

$$Y_4 = 17.337 - 1.577X_1 + 0.313X_2 + 7.500X_3 - 0.081X_4 + 0.065X_5 - 0.088X_6$$

Where, Y_4 = Available Mn

It is evident from table 4, that the main contributing factors responsible for variation (72.28%) in available Mn were pH, OC and CaCO_3 . Inclusion of EC, clay and CEC could slightly improve the prediction value to 80.07% only.

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Correlation Studies on Micronutrients *vis-à-vis* Soil Properties in Some Soils of Nagaur District in Semi-arid Region of Rajasthan

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Abstract: Status of micronutrients and effect of soil properties on their status were studied in some soils of the semi-arid region of Rajasthan. Zinc, Cu, Fe, Mn and B showed positive correlations with silt plus clay and organic carbon, and negative correlations with pH and calcium carbonate content. Molybdenum showed negative correlation with silt plus clay and organic carbon, and positive

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correlation with pH and calcium carbonate content. Available Zn, Cu, Fe, Mn, B and Mo contents ranged from 0.1 to 1.7, 0.5 to 3.9, 1.0 to 6.6, 2.7 to 7.2, 0.2 to 2.0 and 0.1 to 1.3 mg kg⁻¹ with the mean values of 0.73, 2.11, 4.32, 5.15, 0.68, and 0.48 mg kg⁻¹, respectively. Silt plus clay, electrical conductivity, pH, organic carbon and calcium carbonate in soils ranged from 7.9 to 21.8 %, 0.11 to 0.52 dSm⁻¹, 8.0 to 9.3, 0.08 to 0.31 and 0.1 to 1.2% with the mean value of 12.9%, 0.28 dSm⁻¹, 8.5, 0.2 and 0.5%, respectively. Available Zn, Fe and B were deficient in 46, 51.5 and 26.5% soil samples, respectively, while Cu, Mn and Mo were adequate in all the soil samples. Multiple regression analysis indicated that available Zn, Cu, Fe, Mn, B and Mo were significantly influenced by soil properties together at the level of 70, 62, 50, 55, 76 and 95%, respectively. (*Key words: Available micronutrient status, soil-site characteristics, and semi-arid areas*)

The stagnation in crop productivity has been found due to deficiency of some micro- and secondary nutrients. Hence, micronutrients have assumed increasing importance in crop production under modern agricultural technology. Introduction of high yielding wheat, rice and maize varieties in Indian agriculture in mid-sixties compelled the farmers to use high doses of inorganic NPK fertilizers which were also free from micronutrients as impurities. Limited use of organic manures as well as recycling of crop residues are some important factors having contributed towards accelerated exhaustion of micronutrients from soil. Deficiency of micronutrients has become a major constraint to productivity, stability and sustainability in many soils. Although widespread Zn, Cu, Fe, Mn and B deficiency has been observed in the soils of arid and semi-arid regions, the information with respect to micronutrient availability *vis-à-vis* soil-site characteristics for semi-arid region of Rajasthan is lacking. Therefore, an attempt was made in the present investigation to correlate micronutrient contents of the soils with soil-site characteristics.

Materials and Methods

The study area covers Nawa *tehsil* of Nagaur district in semi-arid region of Rajasthan. Physiographically, it is undulated and marked with sand dunes. The soils of the area are characterized by light texture, high pH, salinity, alkalinity and low organic matter content. The semi-arid climate of the area is characterized by wide range of temperature between summer and winter with an average annual rainfall around 450 mm of which 85% is contributed by southwest monsoon during July to August. Random soil samples (0-15 cm) were collected from 200 sites covering 56 *Gram Panchayats*, keeping in view the physiographic characteristics in different cross-sections of the area as well as the variation in soil texture. The processed soil samples were analysed for physical and chemical properties using standard procedures (Jackson 1973). The available Zn, Cu, Fe and Mn were

extracted with a solution of 0.005 M DTPA, 0.01 M CaCl₂ and 0.1 M Triethanolamine (adjusted to pH 7.3) as outlined by Lindsay and Norvell (1978). The concentration of these micronutrients in the extracts was determined using Atomic Absorption Spectrophotometer. Hot water soluble B was determined by Azomethine-H colorimetric method (Page *et al.* 1982). Acid ammonium oxalate at pH 3.3 (Griggs reagent) was used as an extracting agent for the determination of available Mo in soils. Toluene-3, 4-dithiol yields a slightly soluble dark green complex with Mo (vi) in mineral acid medium, which can be extracted by an organic solvent. The resulting green coloured complex is used for the colorimetric determination of Mo as described by Tandon (1995).

Simple correlation coefficients and multiple regression equations were computed relating micronutrient content with different physico-chemical properties of the experimental soils as suggested by Panse and Sukhatme (1961).

Results and Discussion

Considering the critical limits of different micronutrients, the available status of Zn, Cu, Fe, Mn, B and Mo were categorised in sufficient and deficient categories. According to the critical limits suggested by Takkar and Mann (1975) for Zn (0.6 mg kg⁻¹ for deficient, 0.6 to 1.2 mg kg⁻¹ for marginal and more than 1.2 mg kg⁻¹ for sufficient level), out of the 200 soil samples 46% were deficient, whereas 41% were marginal and 13% were sufficient in available Zn. It was observed that 52% soil samples were deficient in available Fe considering 4.5 mg kg⁻¹ as critical limit, suggested by Lindsay and Norvell (1978). All the soil samples were sufficient in available Cu and Mn considering 0.2 mg kg⁻¹ for Cu and 1.0 mg kg⁻¹ for Mn as critical limits as suggested by Lindsay and Norvell (1978). Takkar and Randhawa (1968-76) suggested 0.5 mg kg⁻¹ hot water soluble B as critical limit. Considering the critical limit, 26.5% samples were found deficient in available B. Kanwar and Randhawa (1974)

have suggested 0.05 mg kg^{-1} ammonium oxalate extractable Mo as the critical limit. Considering this, all the soil samples were adequate in available Mo. The weighted means of soil properties and micronutrient contents are presented in table 1.

Influence of pH on Availability of Micronutrients

Zinc, Cu, Fe, Mn and B were negatively correlated with pH while Mo was positively correlated (Tables 2 and 3).

In alkaline range, particularly above pH 7.85, Zn forms negatively charged ions called zincate ions. The acid zincate ZnO_2^{2-} is the prevalent form in lower concentration of alkali. Probably in alkali solutions, the hydroxides of Zn are formed (Kanwar 1976). A change in pH may alter the stability of soluble and insoluble organic complexes of Zn or the solubility of antagonistic ions (Singh and Singh 1981). Rupa and Shukla (1998) also found significant negative correlation between Cu fractions and pH of the soil and opined that this may probably be due to precipitation of Cu as hydroxides at higher pH. Thus, newly formed hydroxides of Cu, would have either become the part of lattice or occluded with the hydroxides of Fe, Al and Mn (Lindsay 1979). Reduction in availability of Fe with an increase in pH may be attributed to conversion of Fe^{2+} ions to Fe^{3+} ions. At high pH, Fe may also precipitate as insoluble $\text{Fe}(\text{OH})_2$. With increase in pH, divalent form (Mn^{2+}) may convert into trivalent or polyvalent forms (Mn^{3+} to Mn^{7+}) which are water insoluble and not easily available to the plants. At higher pH (>8.0), B may convert into sparingly soluble Ca-borate or boro-silicate. A significant positive correlation was found between pH and available Mo in soils under investigation. At higher soil pH, the plants are able to utilize more Mo because of increased solubility in the soil and better absorption within the plants. Tisdale and Nelson (1966) attributed the increased Mo availability with increase in pH due to the replacement of MoO_4^{2-} by OH^- ions.

Influence of Organic Carbon on Availability of Micronutrients

A significant positive correlation of Zn, Cu, Fe, Mn and B was observed with organic carbon while negative between Mo and organic carbon (Table 2 & 3).

It has been reported that organic matter plays an important role in controlling the availability of Zn particularly in alkaline soils. Decomposition of organic matter reduces pH of soil locally, which helps in increasing solubility of Zn from soil materials. Ad-

dition of organic matter improves the soil structure and aeration, which increase the availability of Fe (Singh and Banerjee 1984; Gupta and Srivastava 1990). Dolui and Mustafi (1997) also observed similar relationship between organic carbon and extractable Fe indicating that organic carbon influenced the solubility and availability of Fe which protects itself from oxidation and precipitation of available Fe into unavailable forms and increase Fe availability in soils. Increase in the availability of Mn with the increase in organic carbon might be due to the influence of organic carbon on the solubility and availability of Mn that protects itself from oxidation and precipitation of available Mn into unavailable forms. The availability of the metal ions (Zn, Cu, Fe, Mn) increases with increase in organic matter content because organic matter may supply chelating agents. The average fixation of applied B is reported to increase from 48% to 60% when the organic carbon content increased from 0.5% to 0.75% (Sakal *et al.* 1985; Sakal 1987). A significant negative correlation was found between organic carbon and available Mo. Similar types of results have been reported by Iyer (1959) and Pathak *et al.* (1968).

Influence of Calcium Carbonate on Availability of Micronutrients

Zinc, Cu, Fe, Mn and B were negatively correlated with calcium carbonate content while Mo was positively correlated (Tables 2 and 3).

Leeper (1947) postulated that CaCO_3 might act as a strong adsorbent for heavy metals while Hazra *et al.* (1987) reported that the increase in CO_3^{2-} content in soils raises the possibility of soluble Zn to precipitate as ZnCO_3 and $\text{Zn}_3(\text{CO}_3)_2(\text{OH})_2$. Calcium carbonate has also been reported to decrease the availability of Cu by bringing a change in the soil reaction. Calcium carbonate may retain considerable amount of Cu in the forms unavailable to plants. A negative relationship of CaCO_3 with available Fe might be due to the fact that increase in CaCO_3 content favours the precipitation or oxidation of Fe^{2+} to Fe^{3+} oxides (Randhawa & Singh 1997) or transformation of available Fe into carbonates or retention by free CaCO_3 present (Halder & Mandal 1987). It is believed that Mn is fixed by adsorption on the surface of the calcium carbonate particles. Decrease in DTPA-extractable Mn with an increase in the CaCO_3 content may be attributed to the transformation of available Mn into insoluble hydroxides and carbonates or retention by free CaCO_3 present (Halder & Mandal 1987). Application of lime in soil may reduce the availability of

Table 1. Salient soil properties (weighted mean) of the study area

Sl. No.	Names of Gram-Panchayats	Number of samples collected	EC (dS/m)	pH	O.C. (%)	CaCO ₃ (%)	Silt+clay (%)	Zn	Cu	Fe	Mn B Mo		
											(ppm)		
1	Ruthpura Torda	4	0.21	8.1	0.27	0.20	20.9	1.6	3.8	6.4	6.9	1.60	0.15
2	Palada	3	0.41	8.4	0.21	0.40	16.3	1.4	3.6	6.0	6.3	0.93	0.33
3	Rasal	2	0.39	8.3	0.25	0.25	15.3	1.3	3.7	6.2	6.5	0.90	0.30
4	Anandpura	4	0.30	8.3	0.23	0.30	15.4	1.2	3.6	6.0	6.4	0.93	0.28
5	Ugarpura	1	0.29	8.6	0.15	0.60	11.8	0.7	3.0	5.3	5.6	0.30	0.60
6	Jeelia	4	0.31	8.5	0.20	0.48	11.9	0.6	3.1	5.4	6.0	0.58	0.45
7	Parewadi	1	0.40	8.5	0.20	0.50	10.4	0.3	3.1	5.6	6.0	0.80	0.50
8	Charnwash	3	0.34	8.5	0.19	0.53	12.3	0.4	3.1	5.5	6.2	0.57	0.40
9	Shiv	1	0.52	8.3	0.23	0.60	13.4	0.6	3.4	5.7	6.4	0.80	0.20
10	Chawandia	4	0.40	8.2	0.30	0.20	15.6	0.9	3.5	5.9	6.6	1.03	0.15
11	Aadakshar	3	0.20	8.5	0.20	0.70	10.5	0.4	3.0	5.3	6.4	0.60	0.73
12	Chitawa	3	0.19	8.5	0.17	0.60	12.5	0.4	3.0	5.3	6.9	0.50	0.57
13	Kukanwali	3	0.38	8.6	0.17	0.60	11.6	0.4	2.4	5.0	5.6	0.43	0.57
14	Panchwa	3	0.38	9.1	0.10	1.13	8.6	0.1	0.9	3.3	4.0	0.23	1.13
15	Sardarpura	5	0.31	9.7	0.16	0.78	11.8	0.4	1.6	3.9	4.5	0.50	0.74
16	Deppura	6	0.30	8.6	0.18	0.62	13.2	0.6	2.2	4.8	5.3	0.61	0.60
17	Hirani	4	0.32	8.3	0.24	0.33	15.0	0.9	2.6	5.2	5.8	0.80	0.28
18	Kharia	2	0.16	8.1	0.27	0.15	16.3	1.2	3.5	5.5	6.3	1.20	0.10
19	Bhanwata	3	0.16	8.3	0.24	0.30	14.5	1.0	2.7	5.0	5.7	0.90	0.30
20	Indokha	5	0.19	8.2	0.26	0.22	15.4	1.2	3.1	5.4	6.0	1.18	0.20
21	Nagwada	3	0.43	8.2	0.25	0.30	14.3	1.1	3.1	5.3	6.0	1.10	0.27
22	Todas	1	0.43	8.4	0.22	0.50	12.8	0.8	2.5	4.7	5.4	0.50	0.40
23	Hudil	3	0.44	8.2	0.26	0.23	13.7	0.9	2.6	4.9	5.6	0.93	0.23
24	Lalas	1	0.20	8.3	0.24	0.30	13.3	0.8	2.5	4.8	5.6	0.80	0.40
25	Khorandi	4	0.28	8.5	0.20	0.48	13.4	0.7	1.9	4.2	4.9	0.40	0.48
26	Endali	3	0.35	8.4	0.20	0.53	13.6	0.8	2.0	4.5	5.2	0.53	0.43
27	Nalot	3	0.33	8.4	0.22	0.40	13.5	0.9	2.3	4.7	5.4	0.67	0.37
28	Ghatwa	4	0.26	8.4	0.20	0.50	13.0	0.8	1.7	4.1	4.9	0.55	0.43
29	Jijot	5	0.33	8.1	0.26	0.10	16.2	1.2	2.7	5.2	5.7	0.78	0.12
30	Khakadki	2	0.33	8.9	0.16	0.80	10.2	0.9	0.9	3.1	3.9	0.35	0.85
31	Khardia	4	0.38	8.8	0.16	0.85	10.5	0.5	0.9	3.2	3.8	0.30	0.78
32	Mandawara	1	0.41	8.3	0.24	0.40	12.5	0.2	2.8	4.6	5.8	0.60	0.30
33	Narayanpura	6	0.23	8.5	0.22	0.53	11.0	0.6	2.0	2.4	5.1	0.55	0.45
34	Sargot	6	0.28	8.9	0.18	1.02	9.9	0.3	0.9	1.4	3.7	0.48	0.90
35	Mithadi	4	0.15	8.2	0.27	0.23	13.4	0.7	2.0	2.5	4.9	0.70	0.23
36	Panchota	1	0.11	8.0	0.29	0.10	15.7	1.1	2.3	2.8	5.2	1.20	0.10
37	Mooana	2	0.30	8.0	0.29	0.10	16.1	1.4	2.9	3.9	5.9	1.30	0.15
38	Bhoonee	3	0.37	8.3	0.24	0.50	13.0	0.8	1.9	3.3	4.8	0.90	0.30
39	Rajlia	1	0.25	8.7	0.17	0.70	10.7	0.3	1.4	3.7	4.5	0.50	0.70
40	Marot	5	0.30	8.8	0.16	0.88	11.9	0.5	1.5	4.0	4.8	0.40	0.86
41	Shyamgarh	5	0.13	9.1	0.14	0.92	10.5	0.3	1.0	3.4	4.3	0.32	0.86
42	Solaya	4	0.17	8.3	0.22	0.43	13.6	0.7	1.5	4.0	4.5	0.55	0.33
43	Bhagwanpura	2	0.35	8.3	0.23	0.35	13.9	0.8	1.8	4.1	4.8	0.70	0.25
44	Maharajpura	7	0.36	8.3	0.22	0.37	13.8	0.9	2.0	4.5	5.1	0.80	0.37
45	Govindi	3	0.12	8.7	0.17	0.73	12.6	0.6	1.6	4.0	4.6	0.43	0.70
46	Jabdinagar	2	0.19	9.2	0.13	0.95	9.0	0.2	0.6	2.9	3.6	0.25	1.10
47	Chosla	3	0.20	9.1	0.14	1.02	10.1	0.2	0.6	2.7	3.5	0.40	0.97
48	Ghoodasalt	3	0.20	8.1	0.26	0.13	12.7	0.9	2.5	4.7	5.4	0.93	0.10
49	Shimbhupura	3	0.31	8.6	0.19	0.63	11.9	0.8	1.7	4.1	5.1	0.57	0.57
50	Warjan	5	0.36	8.6	0.18	0.70	12.4	0.5	1.4	3.8	4.3	0.52	0.64
51	Deoli	7	0.23	8.5	0.19	0.59	11.9	0.6	1.7	4.0	4.6	0.53	0.50
52	Minda	6	0.31	9.1	0.12	1.05	9.1	0.5	0.8	3.1	3.8	0.30	0.98
53	Moongashoe	5	0.32	8.5	0.19	0.58	12.4	0.6	1.6	4.8	4.7	0.56	0.48
54	Loonwa	3	0.28	8.3	0.21	0.37	13.1	0.8	1.8	4.2	4.7	0.80	0.33
55	Nawa	9	0.24	8.3	0.24	0.38	13.1	1.0	2.2	4.6	5.2	0.96	0.31
56	Kuchaman	7	0.22	8.5	0.21	0.50	11.9	0.8	2.3	4.7	5.6	0.63	0.49

Table 2. Correlation coefficient (r) values of pH, electrical conductivity, organic carbon, calcium carbonate and silt plus clay with micronutrients

Dependent variable	Soil properties					
	pH	EC	Organic Carbon	CaCO ₃	Silt plus clay	
Available Zn	-0.745**	0.004	0.747**	-0.779**	0.772**	
Available Cu	-0.740**	0.049	0.680**	-0.744**	0.693**	
Available Fe	-0.566**	0.105	0.469**	-0.595**	0.624**	
Available Mn	-0.704**	0.009	0.632**	-0.709**	0.646**	
Available B	-0.787**	-0.078	0.854**	-0.793**	0.729**	
Available MO	0.957**	-0.002	-0.922**	0.959**	-0.739**	

** Significant at 1% level.

Table 3. Regression equations representing the relationship between micronutrients and different soil properties

Micronutrient	Soil property			
	pH	Organic Carbon	CaCO ₃	Silt plus clay
Available Zn	Y = -0.84x + 7.860	Y = 5.78x - 0.451	Y = -0.96x + 1.232	Y = -0.11x - 0.686
Available Cu	Y = -1.964x + 18.790	Y = 12.457x - 0.440	Y = -2.11x + 0.960	Y = 0.242x - 0.991
Available Fe	Y = -1.916x + 20.578	Y = 10.955x + 2.070	Y = -2.227x + 5.489	Y = 0.227x + 0.760
Available Mn	Y = -1.954x + 21.173	Y = 12.109x + 2.667	Y = 2.170x + 6.294	Y = 0.236x + 2.126
Available B	Y = -0.76x + 7.099	Y = 5.67x - 0.487	Y = -0.84x + 1.119	Y = 0.09x - 0.505
Available MO	Y = 0.88x - 7.000	Y = -5.86x + 1.687	Y = 0.97x - 0.028	Y = 0.09x + 1.631

hot water soluble B due to the formation of Ca-borate and B-silicate. Available Mo was positively correlated with calcium carbonate content in the soils. Similarly a significant positive correlation between calcium carbonate and available Mo was also observed by Grewal (1967), Rai *et al.* (1970) and Nayyar (1972).

Influence of Silt Plus Clay on Availability of Micronutrients

A significant positive correlation of Zn, Cu, Fe, Mn and B was observed with silt plus clay while negative with Mo and silt plus clay (Table 2 and 3).

Adsorbed metal ions (Zn, Cu, Fe, Mn) are in equilibrium with the soil solution. Thus, a soil having greater surface is expected to adsorb greater amount of these ions and *vice-versa*. Increase in the finer fraction of the soil leads to increase in the surface area for ion exchange and hence can contribute to greater DTPA-extractable forms of metal ions. In addition to clay minerals, organic and inorganic soil colloids also provide the exchange sites that retain the plant nutrient elements. Fine textured soils retain more B than the coarse textured soils. Hence, B is less liable to leaching from the fine textured soils. An increase in clay content from <3 to >6% in the soils significantly increased the average fixation of added B from 43 to 63% (Singh and Sinha 1976). Available Mo showed a significant negative correlation with silt plus clay in the soils. Similar results were also reported by Verma and Jha (1970) and Chakraborty *et al.* (1982).

Influence of Electrical Conductivity on Availability of Micronutrients

Non-significant correlations were found between electrical conductivity and available Zn, Cu, Fe, Mn, B and Mo.

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