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Soil tests for available zinc and their relation with inorganic zinc fractions in acid soils of Karnataka

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Abstract : Six extractants were tried *viz.* 0.1 N HCl, 0.05 N HCl + 0.025 N H_2SO_4, DTPA (pH 7.3), EDTA-NH_4OAc, EDTA (pH 9) and 2 N $MgCl_2$ to asses the available Zn status of the acid soils of Karnataka. The extracted amounts of Zn by varioius extractants were correlated with inorganic Zn fractions. The extracting power of different extractants was in the order of 0.1 N HCl > 0.05 N HCl + 0.025 N H_2SO_4, > DTPA (pH 7.3) > EDTA (pH 9) > 2 N $MgCl_2$ > EDTA-NH_4OAc. Simple correlation revealed that DTPA (pH 7.3) had a better correlation with exchangeable (r=0.68**), organically bound (r=0.61**), manganese oxide bound (r=0.56**), amorphous iron oxide bound (r=0.47*) and crystalline iron oxide bound (r=0.38*) zinc.
(Key words : Soil test methods, Zn - fractions, Available zinc, Extractants, Acid soils).

Occurrence of zinc deficiency in soils growing rice and plantation crops and spectacular responses to zinc appication have been reported under base unsaturated soils (Dwivedi, *et al.* 1993). It is apparent that hidden trace element deficiencies are wide spread than generally estimated (Takkar and Randhawa, 1978). Selection of promising extractant assumes great importance for rational use of zinc fertilizers in acid soils as meager information exists. A number of soil testing procedures involving various chemicals such as dilute acids, chelating and complexing agents and neutral salts have been employed with varying degrees of success for the determination of available zinc. Calibration of a zinc soil test would be best based on yield response to applied zinc. But reaction of zinc in soil is associated with specific soil properties or cropping systems. Consequenly consideration of other soil properties is essential in the development of a zinc soil test.

Materials and Methods

Twelve surface soil samples were collected from six districts belonging to different agro-climatic situations and land use patterns of Karnataka *viz.*, Harave (Southern transition zone), Annamale, Malalli, Mudigere, Theralu, Bettageri and Thirthahalli (Hilly zone), Gundmi, Hosur, Hubbanageri, Aggragona and Admar (Coastal zone). Available zinc in the soil was estimated by six different extractants like 0.1 N HCl (1:4 soil-solution ratio), time of shaking 15 minutes, (Wear and Evans, 1968), 0.05 N HCl + 0.025 N H_2SO_4 (1:4 soil - solution ratio), time of shaking 15 minutes (Wear and Evans, 1968), 0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA, pH 7.3 (1:2 soil-solution ratio), time of shaking 120 minutes, (Lindsay and Norvell, 1978), 2 N $MgCl_2$, pH 6 (1:5 soil-solution ratio), time of shaking 60 minutes (Bergh, 1948), 0.02 M Na_2 EDTA, pH 9 (1:5 soil-solution ratio) time of shaking 15 minutes (Viro, 1955), 0.01 M EDTA + 1N NH_4OAc, pH 7 (1:5 soil-solution ratio), time of shaking 15 minutes, (Tiller, *et al.*, 1972).

Some important physico-chemical parameters of the soil were estimated by following standard procedures. The pH of the soil ranged from 4.20 to 5.40, Organic carbon from 3.31 to 36.9 g Kg^{-1}, Clay content from 7.0 to 35%, Base saturation from 22.4 to 58.1%, ECEC (Effective Cation Exchange Capacity) from 3.17 to 9.23 c mol (P^+) Kg^{-1}, Free Al_2O_3 from 0.04 to 2.28%, Free Fe_2O_3 from 1.46 to 4.60%, Total Al_2O_3 from 8.36 to 24.5%, Total Fe_2O_3 from 6.93 to 15.31%, and Total Sesque Oxides from 15.57 to 33.85%. The soils were analyzed for different inorganic Zn fractions *viz.*, exchangeable - Zn, Organically bound - Zn, Mn Oxide bound - Zn, Amorphous iron oxide bound Zn, Crystalline iron oxide bound Zn and residual Zn by adopting the procedure given by Singh *et al.* (1988). Simple and multiple regression and path analysis were carried out to evaluate the relationship between inorganic Zn fractions and Zn extracted by different soil extractants.

Results and Discussion

Available Zn

Available Zn in soils as estimated by different extractants is presented in Table 1. The range of available Zn extracted by different extractants was found to be 1.67 to 4.43 µg g^{-1} (01. N HCl), 1.91 to 4.97 µg g^{-1} (0.05 N HCl + 0.025 N H_2SO_4), 0.73 to 2.63 µg g^{-1} (DTPA pH 7.3), 0.12 to 2.02 µg g^{-1}

Table 1. Available zinc by different extractants (μg g^{-1})

Soil	O.1 N HCl	0.05N HCI + 0.025 N H_2SO_4	DTPA pH 7.3	EDTA-NH_4OAc	NH_4OAc pH 4.6	0.02 M EDTA pH 9.0	2N $MgCI_2$
Harave (Ustic haplustalfs)	2.644	2.454	2.26	0.713	3.160	2.240	0.475
Anamale (Oxic humitropepts)	3.994	3.188	1.840	0.770	12.460	0.865	0.628
Malalli (Ustic dystropepts),	3.096	3.296	1.190	0.170	6.320	0.680	0.320
Gundmi (Typic dystropepts)	2.224	2.558	0.856	0.540	9.210	2.280	0.620
Hosur (Typic dystropepts),	2.926	1.910	0.730	0.808	12.920	0.025	2.380
Hubbanagari (Aquic ustrothents)	1.674	2.678	0.829	1.635	8.090	0.605	1.640
Aggragona (Typic ustipsamments)	1.998	2.700	0.955	0.460	7.060	0.880	0.428
RRS, Mudigere (Ustic haplohumults)	2.464	2.796	1.772	0.750	7.230	0.380	0.950
Teralu (Typic paleustalfs)	3.736	2.304	1.220	0.120	6.380	1.285	0.310
Bettageri (Fluventic ustropepts)	2.680	2.490	1.210	2.015	4.580	0.945	0.925
Theerthahalli (Fluventic ustropepts)	4.172	4.968	2.634	2.000	11.740	4.555	1.835
Admar (Ultic paleustalf)	4.428	3.728	2.080	0.700	7.340	1.740	0.563
Mean	3.003	2.920	1.465	0.890	8.040	1.373	0.923

Table 2. Correlation co-efficient between various zinc fractions and available zinc extracted by different extractants

Treatment	Exch. Zn	OrgamcaRy Complexed Zn	Mn Ox bound Zn	Am. FeOx bound Zn	Cryst. FeOx bound Zn	Res. Zn	Total Zn
O.1 N HCI	0.665**	0.023	0.440*	0.762**	0.552**	0.246	0.428*
0.05N HCI+0.025N H_2SO_4	0.858**	0.093	0.753**	0.492**	0.162	0.299	0.414*
DTPA	0.684**	0.610*	0.567**	0.474*	0.382*	0.027	0.065
EDTA-NH_4OAc	0.546**	-0.037	0.137	-0.073	0.313	-0.064	-0.006
NH_4OAc pH4.6	0.468*	-0.339	0.299	0.026	-0.160	-0.284	-0.272
EDTA	0.717**	0.412*	0.573**	0.339	0.124	0.012	0.116
$MgCI_2$	0.221	-0.283	0.104	-0.169	-0.198	-0.142	-0.177

Exch : Exchangeable zinc, MnOx: Manganese Oxide bound zinc, Am Fe Ox: Amorphous Iron Oxide bound zinc, Cryst. Fe Ox: Crystaline Iron Oxide bound zinc, Res. Zn: Residual zinc,
* Significance at 5%, ** Significance at 1%.

(EDTA-NH_4OAc), 0.025 to 4.55 µg g^{-1} (0.02 M EDTA pH 9) and 0.31 to 2.38 µg g^{-1} (2N $MgCl_2$). 0.1 N HCl extracted maximum amount of available zinc from twelve surface soils with a mean of 3.0 µg g^{-1}. The higher solubility in 0.1 N HCl may be due to solubility of many acid soluble compounds in the soil by the acid which destroy the occluded zinc that are normally inaccessible to plants (Trierweiler and Lindsay, 1968). The lowest quantity of Zn was extracted by EDTA-NH_4OAc (0.89 µg g^{-1}) and 2N $MgCl_2$ (0.92 µg g^{-1}). This may be due to minimum and very slow rate of reaction of neutral buffering agents and neutral salts with soil (Tiller, *et al.* 1972). The zinc extracting power of different extractants was in the following order of 0.1 N HCl > 0.05 N HCl + 0.025 N H_2SO_4 > DTPA pH 7.3 > 0.2 M EDTA pH 9 > 2N $MgCl_2$ > EDTA-NH_4OAc.

Correlations

Many of the soil tests developed earlier are not based upon the evaluation of soil Zn fractions which contribute to the supply of available Zn to growing plants. But, few workers attempted for quantification of contribution of various inorganic fractions towards available Zn (Lins and Cox, 1988). Now soil tests are related to different forms of inorganic Zn for a better understanding of the performance of these tests. Simple correlation studies revealed that DTPA (pH 7.3) had a very good correlation with exchangeable Zn (0.68**), organically bound Zn (0.61 **), Manganese oxide bound Zn (0.56**), amorphous iron oxide bound Zn (0.47*) and crystalline iron oxide bound Zn (0.38*) (Table 2). The acid extractants 0.1 N HCl and 0.05 N HCl + 0.025 N H_2SO_4 significantly and positively correlated with all the fractions except organically bound zinc and residual zinc. Another chelating agent EDTA was correlated with exchangeable Zn (0.71**), organically bound Zn (0.41*), and Manganese oxide bound Zn (0.57**) only. The $MgCl_2$ did not show any significant correlation with any inorganic Zinc fractions.

Multiple regression equations were computed relating available zinc extracted by different extractants and various zinc fractions. The equations are as follows.

$$Y_1 = 1.77 + 0.48X_1 - 0.12\,X_2 - 0.05\,X_3 + 0.18\,X_4 + 0.06\,X_5 + 0.01\,X_6 \quad (R^2=0.77)$$

$$Y_2 = 1.69 + 0.83X_1 - 0.25\,X_2 + 0.35\,X_3 - 0.02\,X_4 + 0.02\,X_5 + 0.01\,X_6 \quad (R^2=0.92)$$

$$Y_3 = 0.08 + 0.29X_1 + 0.57\,X_2 + 0.24\,X_3 - 0.01\,X_4 + 0.06\,X_5 + 0.01\,X_6 \quad (R^2=0.89)$$

$$Y_4 = 0.61 + 0.67X_1 - 0.13\,X_2 - 0.02\,X_3 - 0.1\,X_4 + 0.03\,X_5 + 0.002\,X_6 \quad (R^2=0.46)$$

$$Y_5 = 0.52 + 1.32\,X_1 + 1.06\,X_2 - 0.01\,X_3 + 0.06\,X_4 - 0.08\,X_5 - 0.01\,X_6 \quad (R^2=0.71)$$

$$Y_6 = 1.38 + 0.57\,X_1 - 0.45\,X_2 - 0.06\,X_3 - 0.06\,X_4 - 0.07\,X_5 + 0.0002\,X_6 \quad (R^2=0.32)$$

Where Y_1 = 0.1 N HCl, Y_2 = 0.05 N HCl + 0.025 NH_2SO_4, Y3 = DTPA, (pH 7.3), Y_4 = EDTA - NH_4OAc, Y_5= EDTA (pH 9) and Y_6 = 2N $MgCl_2$ and X_1, X_2, X_3, X_4, X_5 and X_6 are exchangeable, organically bound, Manganese oxide bound, amorphous iron oxide bound, crystalline iron oxide bound and residual zinc fractions respectively.

Multiple regression equations show that contribution of different inorganic fractions to 0.05 N HCl + 0.025 N H_2SO_4 extractable Zn is 92 per cent and that of DTPA (pH 7.3) is 89 per cent. However, a major criticism of strong acid extractants is that many acid soluble compounds in the soil are destroyed and occluded Zn that are normally inaccessible to plants (Norvell, 1984). The chelating agents combine with free metal ions in solution forming soluble complexes and thereby reduce the activity of free metal ions in solution. Consequently, metal ions desorb from soil surface or dissolve from labile solid phase to replenish the free metal ions in solution. Thus it is possible to use DTPA as an extractant under different soil pH conditions.

Contribution of individual fractions to available pool extracted by different extractants is estimated with the help of path analysis (Fig 1). The path analysis for HCl + H_2SO_4 extractable Zn showed direct contribution of exchangeable, Manganese Oxide bound and residual Zn to extractable pool. All the fractions indirectly contribute through exchangeable Zn. The negative correlation and direct influence of total Zn to extractable pool suggest that it is not contributing to extractable zinc by HCl + H_2SO_4 extraction.

The results of path co-efficient analysis for DTPA extractable Zn showed that exchangeable, organically bound, manganese oxide bound, crystalline iron oxide bound and total zinc directly contributed to DTPA extractable Zn. Residual fraction did not contribute to extractable Zn pool. But all forms indirectly contributed to extractable Zn through exchangeable zinc (Fig. 1).

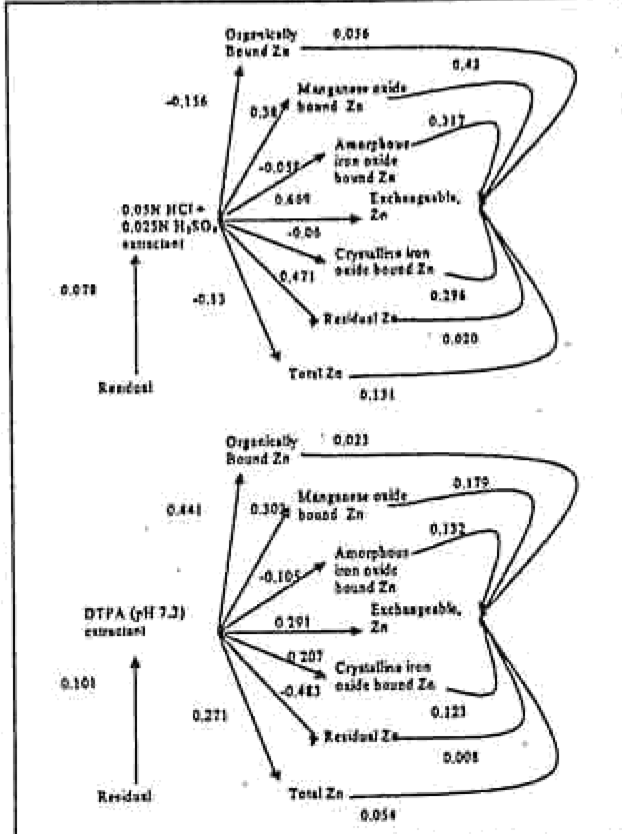

Fig.1 Path diagram for 0.05N HCl + 0.025N H_2SO_4 and DTPA extractants showing direct and indirect effects.

Although these significant values are quantitative in nature, these do give an idea about the relationship of Zinc fractions and soil test procedures. The highly significant and positive correlation observed between DTPA (pH 7.3) and different forms of Zn clearly indicate the suitability of extractant in the acid soils of Karnataka. Crop response studies conducted in red and laterite soils by Iyengar and Deb (1976) and in rice growing soils of Kerala and Tamil Nadu by Rajendran and Aiyer (1981) also indicate the positive correlation between crop uptake and available Zinc extracted by DTPA (pH 7.3).

Although all forms of Zn in the soil are known to supply the nutrient to soil solution, their relative contribution to the labile pool from which plants absorb the nutrient depends mainly on the solubility of the several zinc compounds as influenced by the relative characteristics of the soil. Hence a soil test method for estimating the available Zn status must be chosen bearing in mind the relative proportion of different Zinc fractions in soil and their solubility as influenced by the physico-chemical characteristics of the soil. Thus we can assess the available Zn status of soils by knowing the contribution of different inorganic zinc fractions to available zinc.

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