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Fractions of ferrous in calcareous *Vertic Haplustepts* as influenced by sixteen years of fertilization and Manuring in LTFE soils

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Abstract
The effect of integrated nutrient management (INM) on fractions of ferrous under groundnut-wheat cropping sequence of a *Haplustepts* soil was studies in a long-term field experiment initiated during *kharif* 1999 at Junagadh, Gujarat. Effect of varying dose of N, NP, NPK with FYM, Zn, S and *Rhizobium* on fractions of ferrous. The study was aimed to find out the effect of continuous application of inorganic fertilizers and organic manure on the distribution of Fe fractions. There was an increase in soil DTPA available Fe status of LTFE soils, while some important forms of Fe such as reducible Fe, total Fe and residual Fe was recorded decline. The conversion of exchangeable to DTPA-Fe was evident. In light of this, overall mean DTPA available Fe was recorded medium values (6.87 ppm) as compared to the critical values. Further the internal turnover of Fe along with other fertilizers could also help avoid the deficiencies of Fe even on a long run. The whole spectrum warranted a need to supply Fe nutrient through suitable sources to stabilize Fe status in the soil. The total form was a predominant component followed by DTPA available Fe. There were inter-conversions from DTPA available as well as total form to the reducible forms in a long run.

Keywords: Integrated Nutrient Management, Fractions of Ferrous, *Haplustepts*, Rhizobium and DTPA available Fe

Introduction
Micronutrient deficiencies in crop plants are widespread in all over the world because of increased micronutrient demands from intensive cropping practices and adaptation of high-yielding cultivars having higher micronutrient demand. Moreover, enhanced production of crops on marginal soils that contain low levels of essential nutrients, increased use of high analysis fertilizers with low amounts of micronutrient contamination, decreased use of animal manures, composts and crop residues, use of soils that are inherently low in micronutrient reserves and involvement of natural and anthropogenic factors that limit adequate plant availability add to the cause (Fageria *et al*., 2002) [1]. In India, intensive cropping with nutrient exhaustive high-yielding varieties coupled with the use of high analysis fertilizers for enhancing food grain production have catalyzed the rapid depletion of available micronutrients in soil in general (Singh, 2009) [11] and available ferrous (Fe) in some areas in particular (Nayyar *et al*., 1990) [4]. Herencia *et al*. (2008) [6] reported that with the addition of organic and mineral fertilization, OM-bound fractions of micronutrients increased their availability and uptake in the soil. To understand the chemical reactions and bioavailability of soil zinc, it is essential to investigate its release behaviour of various fractions in soils (Saviour and Stalin (2014) [12]. Dhaliwal and Walia (2008) [2] reported that incorporation of manures increased the availability of the micronutrients like Fe, Mn, Zn and Cu. Long-term experiments (LTE) offer a better platform to visualize the status of micronutrients in soil under intensive cropping and their contribution to sustained production. Uptake of ferrous by crop plants is determined by soil properties, plant factors, and their interactions at the soil-root interface. Knowledge of the reactions at the interface is basic to the prediction of soil Fe availability and to an understanding of soil-plant-Fe relationships. Medium black soils of Saurashtra region derived from trap basalt, sand stone and lime stone under semi-arid climate have unique properties of calcareousness which affect the physico-chemical properties, nutrient availability and plant growth. Very little or no work was done on Fe nutrition, status and different forms in soils of Saurashtra region so far. Hence, there is a need for depth study of dynamics of different forms of Fe under intensive agriculture, present investigation was carried out.

Materials and Methods

Surface soil samples (0-15 cm) were collected from the AICRP-LTFE soils conducted on groundnut-wheat sequence in RBD, replicated four times, at Instructional Farm, Junagadh Agricultural University, Junagadh during the year 1999 (initial) and 2014-15 (16th year, after wheat). Initial soil properties of LTFE soil was soil pH 8.2, soil EC 0.37 dS/m. $CaCO_3$ 32.2 g/kg, CEC 36.8 c mol (P^+)/kg, soil OC 8.9 g/kg, soil Av. N 161 kg/ha, soil Av. P_2O_5 9.48 kg/ha, soil Av. K_2O 184 kg/ha, soil Av. S 17.4 mg/kg, Fe 13.7 mg/kg, Mn 10.01 mg/kg, Zn 1.47 mg/kg and Cu 3.24 mg/kg, respectively.

Tr.No.	Treatment Details
T_1:	50% N P K of recommended doses in G'nut -Wheat sequence
T_2:	100% N P K of recommended doses in G'nut -Wheat sequence
T_3:	150% N P K of recommended doses in G'nut -Wheat sequence
T_4:	100% N P K of recommended doses in G'nut -Wheat sequence + $ZnSO_4$ @ 50 kg/ha once in three year to G'nut only (i.e. '99, 02, 05 etc)
T_5:	N P K as per Soil Test
T_6:	100% N P of recommended doses in G'nut -Wheat sequence
T_7:	100% N of recommended doses in G'nut -Wheat sequence
T_8:	50% N P K of recommended doses in G'nut -Wheat sequence + FYM @ 10 t/ha G'nut and 100% N P K to Wheat
T_9:	Only FYM @ 25 t/ha to G'nut only
T_{10}:	50% N P K of recommended doses in G'nut -Wheat sequence + Rhizobium + PSM to G'nut and 100% N P K to Wheat
T_{11}:	100% N P K of recommended doses in G'nut -Wheat sequence (P as S S P)
T_{12}:	Control

Iron Fractionation method

The sequential extraction technique employed to separate the various forms of manganese was Tessier's procedure by Jackson (1973) [3] and Viets (1962) [5] as water soluble, exchangeable, DTPA available, and reducible form. Total Fe status was determined by digesting the soil using HF: $HClO_4$ (5:1). These extracts were analyzed for their Fe content on Atomic Absorption Spectrophotometer. Residual form of Fe was calculated by deducting water soluble + exchangeable + DTPA available + reducible (i.e available total) from the total Fe status of the soil. The per cent available Fe status was calculated as available total of the total Fe status of the soil.

Results and Discussion

Fe- Water Soluble

The water soluble Fe showed non significant difference among treatment, when pooled over years and also Y x T interaction was not significant. In a long run after 16^{th} year, the significant values were recorded in T_{12} (0.06 ppm) treatment followed by T_{10} and T_6 treatment. The results are indicative of enhancing water soluble iron utilization by the application of fertilizers in a long run. Overall there were a no changes in the water soluble iron content over a period of time (Table 1). The amount of water soluble ferrous was practically nil in almost all cases (Joshi and Dhir, 1982) [7].

Table 1: Status of water soluble form of iron in soils of LTFE experiment in Initial and 16^{th} year

Treat.	Iron water soluble from in soil (ppm)			
	Initial year	16^{th} year		pooled
T_1	0.04	0.03		0.03
T_2	0.05	0.03		0.04
T_3	0.05	0.03		0.04
T_4	0.04	0.03		0.03
T_5	0.03	0.02		0.02
T_6	0.03	0.04		0.03
T_7	0.03	0.01		0.02
T_8	0.03	0.03		0.03
T_9	0.04	0.02		0.03
T_{10}	0.02	0.07		0.05
T_{11}	0.02	0.02		0.02
T_{12}	0.04	0.08		0.06
SEm±	0.00	0.02		0.01
CD at 5%	0.01	0.01		NS
C.V.%	19.64	144.11		100.03
Mean	0.03	0.03		0.03
Y * T	S.Em.±	0.02	C.D. at 5%	NS

Fe – Exchangeable

The exchangeable iron content did not showed any significant differences either through treatments or through years (Table 2). Exchangeable Fe ranged between 2 -8 ppm observed by Joshi *et al.* (1988) [8].

Table 2: Status of exchangeable form of iron in soils of LTFE experiment in Initial and 16^{th} year

Treat.	Iron exchangeable form in soil (ppm)			
	Initial year	16^{th} year		pooled
T_1	0.03	0.03		0.03
T_2	0.03	0.04		0.04
T_3	0.03	0.03		0.03
T_4	0.02	0.02		0.02
T_5	0.03	0.02		0.03
T_6	0.03	0.03		0.03
T_7	0.02	0.02		0.02
T_8	0.04	0.04		0.04
T_9	0.03	0.03		0.03
T_{10}	0.02	0.05		0.03
T_{11}	0.04	0.04		0.04
T_{12}	0.02	0.02		0.02
SEm±	0.00	0.01		0.01
CD at 5%	NS	NS		NS
C.V.%	24.50	85.62		65.03
Mean	0.03	0.03		0.03
Y * T	S.Em.±	0.01	C.D. at 5%	NS

Fe – DTPA Available

The DTPA available iron was significant when pooled over year and also Y x T interaction was significant and highest value was observed under application of 100% N P of recommended doses in G'nut -Wheat sequence (7.38 ppm). Most of the treatments have higher significant value as compared to control in pooled results (Table 3). Overall mean value was increased over a long period. The DTPA extractable Fe varied from 1.0 to 21.4 ppm with a mean value of 7.2 ppm (Randhawa and Singh, 1996) [9].

Table 3: Status of DTPA available form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Iron DTPA available form in soil (ppm)			
	Initial year	16th year		pooled
T_1	4.09	8.31		6.20
T_2	4.42	9.89		7.15
T_3	4.31	8.57		6.44
T_4	5.68	8.28		6.98
T_5	4.47	8.87		6.67
T_6	5.01	9.74		7.38
T_7	4.11	8.58		6.34
T_8	4.86	7.52		6.19
T_9	4.88	8.84		6.86
T_{10}	5.40	9.26		7.33
T_{11}	4.74	9.11		6.92
T_{12}	4.48	7.98		6.23
SEm±	0.27	1.08		0.56
CD at 5%	0.78	1.10		0.97
C.V.%	11.57	23.98		22.99
Mean	4.70	9.03		6.87
Y * T	S.Em.±	0.69	C.D. at 5%	2.98

Fe – Reducible

The reducible form of iron was not significant when pooled over year but Y x T interaction was significant. The highest value was recorded under application of 100% N P of recommended doses in G'nut -Wheat sequence (9.88 ppm) followed by T_7, T_9, T_{12} and T_{11} after 16th years (Table 4). In the chemical fertilizer application resulted in unutilization of reducible iron. Overall mean value is depleted on long term basis. The addition of organic matter showed a positive balance in reducible Fe fractions but their values were lower than the values without added organic matter were observed by Nirupama *et al.* (1999) [10].

Table 4: Status of reducible form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Iron reducible form in soil (ppm)			
	Initial year	16th year		pooled
T_1	9.76	5.16		7.46
T_2	9.88	5.74		7.81
T_3	9.16	6.03		7.59
T_4	8.01	6.51		7.26
T_5	6.18	6.33		6.26
T_6	7.20	12.55		9.88
T_7	6.94	8.18		7.56
T_8	7.93	4.39		6.16
T_9	7.20	7.47		7.34
T_{10}	8.46	6.17		7.32
T_{11}	8.22	6.86		7.54
T_{12}	7.31	6.94		7.13
SEm±	0.77	1.58		0.88
CD at 5%	2.22	2.01		NS
C.V.%	19.23	45.93		33.34
Mean	8.02	6.86		7.44
Y * T	S.Em.±	1.24	C.D. at 5%	3.50

Fe – Total

The total iron content showed significant change, when pooled over the year and Y x T interaction was also significant. The highest value was recorded under application of FYM @ 25 t/ha to G'nut (29902.85 ppm). Overall mean value was depleted on long term basis (Table 5). The application of chemical fertilizer resulted in enhancement of the utilization of total iron or conversion of total to available form by the soil reaction and under utilization by the plants.

Table 5: Status of total form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Iron total form in soil (ppm)			
	Initial year	16th year		pooled
T_1	27229.25	25862.98		26546.11
T_2	29254.75	25493.08		27373.91
T_3	29548.00	25581.55		27564.78
T_4	27815.25	23374.85		25595.05
T_5	28229.25	25782.85		27006.05
T_6	31348.00	25734.80		28541.40
T_7	27905.00	25358.48		26631.74
T_8	31487.50	25976.48		28731.99
T_9	33765.75	26039.95		29902.85
T_{10}	29995.00	25760.45		27877.73
T_{11}	29457.25	25716.83		27587.04
T_{12}	26564.75	25460.38		26012.56
SEm±	899.16	695.33		568.32
CD at 5%	2587.10	2477.21		1908.44
C.V.%	6.12	5.45		5.86
Mean	29383.31	25511.89		27447.60
Y * T	S.Em.±	803.73	C.D. at 5%	2269.39

Fe – Residual

Like wise total form, residual iron was also showed significant differences when pooled over the year and Y x T interaction was also significant (Table 6). The highest value was recorded under application of FYM @ 25 t/ha to G'nut (29888.59 ppm).

Table 6: Status of residual form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Iron residual form in soil (ppm)			
	Initial year	16th year		pooled
T_1	27215.34	25849.45		26532.39
T_2	29240.37	25477.38		27358.87
T_3	29534.45	25566.90		27550.68
T_4	27801.50	23360.01		25580.76
T_5	28218.55	25767.61		26993.08
T_6	31335.73	25712.44		28524.08
T_7	27893.89	25341.69		26617.79
T_8	31474.65	25964.50		28719.58
T_9	33753.60	26023.59		29888.59
T_{10}	29981.10	25744.90		27863.00
T_{11}	29444.24	25700.79		27572.52
T_{12}	26552.89	25441.97		25997.43
SEm±	899.05	695.64		568.38
CD at 5%	2586.79	2459.30		1949.21
C.V.%	6.12	5.46		5.86
Mean	29370.53	25495.93		27433.23
Y * T	S.Em.±	803.81	C.D. at 5%	2269.60

Fe – Percentage Availability

It was significant when pooled over the year and interaction was also significant (Table 7). The application of 50% N P K of recommended doses in G'nut -Wheat sequence + FYM @ 10 t/ha G'nut and 100% N P K to Wheat showed the significantly higher values as compared to Control.

Table 7: Status of percentage available form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Percentage available of Iron in soil			
	Initial year	16th year		pooled
T_1	0.05	0.05		0.05
T_2	0.05	0.06		0.06
T_3	0.05	0.06		0.05
T_4	0.05	0.07		0.06
T_5	0.04	0.06		0.05
T_6	0.04	0.09		0.06
T_7	0.04	0.07		0.05
T_8	0.04	0.05		0.04
T_9	0.04	0.06		0.05
T_{10}	0.05	0.06		0.08
T_{11}	0.04	0.06		0.05
T_{12}	0.04	0.07		0.06
SEm±	0.00	0.01		0.00
CD at 5%	0.01	0.02		0.01
C.V.%	13.52	22.52		20.35
Mean	0.04	0.06		0.05
Y * T	S.Em.±	0.01	C.D. at 5%	0.02

Fe – Available Total

Total available form of iron was also exhibited more or less same trend. Pooled effect was significant and also Y x T interaction was significant. Highest value was recorded in T_6 treatment followed by T_2 and T_{10}. Overall mean value was increase over the time. After 16th year chemical fertilizers in general showed increasing trend of Fe available total. While in FYM and control treatment it was also increasing. The accumulation in soil was observed by virtue of conversion to available form (Table 8).

Table 8: Status of total available form of iron in soils of LTFE experiment in Initial and 16th year

Treat.	Total available forms of Iron in soil (ppm)			
	Initial year	16th year		pooled
T_1	13.91	13.53		13.72
T_2	14.38	15.70		15.04
T_3	13.55	14.65		14.10
T_4	13.75	14.84		14.29
T_5	10.70	15.24		12.97
T_6	12.27	22.36		17.32
T_7	11.11	16.79		13.95
T_8	12.85	11.97		12.41
T_9	12.15	16.36		14.26
T_{10}	13.90	15.55		14.72
T_{11}	13.01	16.03		14.52
T_{12}	11.86	18.41		15.13
SEm±	0.79	1.56		0.87
CD at 5%	2.29	4.48		3.73
C.V.%	12.43	19.50		17.19
Mean	12.79	15.95		14.37
Y * T	S.Em.±	1.24	C.D. at 5%	3.49

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