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Dynamics of zinc fraction in a calcareous *Vertic haplustept* under AICRP-LTFE soils

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Abstract
This investigation initiated which comprised of samples derived from long term fertilizer experiment started 20 years back on *Vertic Haplustept* calcareous medium black clayey soils of Junagadh. The samples were subjected to fractionation of micronutrient *viz.*, Zn. The LTFE experiment involved 12 treatments including untreated control and 4 replication which was subjected to analysis of variance in order to find out the effect of various treatments on yield, correlation, regression, path and fractions of Zinc were also change in a long term cycle of 1, 10 and 20 years. The results revealed that DTPA available Zn was maintained high quite above critical values (0.5 to 1.0 ppm) and did not indicate any need to supplement Zn nutrient in near future. Particularly DTPA available Zn recorded significantly higher value under T_4 (100% NPK+ $ZnSO_4$ @ 50 kg ha^{-1}) Followed by T_8 and T_9. FYM is essential for maintaining soil fertility at long run.

Keywords: Dynamic, micronutrient fraction, *Haplustept*

Introduction

With globalization, Indian agriculture is passing through a critical phase. It is confounded with increasing crop production, sustainability and environmental quality issues. Answers to these questions can be sought by the long-term experiments, which are valuable repositories of information regarding the sustainability of intensive agriculture. Sustainability in crop production has always been tough task. The importance of micronutrients has been realized during the past three decades when widespread micronutrient deficiencies were observed in most of the soils in our country, where intensive agriculture is practiced with high analysis fertilizers and high yielding varieties. The overall deficiency of micronutrients in Indian soils was found to be 13 per cent for Fe, 4 per cent for Mn, 47 per cent for Zn and 2 per cent for Cu (Sakal and Singh, 2001) [10] while overall percentage deficiency of micronutrients in Gujarat soils was found 8 per cent for Fe, 4 per cent for Mn, 24 per cent for Zn and 4 per cent for Cu (Anon, 1999) [1].

Zinc is one of the eight essential micronutrients. It is needed by plants in small amounts, but yet crucial to plant development. In plants, zinc is key constituent of many enzymes and proteins. It plays an important role in wide range of processes, such as growth hormone production and internode elongation.

The availability of the micronutrients in soil is also influenced by the soil properties like pH, EC, content of organic matter, free lime, moisture, proportion of clay and silt fractions, type of clay, concentrations of interacting ions, *etc*. Micronutrient cations are usually held very strongly by the organic legends. Micronutrient cations exist in the soils in different pools. Viet (1962) [12] postulated existence of five distinct pools of micronutrient cations in soil *viz.*, (i) soil solution or water soluble, (ii) exchangeable, (iii) adsorbed, complexed and chelated, (iv) associated with secondary minerals and as insoluble metal oxides and hydroxides, and (v) associated with primary minerals. First 3 pools exist in a state of dynamic equilibrium and constitute the labile pool from which the plants off take micronutrients. Consequently, a number of sequential fraction procedures have been developed for studying the relative abundance of different fractions in the soils and their relative importance in supplying micronutrients to the growing crops. The long term fertilizer experiments are of immense value in assessing the sustainability of agricultural systems and practices. Our aim is to study the trend of the pools of micronutrients in long run.

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Future strategy of soil fertility and its management will be achieved only through scientific information generated via different pools of soil micronutrient like, Zn over a periods of time. The study of these eminent pools of soil micronutrients is only possible with the inclusion of long term fertilizer experiment.

Materials and Methods
The long term fertilizer experiment was started in the year 1999 at Instructional Farm, College of Agriculture, Junagadh Agricultural University, Junagadh. Surface soil samples (0-15 cm) were collected from the AICRP-LTFE soils conducted on groundnut-wheat sequence in Randomized Block Design replicated four times at Instructional Farm Junagadh Agricultural University, Junagadh during the year 1999-2000 (1st year, after wheat), 2008-09 (10th year, after wheat) and 2018-19 (20th year, after wheat). The treatments were T_1- 50% NPK of recommended doses in G'nut-wheat sequence, T_2- 100% NPK of recommended doses in G'nut -wheat sequence, T_3- 150% NPK of recommended doses in G'nut -wheat sequence, T_4- 100% NPK of recommended doses in G'nut -wheat sequence + ZnSO4 @ 50 kg ha^{-1} once in three year to G'nut only (i.e. '99, 02, 05 etc), T_5- NPK as per soil test, T_6- 100% NP of recommended doses in G'nut -wheat sequence,

T_7- 100% N of recommended doses in G'nut wheat sequence, T_8- 50% NPK of recommended doses + FYM @ 10 t ha^{-1} to G'nut and 100% NPK to wheat, T_9- Only FYM @ 10 t ha^{-1} to Groundnut and @ 15 t ha^{-1} to wheat, T_{10}- 50% NPK of recommended doses + Rhizobium + PSM to G'nut and 100% NPK to wheat, T_{11}- 100% NPK of recommended doses in G'nut -wheat sequence (P as SSP) and T_{12}- Control. The soil samples were collected and air-drying ground with wooden mortar and pestle to pass through a 2 mm plastic sieve and analyzed for micronutrient by Atomic Absorption Spectrophotometer method (Lindsay and Norvell, 1978) [8]. Micronutrient fraction of Zn by Sequential fraction Jackson (1979) [7], Viet (1962) [12].

Results and Discussion
Effect of treatment on Zinc Fractions
Zn – Water Soluble: Water soluble Zn showed significant difference due to treatments pooled over year and Y x T interaction were significant. (Table 1). The Higher significant value was observed under treatment T_4 (100% N P K + ZnSO$_4$ @ 50 kg ha^{-1} once in three year to G'nut only). Over all mean value decrease over a period of time. Fraction of Zn in soil samples showed that zinc in water soluble pools were virtually non-existent, (Shinghal and Rattan, 1995) [11].

Table 1: Status of water soluble form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc water soluble form in soil (ppm)			
	1st year	10th year	20th year	pooled
T_1	0.118	0.121	0.075	0.105
T_2	0.119	0.108	0.086	0.104
T_3	0.132	0.116	0.094	0.114
T_4	0.169	0.136	0.108	0.137
T_5	0.127	0.118	0.098	0.114
T_6	0.116	0.109	0.056	0.093
T_7	0.110	0.120	0.065	0.098
T_8	0.118	0.120	0.062	0.100
T_9	0.141	0.133	0.094	0.123
T_{10}	0.132	0.117	0.079	0.109
T_{11}	0.127	0.116	0.083	0.108
T_{12}	0.119	0.108	0.128	0.118
S.Em.±	0.010	0.006	0.008	0.005
C.D. at 5%	0.029	0.017	0.023	0.013
C.V.%	16.0ss40	10.230	18.580	14.940
Mean	0.127	0.118	0.085	0.110
Y * T	S.Em.±	0.008	C.D. at 5%	0.023

Zn Exchangeable
Exchangeable form of Zn showed significant difference in treatments pooled over year and Y x T interaction were significant. (Table 2). The significantly higher value was recorded in T_9 followed by T_4. Mean value was slightly

increase after 10 year interval and declined after 20 year of experimentation. Variation in the activation of Zn fractions were observed due to decomposition of FYM which affects the dynamics of their inter conversion from one fraction to other (Dhaliwal *et al.* 2010) [5].

Table 2: Status of exchangeable form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc exchangeable form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	0.203	0.155	0.131	0.163
T_2	0.129	0.144	0.151	0.141
T_3	0.139	0.135	0.194	0.156
T_4	0.188	0.215	0.176	0.193
T_5	0.118	0.140	0.117	0.125
T_6	0.145	0.151	0.126	0.141
T_7	0.145	0.152	0.137	0.145
T_8	0.160	0.163	0.169	0.164
T_9	0.179	0.205	0.216	0.200
T_{10}	0.122	0.157	0.162	0.147
T_{11}	0.138	0.146	0.124	0.136

T_{12}	0.173	0.136	0.162	0.157
S.Em.$\pm$	0.013	0.009	0.009	0.006
C.D. at 5%	0.037	0.025	0.027	0.017
C.V.%	17.00	10.86	11.89	13.45
Mean	0.153	0.158	0.155	0.155
Y * T	S.Em.$\pm$	0.01	C.D. at 5%	0.03

Zn–DTPA Available

This forms showed significant difference among the treatments when pooled over years and Y x T interaction were significant. The significantly higher values was recorded under treatment T_4 (100% N P K + $ZnSO_4$ @ 50 kg ha^{-1} once in three year to G'nut only) after 20th year, followed by T_9 and T_{10}. Similar result found In pooled, initial and 10th year significantly higher value observed under T_4. Overall mean value was increased after a span of 20th year (Table 3). Available Zn content of Saurashtra soil ranged from 0.1 to 2.25 mg kg^{-1} with a mean value of 0.80 mg kg^{-1} (Anon., 1975-76) [2].

Table 3: Status of DTPA available form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc DTPA available form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	0.929	1.715	1.069	1.238
T_2	0.802	1.237	1.383	1.141
T_3	0.801	0.937	1.316	1.018
T_4	1.506	1.807	2.514	1.943
T_5	0.755	1.070	1.513	1.113
T_6	0.724	1.243	1.652	1.206
T_7	0.736	1.652	1.519	1.302
T_8	0.637	1.723	1.632	1.331
T_9	0.844	1.762	2.353	1.653
T_{10}	0.849	1.091	2.262	1.401
T_{11}	0.864	1.319	2.035	1.406
T_{12}	0.833	1.007	1.614	1.151
S.Em.$\pm$	0.079	0.132	0.144	0.070
C.D. at 5%	0.227	0.380	0.413	0.197
C.V.%	18.420	19.130	16.510	18.330
Mean	0.857	1.380	1.739	1.325
Y * T	S.Em.$\pm$	0.121	C.D. at 5%	0.341

Zn – Reducible

The pooled and Y x T differences were significant (Table 4). The significantly highest values were recorded under application of 100% N P K + $ZnSO_4$ @ 50 kg ha^{-1} once in three year to G'nut only (T_4). Thus, the complete recommended doses of fertilizer with $ZnSO_4$ recorded the highest value compare to other treatment. The residual Zn which contributed the major fraction in soil and apparently associated with soil minerals, showed a higher mean value of 24.6 ppm (Gowrisankar and Murrigappan, 1998) [6].

Table 4: Status of reducible form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc reducible form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	0.321	0.658	0.350	0.443
T_2	0.468	0.583	0.305	0.452
T_3	0.483	0.615	0.378	0.492
T_4	0.565	0.911	0.777	0.751
T_5	0.483	0.598	0.424	0.501
T_6	0.410	0.652	0.508	0.523
T_7	0.470	0.490	0.487	0.482
T_8	0.297	0.658	0.487	0.481
T_9	0.529	0.729	0.536	0.598
T_{10}	0.318	0.560	0.753	0.544
T_{11}	0.433	0.559	0.553	0.515
T_{12}	0.324	0.494	0.413	0.410
S.Em.$\pm$	0.04	0.05	0.03	0.02
C.D. at 5%	0.11	0.14	0.08	0.06
C.V.%	17.89	15.50	11.85	15.28
Mean	0.42	0.63	0.50	0.52
Y * T	S.Em.$\pm$	0.04	C.D. at 5%	0.11

Zn – Total

Total forms of Zn differed significantly when pooled over years and Y x T interaction were significant (Table 5). The higher value was recorded under application of FYM @ 10 t ha^{-1} to G'nut and @ 15 t ha^{-1} to wheat (T_9). In a long run over all mean value was slightly decline. In general, total Zn converted into available Zn under its depletion status of soil, which might utilize by crop. The total soil zinc concentration ranged from 38.1 to 113.8 ppm (Chaudhary *et al.* 1997) [4].

Table 5: Status of total form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc total form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	32.12	30.53	26.25	29.63
T_2	33.76	30.46	24.97	29.73
T_3	33.80	30.88	23.47	29.38
T_4	32.66	32.75	37.26	34.22
T_5	32.98	30.27	25.13	29.46
T_6	34.68	31.53	20.64	28.95
T_7	32.43	30.26	29.44	30.71
T_8	36.99	33.02	30.98	33.66
T_9	38.34	33.89	38.61	36.95
T_{10}	34.83	34.05	35.01	34.63
T_{11}	34.46	30.87	33.78	33.04
T_{12}	31.57	29.21	30.07	30.28
S.Em.±	1.03	0.74	1.19	0.58
C.D. at 5%	2.96	2.12	3.42	1.62
C.V.%	6.04	4.68	8.01	6.32
Mean	34.05	31.48	29.63	31.72
Y * T	S.Em.±	1.002	C.D. at 5%	2.810

Zn – Residual: Likewise total, the residual form of Zn also differed significantly when pooled over years and Y x T interaction also was significant (Table 6). The highest value was recorded under application of FYM @ 10 t ha⁻¹ to G'nut and @ 15 t ha⁻¹ to wheat (T_9). In a long run depletion was observed in all the treatment. The residual zinc fraction constituted higher per cent of total zinc fraction observed by Shinghal and Rattan (1995) [11].

Table 6: Status of residual form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc residual form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	30.55	27.88	24.63	27.69
T_2	32.24	28.39	23.04	27.89
T_3	32.24	29.07	21.48	27.60
T_4	30.24	29.68	33.68	31.20
T_5	31.50	28.34	22.98	27.61
T_6	33.28	29.37	18.30	26.98
T_7	30.97	27.85	27.23	28.68
T_8	35.78	30.35	28.63	31.59
T_9	36.65	31.06	35.41	34.37
T_{10}	33.41	32.12	31.75	32.43
T_{11}	32.90	28.73	30.99	30.87
T_{12}	30.12	27.46	27.76	28.45
S.Em.±	1.04	0.78	1.25	0.60
C.D. at 5%	2.98	2.25	3.61	1.69
C.V.%	6.38	5.35	9.24	7.04
Mean	32.49	29.19	27.16	29.61
Y * T	S.Em.±	1.042	C.D. at 5%	2.925

Zn – Per cent Availability

Pooled differences found non significant but in all year and Y x T interaction were significant (Table 7). In initial year significantly higher value was recorded under the application of 100% N P K + ZnSO₄ @ 50 kg ha⁻¹ once in three year to G'nut (T_4) and similar result found in 10th year followed by T_1, T_9, T_8 & T_7. In 20th year significantly higher value was found in T_6 followed by T_4 & T_{10}. The application of chemical fertilizers appeared to trigger the utilization of available Zn. In T_4, T_9 and T_6 the utilization was not triggered but in a long run because of soil reaction there is a possibility of conversion to available Zn from total, hence, the values are higher in 20th year as compare to initial year (Fig 4.4.2).

Table 7: Status of per cent available form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc per cent available form in soil (ppm)			
	1st year	10th year	20th year	Pooled
T_1	4.900	8.705	6.195	6.600
T_2	4.501	6.855	7.695	6.351
T_3	4.627	5.846	8.481	6.318
T_4	7.450	9.380	9.615	8.815
T_5	4.524	6.366	8.630	6.507
T_6	4.031	6.855	11.345	7.410
T_7	4.509	7.942	7.514	6.655
T_8	3.290	8.102	7.748	6.380

T_9	4.426	8.369	8.336	7.044
T_{10}	4.103	5.648	9.496	6.416
T_{11}	4.538	6.920	8.322	6.593
T_{12}	4.581	6.009	7.703	6.098
S.Em.±	0.294	0.564	0.687	0.312
C.D. at 5%	0.846	1.622	1.977	NS
C.V.%	12.730	15.560	16.320	15.980
Mean	4.623	7.250	8.423	6.766
Y * T	S.Em.±	0.541	C.D. at 5%	1.517

Zn – Available Total: Total available Zn showed significant differences when pooled over years and Y x T interaction were also significant (Table 8). The higher value observed in T_4 (100% N P K + $ZnSO_4$ @ 50 kg ha^{-1} once in three year to G'nut). Overall mean value was increase after a span of 20 year. This gives an indication of supplementation and faster utilization of available Zn by the application of chemical fertilizers. Thus in a long run after 20th year in T_4 and T_9 the values remained higher by virtue of conversion of total to available form by the soil reaction.

Table 8: Status of total available form of zinc in soils of LTFE in 1st, 10th and 20th year of LTFE

Treat.	Zinc total available form in soil (ppm)			
	1st year	10th year	20th year	pooled
T_1	1.571	2.648	1.625	1.948
T_2	1.517	2.073	1.924	1.838
T_3	1.555	1.802	1.981	1.779
T_4	2.427	3.069	3.575	3.023
T_5	1.482	1.926	2.151	1.853
T_6	1.395	2.154	2.341	1.963
T_7	1.460	2.413	2.208	2.027
T_8	1.213	2.663	2.349	2.075
T_9	1.692	2.828	3.198	2.573
T_{10}	1.421	1.925	3.256	2.201
T_{11}	1.562	2.140	2.794	2.165
T_{12}	1.448	1.744	2.317	1.836
S.Em.±	0.084	0.159	0.143	0.077
C.D. at 5%	0.241	0.457	0.412	0.215
C.V.%	10.730	13.920	11.550	12.580
Mean	**1.562**	**2.282**	**2.476**	**2.107**
Y * T	S.Em.±	0.133	C.D. at 5%	0.372

Correlation among different forms of Zn
The DTPA available zinc showed highly significant positive relationship with reducible (r = 0.296), available total (r = 0.829) and per cent available (r = 0.949). This indicated DTPA available zinc as the pre dominant component of available zinc. Other forms such as water soluble form showed highly significant relationship with exchangeable and total. Exchangeable form showed highly significant negative relationship with available and available total. These was highly significant positive relationship of reducible with total (r = 0.346) and residual (r = 0.402). The reducible showed highly significant positive relationship with per cent available. Water soluble, total and per cent available showed highly significant positive relationship with residual. Available total showed highly significant positive relation with per cent available. Per cent available showed significant negative with exchangeable form. Total and water soluble showed significant negative relationship with per cent available. (Table 9).

Table 9: Correlation coefficient between different forms of Zn to among forms of LTFE soils in the 1st, 10th and 20th year

Sr. no.	Correlation between	
	Zn Form to among forms	
1	Zn WS v/s Zn EF	0.651**
2	Zn WS v/s Zn T	0.373**
3	Zn WS v/s Zn PA	-0.322**
4	Zn EF v/s Zn AV	-0.395**
5	Zn EF v/s Zn T	0.346**
6	Zn EF v/s Zn RES	0.402**
7	Zn EF v/s Zn TA	-0.290**
8	Zn AV v/s Zn WS	-0.188*
9	Zn AV v/s Zn RED	0.296**
10	Zn AV v/s Zn PA	0.829**
11	Zn AV v/s Zn TA	0.949**
12	Zn RED v/s Zn PA	0.392**
13	Zn T v/s Zn RES	0.986**
14	Zn T v/s Zn PA	-0.424**
15	Zn RES v/s Zn WS	0.403**
16	Zn PA v/s Zn RES	0.554**
17	Zn PA v/s Zn EF	-0.435**
18	Zn TA v/s Zn PA	0.863**

Regression
The high values of multiple correlation co-efficient obtained in the stepwise regression of zinc with its various forms thereby explaining most of the variations in DTPA available Zn. The available total Zn had the maximum influenced followed total form.

Path Zn: Form to Forms
The total, available total and per cent available Zn had a positive direct effect on DTPA available Zn. These relationships might be due to indirect negative effects of per cent available forms through residual Zn. (Fig. 1)
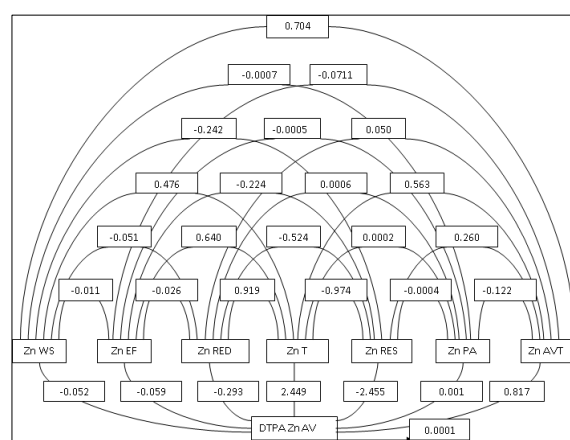

Fig 1: Path diagram of the effect of different forms of Zn on DTPA-Zn in the LTFE soils

Conclusion

On the basis of the results obtained, it seems quite logical to conclude that The predominant form in Zinc was the DTPA available form and it was exhibited increase over time in soil long run *viz.*, 20 years. In most of form over all mean value was decrese over a period of time. The chemical fertilizers appeared to trigger the utilization of micronutrient like Zn. The dynamics of Zinc Fractions along with its forms, in general, exhibited gross negative trend with varying magnitude according to the soil. Application of FYM not only sustains fertility, but also increases soil nutrient status as like here in Zinc status of the LTFE soil. In treatments which received FYM, increased Zinc status in LTFE soils. The combined application of organic and inorganic fertilizers in continuous manner, have sustain the crop yield.

The high residual values in multiple correlation and regression analysis, the soil properties had little influence on DTPA available micronutrients. This is because the soil of the experimental block was same and the fertilizer and manure treatment could not changed the soil properties in the span of twenty years. The path co-efficient analysis of DTPA available Zinc as influenced by various forms revealed that total form had a direct positive effect on DTPA extracted Zn.

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