm yard manure. However, a low [Fe] ranging from 2.12 to 3.17 mg kg⁻¹ was observed by Tunio (2001) in tubewell irrigated soils of Tandojam. The low [Fe] in these soils might be due to insufficient application of Fe in fertilizers.

Manganese. In summer 2000, the concentration of Mn [Mn], ranged from 4.31 to 47.20 and 2.63 to 41.85 with the average values of 15.87 and 14.14 mg kg⁻¹ in surface and sub-surface soil samples, respectively. During the winter 2000, [Mn] ranged from 6.27 to 16.11 in surface and 5.13 to 19.13 mg kg⁻¹ in sub-surface soil samples having mean concentration of 8.98 and 7.62 mg kg⁻¹, respectively (Table II). Similarly, [Mn] ranged from 9.16 to 34.86 with the average value of 17.07 mg kg⁻¹ in surface soils and 5.22 to 24.26 having mean value of 12.68 mg kg⁻¹ in sub-surface soils, during summer 2001. However, in winter 2001, [Mn] varied between 7.02 to 17.08 and 4.66 to 15.46 mg kg⁻¹ with an average value of 11.57 and 8.66 mg kg⁻¹ in surface and sub-surface soil samples, respectively (Table II). The data showed that [Mn] tended to increase in summer compared to winter and decreased with soil depth. The overall mean concentration of Mn in effluent irrigated soil samples was 13.02 and 10.88 mg kg⁻¹ in surface and sub-surface soil samples, respectively. While, the mean values in tube well irrigated soil samples were 5.29 and 3.43 mg kg⁻¹ for the

given respective soil surfaces (Table III).

The analysis of variance showed that [Mn], was significantly higher in summer season compared to winter and similarly significantly higher in surface soils than that in sub-surface soils (Table I). According to t-test comparison, [Mn] in effluent irrigated soils was significantly higher than that in tube well irrigated soil (Table III).

Bansal *et al.* (1992) reported similar results, who observed Mn content of 12.8 mg kg⁻¹ in industrial waste water irrigated soils near Ludhiana, Punjab (India). Havlin and Soltanpour (1981) reported that AB-DTPA Mn concentration above 1.8 mg kg⁻¹ could be considered adequate for plant growth. By comparing, all the values were found in adequate range as shown in Table II. Memon (1985) and Tunio (2001) reported similar results and found an adequate amount of Mn in soils of Hyderabad and Tandojam (Sindh), respectively. Although tubewell water was used for irrigation on these soils but due to application of organic as well as inorganic fertilizers the adequacy of [Mn] was achieved.

An effort was also made to study the correlation between chemical properties and AB-DTPA extractable micronutrients concentrations. The pH of surface soil showed negative and significant correlation with Zn, Cu and Fe while non-significant correlation with Mn. However, in sub-surface soils the pH showed negative and significant correlation with Zn, Fe and Mn while non-significant correlation with Cu. The concentrations of Zn, Cu and Fe showed positive and significant correlation with organic matter at both depths (0-20 & 20-40 cm) as given in Table IV. The changes in soil chemical properties and their correlation with micronutrients (Zn, Cu, Fe & Mn) may be due to variations in composition of effluent used for irrigation. The composition of industrial effluents varies from time to time because of the different chemicals used by various industries in the Korangi Industrial Area, Karachi. The exercise of using industrial effluents for irrigation to grow seasonal vegetables is widely practiced in this area for a very long time. So, the industrial effluents containing a variety of chemicals might have affected soil chemical properties and micronutrients accumulation. Moreover, the data showed that micronutrient concentrations tended to increase in summer as compared to winter and decreased with depth, which can be associated with changes in temperature, pH, microbial activities and variations in climatic conditions (rain fall) because surface soils are more exposed to effluents and other site related complex factors.

Based upon the above discussion it can be concluded that effluent irrigation has made fair micronutrient accumulation in soil, which could be considered adequate for crop growth, but the long term application of industrial and domestic wastewater via irrigation water may cause the build up of these elements in soils to undesirable and phytotoxic levels. So, the excessive addition of micronutrients would neither be economical nor safe from environmental point of view.

Table V. Chemical characteristics of different soil samples collected from Korangi Industrial Area Karachi, Sindh during different seasons of the years 2000 and 2001

Parameter	Soil Depth (cm)	2000		2001		Mean Values (n=40)
		Summer (n=10)	Winter (n=10)	Summer (n=10)	Winter (n=10)	
pH	0-20	8.09	8.01	8.04	8.06	8.05
	20-40	8.12	8.11	8.07	8.11	8.10
EC (dSm ⁻¹)	0-20	0.33	0.20	0.41	0.35	0.32
	20-40	0.31	0.16	0.44	0.39	0.32
Lime (%)	0-20	23.04	20.95	22.47	22.25	22.17
	20-40	22.1	23.25	19.15	18.7	20.8
O.M (%)	0-20	0.84	0.91	0.97	1.14	0.96
	20-40	0.72	0.70	0.72	0.87	0.75

REFERENCES

- Adrian, D.C., 1986. *Trace Elements in the Terrestrial Environment*, p. 56. Springer, N.Y.
- Bansal, R.L., V.K. Nayyar and P.N. Takkar, 1992. Accumulation and bioavailability of Zn, Cu, Mn, and Fe in soils polluted with industrial wastewater. *J. Ind. Soc. Soil Sci.*, 40: 796-9
- Bernard, D., Knezek and B.G. Ellis, 1980. Essential micronutrients IV: Copper, Iron, Manganese and Zinc. In: Davies, B.E. (ed.), *Appl. Soil Trace Elements*, pp. 259-86. John Wiley and Sons Ltd. UK
- Berrow, M.L., 1986. An Overview of soil contamination problems. In: Lester, J.N. *et al.* (eds.), *Proc. Int. Conf. Chemical in the environment*. pp. 543-52. Selper Ltd. London
- Bozdar, L., 1991. Assessing Zn availability status of wheat areas of district Hyderabad, through analysis of soil and associated plant tissue. *M.Sc (Agri.) Thesis*, submitted to Sindh Agric. Univ. Tandojam
- Bride, M.B.M.C., 1986. *Environmental Chemistry of Soil*. p. 184. Oxford Univ. Press, N.Y.
- Gee, G.W. and J.W. Bander, 1986. Particle size analysis. In: Kiute, A. (ed.), *Methods of Soil Analysis*, pp. 383-411. Am. Soc. Agron. Madison WI.
- Havlin, J.L. and P.N. Soltanpour, 1981. Evaluation of the NH₄ HCO₃-DTPA soil test for iron and Zinc. *Soil Sci. Soc. Am. J.*, 45: 70-5
- Kabata-Pendias, A. and H. Pendias, 1984. *Trace Elements in Soils and Plants*, pp. 28-34. CRC Press, Inc., Florida, USA
- Lindsay, W.L. and W.A. Norvell, 1978. Development of DTPA soil test for Zn, Cu, Fe and Mn. *Soil Sci. Soc. Am. J.*, 42: 421-8
- Mclean, E.O., 1982. Soil pH and Lime requirement. In: Page, A.L., M.H. Miller and D.R. Keeny (eds.), *Methods of Soil Analysis*, pp. 209-23. Part 2, 2nd ed. Am. Soc. Agron. Madison. WI.
- Memon, K.S., 1984-85, 1985-86. Cooperative research program on micronutrient status of Pakistan-soils. 2nd Annual Report Department of Agric. Chemistry, Sindh Agric. Univ. Tandojam
- Mengal, K. and E.A. Kirby, 1987. *Principles of Plant Nutrition*. p. 80. International Potash Institute, Worblaufen-Bern, Switzerland
- Nelson, D.W. and L.E. Sommer, 1982. Total carbon, organic carbon and organic matter. In: Page, A.L. M.H. Miller and D.R. Kenny (eds.), *Methods of Soil Analysis*, pp. 539-77. Part 2, 2nd ed. Am. Soc. Agron. Madison. WI. New York, USA
- Rhoades, J.D., 1982. Soluble salts. In: Page, A.L., M.H. Miller and D.R. Keeny (eds.) *Methods of Soil Analysis*, pp. 167-79. Part 2, 2nd ed. Am. Soc. Agron. Madison. WI.
- Richards, L.A., 1954. *Diagnosis and Improvement of Saline and Alkali Soils*. Hand Book 60 USDA
- Sillanpaa, M., 1982. Micronutrients and the nutrient status of soils, a global study. *F.A.O. Soil Bull.* 48; Rome
- Steel, G.D.R. and J.H. Torrie, 1980. *Principles and Procedures of Statistics. A Biometrical Approach*, 2nd ed. McGraw Hill, Inc. New York, USA
- Tunio, S.P., 2001. The micronutrient status of the soil of Latif Farm. Block B and C. *M.Sc (Agri.) Thesis*, Submitted to Sindh Agri. Univ. Tandojam

(Received 20 November 2003; Accepted 10 December 2004)