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Micronutrients status and zinc forms distribution in soils under paddy land cover in Sringeri taluk in hilly zone of Karnataka

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Abstract
Rice is staple crop for most of the people in Karnataka, in due days its productivity and production is reducing due to improper application of fertilizers, specially, the zinc. This study was undertaken to know the status of micronutrients and zinc fractions in soils under paddy land cover in Sringeri taluk. The results showed that, the soils are acidic in nature with pH of 4.22 to 5.03, organic carbon in range of 4.5 to 21.00 g kg-1. The available zinc ranged from 0.39 to 2.81 mg g-1, it showed that 94.74 per cent of soils were sufficient in zinc nutrition. The distribution of zinc fractions followed the order: water-soluble < carbonate bound < organic matter bound < easily reducible manganese bound < iron and aluminum oxide bound < sorbed zinc < residual zinc.

Keywords: micronutrients, zinc, fractions, hilly zone

Introduction
Sringeri taluk of chickamagaluru district co0mes under hilly zone (zone 9) of Karnataka featured by high rainfall, humid weather which influenced the formation of lateritic soils. The soils are acidic in nature, which influence in high iron content in soil and deficiency of zinc in soils. Due to leaching of bases and kaolinite type clay minerals in soils influence the low CEC in soils. Major crops grown in this region are coconut, arecanut, coffee, pepper, cardamom and rice also grown in low land areas.

Among the micronutrients zinc plays important role in production and productivity of rice. It is being deficient in soils hinder the growth and metabolic activity of the crop and also cause Khaira disease in acute deficiency. Zinc in soil exists in various chemical forms and their contribution to available zinc vary widely depending upon physical and chemical properties of soils. Knowledge on different forms of zinc which control the distribution of zinc between active soil zinc constituents and soil solution are fundamental to an understanding of the chemistry of soil zinc and are indicators of bioavailability of zinc in soils

Material and Methods
Study area and collection of soil samples
Nineteen soil samples were collected randomly from soils under paddy land cover from different RSKs in Sringeri taluk. The samples were air dried, powdered and sieved in 2mm sieve for chemical properties and 0.5mm sieve for organic carbon determination. The samples were stored in polythine bags and kept in dry place.

Soil analysis
Particle size analysis was carried out by feel method. Soil pH was determined in 1:2.5 soil to water suspension by dipping the combined electrode of a digital pH meter as described by Jackson (1973) [8]. Electrical conductivity of soil samples was measured in 1:2.5 soil to water extract using conductivity bridge as outlined by Jackson (1973) [8] under suitable measuring conditions, the results were expressed in terms of dSm-1 at 25^{0}C. Easily oxidizable organic carbon content of soil samples was determined by Walkley and Black's wet oxidation method. In this method, a known weight (0.5g) of sample was treated with a known excess volume of potassium dichromate in presence of conc. Sulphuric acid to oxidize the organic carbon to carbon dioxide and the unreacted potassium dichromate was back titrated against standard ferrous ammonium sulphate using ferroin indicator (Walkley and Black, 1934) [29].
Calcium carbonate content was determined by concentrated HCl method as prescribed by Jackson (1973) [8]. CEC of the soil selected samples were determined by leaching ten grams of soil with neutral N ammonium acetate solution for several times followed by washing with

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alcohol to remove excess of electrolyte. Then, the adsorbed NH_4^+ ions were displaced by K^+ ions by leaching the soil with 10 per cent KCl solution. Finally, NH_4^+ in the leachate was determine by distillation method as described by Page et al. (1982) [17].

DTPA-extractable zinc, iron, copper and manganese
Available zinc in soils for plant nutrition was extracted using Diethylene Triamine Penta Acetic acid extractant (pH 7.3) at 1:2 soil to extractant ratio as described by Lindsay and Norwell (1978) [13]. The concentration of zinc in the extract was determined using Atomic Absorption Spectrophotometer (AAS) using Zn-HCL lamp under suitable measuring conditions (Page et al., 1982) [17]. The same extractant was used to determine the concentration of other three micronutrients in AAS with the help of respective hallo cathode lamps.

Fractions of zinc in soils
Zinc in soils was fractionated into forms designated as water soluble (WS), sorbed (SORB), easily reducible manganese bound (ERMn), carbonate bound (CA), organic bound (OM), Fe & Al oxides bound (Fe & Alox) and residual (RES) forms. Each chemical form is operationally defined as given below (Ma and Uren, 1995) [14].

Table: Operational definition, Step and Fraction

Operational definition	Step	Fraction
Distilled water (1:5), shaken for 2 hrs	1	Water soluble (WS)
1% Na Ca-HEDTA in 1M NH4OAc, pH 8.3 (1:10) shaking for 2 hrs	2	Sorbed (SORB)
0.2 % quinol in 1M NH4OAc, pH 7.0 (1:10) shaking for 2 hrs	3	easily reducible manganese bound (ERMn)
0.5 % Na/H acetate, pH 4.74 (1:10), soaking for 15 hrs or shaking of 3 hrs	4	Carbonate bound (CA)
5 ml of 30 % H_2O_2 pH 4.74, digested twice at 25^0C and extract as for carbonate fraction (1 hr)	5	Organic bound (Om)
0.175M $(NH_4)_2C_2O_4$ in 0.1M $H_2C_2O_4$, pH 3.25 (1:10) soaking for 15 hrs or shaken for 2 hrs	6	Fe & Al oxides bond (Fe&Alox)
Total – Σ extractable amounts	7	Residual (RES)

In the above scheme of fractionation, extractions were conducted in 50 ml polypropylene centrifuge tubes with three grams of soil. Between each successive extraction, the supernatant was obtained by centrifuging for 15 minutes (3000 rpm) and filtering. The concentration of zinc in the extracts was determined using atomic absorption spectrophotometer under suitable measuring conditions (Page et al., 1982) [17].

Total zinc in soils
Finely powdered, 1M $(NH_4)_2CO_3$ washed and oven dried soil sample of 0.2 g was taken in a polypropylene bottle. To this 2 ml, of aqua regia (HNO_3 + HCl) was added to decompose the carbonates present and also to disperse the sample. Then 20 ml of HF was added, and the bottled was capped immediately. The contents of the bottle were shaken for 8 to 10 hours. After this treatment, about 50 ml of saturated H_3BO_3 was added, shaken for 2 hours and kept for a week to dissolve the sample completely. Finally, the volume of the digested sample was made up to 100 ml, as described by Sridhar and Jackson (1974) [26]. The concentration of zinc in the above solutions were determined by atomic absorption spectrophotometer under suitable measuring conditions (Page et al., 1982) [17].

Results and Discussion
Results presented in Table 1 indicated that, the soil samples collected from Sringeri taluk were acidic in reaction (pH) and it varied from 4.22 to 5.03 with mean value of 4.58. The acidic nature of these soils may be attributed to the high intensity of weathering coupled with intensive leaching of bases due to heavy rainfall. Similar results also reported by (Sathyanarayana and Biswas, 1970) [21].

Electrical conductivity of these soils ranged from 0.03 to 0.09 dS m^{-1} at 25 ^0C with a mean of 0.07 dS m^{-1} at 25 ^0C revealing that soils were normal with respect to soluble salts and found to be low or within the in normal range. This might be due to leaching of bases due to heavy rain fall leaving acidic constituents in soils. (Kabey and Shankar, 2013; Padhan et al., 2016) [11, 16]

Organic carbon status was in the range of 4.5 to 21.0 g kg^{-1} with mean value of 13.8 g kg^{-1}, indicating that organic carbon in soils was in the range of low to high status. The low organic carbon content in soils might be due to coarse texture and lower application of organic matter to the soil (Dudal, 1965) [4], higher status of organic carbon in soils might be attributed to the submerged condition and decreased in the rate of organic matter decomposition due to lack of aeration and also incorporation of paddy straw into the soils. Similarly, Chidanandappa (2003) [2] reported that organic manures addition enhanced the organic carbon content in soils.

Calcium carbonate equivalent in soils varied between 0.03 to 0.50 per cent with mean value of 0.25 per cent and found to be very low probably because of the acidic nature of these soils. Under acid condition of soils, $CaCO_3$ dissolved and leached down heavy rain fall (Wijebandara, 2007) [30]. The CEC of selected samples varied from 7.06 to 8.85 cmol (p^+) kg^{-1} (Table 2). A variation in CEC of these soils probably vary due to soil pH and clay content of these soils. Further, low CEC of the soils may be attributed to the lower amount of clay and dominated by Kaolinite, Fe and Al oxides (Tripathi et al., 2006; Padhan et al., 2016) [16].

DTPA- extractable iron ranged from 88.20 to 282.19 mg kg^{-1} with mean of 184.97 mg kg^{-1}, copper ranged from 26.84 to 281.61 mg kg^{-1} with mean of 110.82 mg kg^{-1} and manganese ranged from 0.84 to 53.00 mg kg^{-1} with mean of 9.35 mg kg^{-1}. Low pH and acidic nature influenced high iron content, and copper and manganese were also recorded at higher range. The results were in accordance Talukdar et al. (2009) [27], Rajesh (2014) [19].

Available zinc status in soils ranged from 0.39 to 2.81 mg kg^{-1} with a mean of 1.21 mg kg^{-1} (Table 1). Out of 19 soil samples studied only 5.26 per cent of soils were deficit in zinc and remaining 94.74 per cent soils were sufficient (Fig. 1). A wide variation in zinc content in soils probabaly due to variation in soil properties like pH, OC, clay, sesquioxides and CEC of these soils. Sufficient or high availble zinc content in soils of this region might be due to weathered and acidic nature of these soils. An increase in soil pH resulted in a decrease in zinc extractability by DTPA due to the conversion of some amount of Zn to $Zn(OH)_2$ (Hazra and Mandal, 1988). Further, an increase in organic matter increased the available zinc content in soils was attributed to the the following reasons:
1. Organic matter acts as source of zinc as a chelating agent.

2. Chelating agents released during the decomposition of organic matter, complexed and mobilized the zinc in soils.

Similar findings were also reported by many workers (Chidanandappa, 2003, Gosavi and Chaudhari, 2016; Kumar and Babel, 2011; Meenakshi *et al*., 2005 and Jena *et al*., 2006) [2, 6, 12, 15, 9].

It was noticed that total zinc ranges from 114.50 to 203.00 mg kg^{-1} with mean value of 146.83 mg kg^{-1} (Table 2), higher concentration of total zinc is described to high organic carbon content and the increase in clay content as reported by Singh and Abrol (1986) [25], Sharma *et al*. (2002) [22] and Jyothi *et al*. (2010) [10]. Among different forms of zinc, such water soluble, sorbed, easily reducible manganese bound, carbonate bound, organic bound, iron and aluminium oxides bound and residual zinc and their distribution in soils ranged from 0.95 to 1.32, 5.95 to 9.11, 1.56 to 2.85, 1.29 to 1.85, 1.92 to 2.95, 3.95 to 6.67 and 94.87 to 181.80 mg kg^{-1} with a mean value of 1.12, 7.08, 2.09, 1.60, 2.42, 5.04 and 127.49 mg kg^{-1}, respectively, constituting 0.53 to 1.10, 3.92 to 5.75, 1.07 to 2.13, 0.73 to 1.38, 1.13 to 2.25, 2.12 to 5.83 and 82.86 to 89.73 per cent of total zinc, respectively. Among forms of zinc found in soils, the residual zinc was recorded as dominant fraction (82.89 to

89.73 % of the total zinc), distribution of native and applied zinc predominantly in residual form has been confirmed by several investigators (Cala *et al*. ,1999; Singh *et al.,* 1999 and Jyothi *et al.,* 2010) [1, 24, 10]. This is because a considerable amount of zinc was found in residual fraction where possibly most of the total zinc was held within the silicate minerals. The water-soluble zinc was found to be least fraction (0.53 – 1.10 % of the total Zn), the contribution of water soluble fraction to the total zinc was considered to be the least in soils. This might be due to the high buffering capacity and high organic carbon status in soils suggesting that organic matter may provide more exchange sites for adsorption of zinc. Similar findings were also reported by Dhane and Shukla (1995) [3] and Shazia *et al*. (2014) [23]. These different zinc fractions followed same order in all soils selected for fractionation studies, here, residual zinc fraction occupied the most dominant fraction and water-soluble fraction as least dominant one, further, the different fractions followed the order: water-soluble < carbonate bound < organic matter bound < easily reducible manganese bound < iron and aluminum oxide bound < sorbed zinc < residual zinc. The results are in accordance with other researchers like Ramzan *et al*. (2014) [20] and Gogoi *et al*. (2017) [5]

Table 1: Soil chemical properties and available micronutrient status in soils under paddy land cover of Sringeri taluk in hilly zone of Karnataka

Sample No.	Texture	pH	EC (dS m^{-1} at 25[0]C)	OC (g kg^{-1})	Calcium carbonate equivalent (%)	Zn	Fe	Cu	Mn
						← ---------- (mg kg^{-1}) ------------- →			
1	sl	4.75	0.08	10.50	0.33	1.73	282.19	193.95	7.98
2	l	4.45	0.08	9.90	0.25	0.63	125.58	64.974	3.192
3	ls	5.03	0.05	11.10	0.35	1.16	203.99	61.824	10.5
4	scl	4.79	0.06	12.30	0.38	1.28	183.54	121.25	23.52
5	sl	4.39	0.07	17.70	0.20	1.11	199.24	97.692	6.636
6	sl	4.48	0.05	11.40	0.18	0.93	157.08	105.58	11.76
7	ls	4.48	0.05	20.70	0.13	1.06	124.74	43.386	5.04
8	s	4.58	0.09	19.80	0.28	1.44	127.51	71.82	2.94
9	cl	4.64	0.09	13.50	0.18	0.82	232.68	86.856	12.6
10	ls	4.85	0.06	11.40	0.15	0.95	141.96	39.774	7.98
11	sl	4.48	0.08	8.70	0.18	1.29	228.06	281.61	7.56
12	cl	4.76	0.07	21.00	0.50	1.71	175.14	201.64	3.36
13	sl	4.48	0.07	16.20	0.20	1.16	207.06	154.60	4.914
14	cl	4.44	0.06	14.70	0.28	1.24	189	150.40	5.46
15	l	4.49	0.08	18.00	0.43	2.81	277.2	131.67	53.004
16	cl	4.54	0.05	15.30	0.38	1.21	151.2	120.07	5.334
17	scl	4.22	0.07	9.60	0.15	1.12	258.3	97.104	2.562
18	scl	4.63	0.03	4.50	0.03	0.39	88.2	26.838	0.84
19	ls	4.47	0.05	15.60	0.15	1.03	161.7	54.6	2.436
Range		4.22-5.03	0.03 - 0.09	4.5 – 21.0	0.03 - 0.50	0.39 - 2.81	88.20 – 282.19	26.84 – 281.61	0.84 – 53.00
Mean		4.58	0.07	13.8	0.25	1.21	184.97	110.82	9.35

Table 2: CEC, total zinc and zinc fractions of soils under paddy land cover in Sringeri taluk in hilly zone of Karnataka

Sample No.	CEC [c mol (p [+]) kg^{-1}]	Zinc fractions (mg kg^{-1})							
		WS	SORB	ERMn	CA	OM	Fe & Alox	RES	TOTAL
1	8.85	1.32 (1.10)	6.49 (5.39)	1.95 (1.62)	1.57 (1.30)	2.22 (1.84)	4.68 (3.88)	102.27 (84.87)	120.50
2	7.40	1.09 (0.81)	5.95 (4.44)	2.85 (2.13)	1.85 (1.38)	1.92 (1.43)	4.15 (3.10)	116.19 (86.71)	134.00
3	8.58	1.12 (0.91)	7.02 (5.73)	1.81 (1.48)	1.65 (1.35)	2.56 (2.09)	5.89 (4.81)	102.45 (83.63)	122.50
4	8.40	1.24 (0.61)	9.11 (4.49)	2.18 (1.07)	1.49 (0.73)	2.29 (1.13)	4.89 (2.41)	181.80 (89.56)	203.00
5	7.06	0.98 (0.53)	7.32 (3.92)	2.19 (1.17)	1.77 (0.95)	2.95 (1.58)	3.95 (2.12)	167.34 (89.73)	186.50
6	7.59	0.95 (0.83)	6.58 (5.75)	1.56 (1.36)	1.29 (1.13)	2.58 (2.25)	6.67 (5.83)	94.87 (82.86)	114.50
Range	7.06 – 8.85	0.95 - 1.32 (0.53 - 1.10)	5.95 - 9.11 (3.92 - 5.75)	1.56 - 2.85 (1.07 - 2.13)	1.29 - 1.85 (0.73 - 1.38)	1.92 - 2.95 (1.13 - 2.25)	3.95 - 6.67 (2.12 - 5.83)	94.87 - 181.80 (82.86 - 89.73)	114.50 - 203.00
Mean	7.98	1.12 (0.80)	7.08 (4.95)	2.09 (1.47)	1.60 (1.14)	2.42 (1.72)	5.04 (3.69)	127.49 (86.23)	146.83

(Figures in parenthesis indicate per cent distribution)
WS: water soluble   **SORB**: sorbed   **ERMn**: easily reducible manganese bound
CA: carbonate bound   **OM**: organic bound   **Fe&Alox**: Fe & Al oxides bond   **RES**: residual
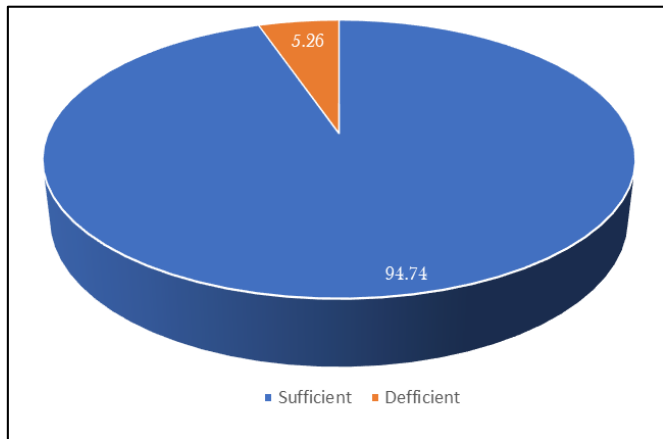
Fig 1: Per cent soil samples distribution of zinc status in soils under paddy land cover of Shrigeri taluk in hilly zone of Karnataka.

Conclution
Available zinc status in the surface layer of soils coming under paddy land cover of hilly zone indicated that, out of 19 soil samples studied, about 95.74 per cent of samples recorded sufficient status and the remaining only 5.26 per cent of samples were deficient in available zinc status, this much recovery of soils from deficient level zinc may be due to regular addition of ZnSO4 to paddy fields. Available zinc *was* found to be positively influenced by total zinc content and soil properties like, organic matter, CEC and clay content of soils. Further the order of distribution of zinc fractions in soils was found in the order of water-soluble < carbonate bound < organic bound < easily reducible manganese bound < Fe and Al oxide bound < sorbed < residual zinc. Water soluble fraction was found to be the least fraction and the residual fraction was found to be the dominant fraction contributing to total zinc in soils of the study area.

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