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Fractionation of zinc and their association with soil properties of Manipur

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Abstract

The Zinc content in six soil chemical fractions was determined in twenty four soil samples collected from different paddy fields of Gamdeiphai, Sadukoireng, Utonglok, Saijang villages of Saikul block of Kangpokpi district of Manipur using Stratified Random Sampling with proportionate allocation, to investigate the form of spontaneously accumulated Zn in the hill soils of Manipur and also to study the correlation coefficient between zinc fractions and soil properties. Sequential extraction was applied to every soil and each Zn fraction was designated. The water soluble and exchangeable zinc fractions (WSEX-Zn) varied from 0.45-0.93 mg kg^{-1} (mean 0.76 mg kg^{-1}), organically bound zinc fractions (OC-Zn) 2.40-6.12 mg kg^{-1} (mean 4.65 mg kg^{-1}), amorphous sesquioxide bound zinc (AMOX-Zn) 2.82-4.70 mg kg^{-1} (mean 3.69 mg kg^{-1}), crystalline sesquioxide bound zinc (CRYOX-Zn) 1.08-2.20mg kg kg^{-1} (mean 1.52 mg kg^{-1}), manganese oxide bound zinc (MN-Zn) 0.98-4.69mg kg^{-1} (mean 2.30 mg kg^{-1}) and residual form of zinc (RES-Zn) varied from 58.91-100.32 mg kg^{-1} (mean 78.99 mg kg^{-1}). Thus the different fractions of zinc viz. WSEX-Zn, OC-Zn, AMOX-Zn, CRYOX-Zn, MN-Zn and (RES-Zn) form constituted 0.83%, 5.06%, 4.01%, 1.65%, 2.50%, 85.95% of total zinc content in soils respectively. All the soil samples were acidic in reaction ranging from pH 4.5 to 6.06 with mean value of 5.20, electrical conductivity is ranging from 0.06 to 0.20 dSm^{-1} with mean value of 0.10 dSm^{-1}, organic carbon content 0.30 to 1.59% with mean value of 0.91%, cation exchange capacity of the soils 9.2 to 23.6 [cmol (p+) kg^{-1}] with mean value of 15.60 [cmol (p+) kg^{-1}] and the clay content of soil varied from 33.50 to 54.40% (mean 45.39%). The DTPA zinc ranged from 0.30-1.36mg kg^{-1} (mean 0.88 mg kg^{-1}) and total zinc 71.94-112.62 mg kg^{-1} (mean 91.90 mg kg^{-1}).

Keywords: Zinc, fractions, paddy, hill soil, Kangpokpi

Introduction

Micronutrient deficiencies are becoming serious because of escalated nutrient demand from more intensive and exploitative agriculture, coupled with use of high analysis fertilizer and low amount of organic manures. Among the micronutrients, zinc is the most limiting nutrient whose deficiency is a wide spread nutritional disorder of wetland rice. Zinc is known to occur in soil in a number of discrete chemical forms differing in their solubility and thus availability to plants (Sarkar and Deb, 1982) [15]. Zinc exists in five distinct pools in soils viz., water soluble, exchangeable, adsorbed, chelated or complexed zinc. These pools differ in strength and therefore in their susceptibility to plant uptake, leaching, and extractability. The equilibrium among the different pools is influenced by pH, Eh, and concentration of zinc and other cations, particularly iron and manganese. The readily available zinc forms viz., water soluble, exchangeable and chelated zinc forms were in reversible equilibrium with each other (Viets, 1962) [18].

The soil is a dynamic system where changes in its properties, management and environmental factors affect the availability of metals. However, in response to soil properties, distribution of ZN varies convincingly. Several properties like pH, organic matter, CEC and soil texture is influenced by the distribution of microelements among the fractions in soil. In view of the above, an attempt was made to study the distribution of zinc fractions in soils of Manipur and their relationships with physico-chemical properties of soils.

Material and Methods

Twenty four soil samples (0-20 cm depth) were collected from different paddy fields of Gamdeiphai, Sadukorireng, Utonglok, Saijang villages of Saikul block of Kangpokpi district of Manipur using Stratified Random Sampling with proportionate allocation. The soil samples were air dried, ground and passed through the 2 mm sieve for laboratory analysis. These samples were analyzed for soil reaction (pH) electrical conductivity (EC) using standard procedures as described by Jackson (1973) [5], organic carbon was determined by wet oxidation method of Walkley and Black (1934) [20], Soil texture by Hydrometer method of Buoyoucous (1962) [2], cation exchange capacity (CEC) by (Borah *et al*., 1987) [1]. Available zinc content of soils was measured in Atomic Absorption Spectrophotometer (AAS) after extracting the soils with 0.005M DTPA (Diethylenetriaminepenta acetic acid) in 1:2 ratio (soil: extractant) following the standard procedure (Lindsay and Norvell, 1978) [11].

A sequential fractionation procedure (Chatterjee and Khan, 1992) [3] was used to partition the Zn into six chemical fractions. Since the fractions were operationally defined, they were specified as water soluble plus exchangeable, bound to Fe/Mn oxides, Amorphous sesquioxide, Crystalline sesquioxide bound, organic matter bound and residual of Zinc in the soil (Table.1). Soil zinc fractions were estimated by subjecting surface soils to fractionation using different extractants of volume 50 ml each. First 5 g of soil was treated with 1 M neutral Mg $(NO_3)_2$, followed by 0.05 M Cu $(OAc)_2$, 0.1 M $NH_2OH.HCl$ (pH-2), 0.2 M, $(NH_4)_2\ C_2O_4$ (pH-3) and 0.1 M ascorbic acid with acidified ammonium oxalate to obtain water soluble and exchangeable, organically bound, manganese oxide bound, amorphous and crystalline sesquioxide bound, zinc fractions, respectively. Residual zinc fraction was calculated by taking difference of total and summation of zinc fractions. The total Zinc in soil was determined by using Atomic Absorption Spectrophotometer after HF and $HClO_4$ digestion method (Page *et al*. 1982). Correlation co-efficient (r) studies between different forms soil zinc and soil properties will be computed by the following formula –

$$r = \frac{\Sigma xy - \frac{\Sigma x - \Sigma y}{N}}{\sqrt{\left[\Sigma x^2 - \frac{(\Sigma x)^2}{N}\right]\left[\Sigma y^2 - \frac{(\Sigma y)^2}{N}\right]}}$$

Where, N is the number of samples, r is given as the ratio of covariance of the variables x and y to the product of the standard deviations of x and y (Gomez and Gomez, 1986) [7].

Table 1: Sequential extraction procedure for zinc in soil (Chatterjee and Khan, 1992) [3]

Fraction	Solution	Soil(g):solution(ml)	Conditions
1. Water soluble + Exchangeable (WSEX)	IM(Mg)NO_3 (pH 7.0)	5:50	2 h shaking
2. Organically complexed (OC)	0.05M $Cu(OAc)_2$	5:50	30 min. shaking
3. Manganese oxide bound (MNOX)	0.1 M $NH_2OH.HCl$ (pH 2.0)	5:50	30 min. shaking
4. Amorphous sesquioxide bound form (AMOX)	0.2 $M(NH_4)_2C_2O_4.H_2O$ (pH 3.0)	5:50	4 h shaking
5. Crystalline sesquioxide bound form (CRYOX)	0.1M Ascorbic acid with acidified ammonium oxalate	1:10	Soil and solution boiling for 30 min. on water bath
6. Residual zinc	Total zinc – sum of all the fractions		

Result and Discussion

All the soil samples were acidic in nature, the soil pH values ranged from 4.45 to 6.06 with the mean value of 5.20. Electrical conductivity of soils ranging from 0.06 to 0.20 dSm^{-1} with mean value of 0.10 dSm^{-1}, organic carbon content is varies from 0.30 to 1.59% with mean value of 0.91%, cation exchange capacity of the soils is 9.2 to 23.6[cmol (p+) kg^{-1}] with mean value of 15.60[cmol (p+) kg^{-1}] and the clay content of soil varied from 33.50 to 54.40% with mean value of 45.39%. The silt and sand contents of the soils ranged from 14.30 to 47.70% (mean 34.44%) and 3.60 to 46.30% (mean 19.97%), respectively. The texture of the soils was mostly clay, though some soils were clay loam, sandy clay and silt clay.

The DTPA zinc ranged from 0.30-1.36 mg kg^{-1}(mean 0.88 mg kg^{-1}) and total zinc 71.94-112.62 mg kg^{-1}(mean 91.90 mg kg^{-1}). The water soluble and exchangeable zinc fractions (WSEX-Zn) varied from 0.45-0.93 mg kg^{-1}(mean 0.76 mg kg^{-1}), organically bound zinc fractions (OC-Zn) 2.40-6.12 mg kg^{-1}(mean 4.65 mg kg^{-1}), amorphous sesquioxide bound zinc (AMOX-Zn) 2.82-4.70 mg kg^{-1}(mean 3.69 mg kg^{-1}), crystalline sesquioxide bound zinc (CRYOX-Zn) 1.08-2.20 mg kg^{-1}(mean 1.52 mg kg^{-1}), manganese oxide bound zinc (MN-Zn) 0.98-4.69 mg kg^{-1}(mean 2.30 mg kg^{-1}) and residual form of zinc(RES-Zn) varied from 58.91-100.32 mg kg^{-1}(mean 78.99 mg kg^{-1}).

Among the all fractions major proportion of soil zinc was in the form of Residual form(RES-Zn) varying from 58.91-100.32 mg kg^{-1}(mean 78.99 mg kg^{-1}) and the least form of soil zinc was water soluble and exchangeable zinc fractions (WSEX-Zn) varied from 0.45-0.93 mg kg^{-1}(mean 0.76 mg kg^{-1}). The organically bound zinc fraction (OC-Zn) 2.40-6.12 mg kg-1(mean 4.65 mg kg^{-1}) was the major proportion of zinc form after residual form of zinc. Crystalline sesquioxide bound zinc (CRYOX-Zn) 1.08-2.20 mg kg^{-1}(mean 1.52 mg kg^{-1}) was more than the water soluble and exchangeable zinc fractions and less than the all remaining fractions.

The different fractions of zinc viz. WSEX-Zn, OC-Zn, AMOX-Zn, CRYOX-Zn, MN-Zn and RES-Zn form constituted 0.83%, 5.06%, 4.01%, 1.65%, 2.50%, 85.95% of total zinc content in soils respectively (Fig. 1). Thus the different fractions were in the order of WSEX-Zn <CRYOX-Zn < Mn-ZnAMOX-Zn < OC-Zn <RES-Zn.

Water soluble and exchangeable zinc fractions (WSEX-Zn)

This fraction varied from 0.45-0.93 mg kg^{-1} (mean 0.76 mg kg^{-1}) and constituted 0.83 per cent of total zinc in soil. The concentration and per cent contribution of this contribution of this fraction to total zinc was the lowest among all the fractions studied (Table 3). Water soluble plus exchangeable zinc correlated negatively with pH (r = -0.222) and EC (r = -0.309) of soil, this is due to increased solubility of zinc at low pH and its subsequent adsorption on clay complex. Similar observations were given by Hazra *et al*., (1987) [8]. Water soluble plus exchangeable zinc positively correlated with organic carbon (r = 0.223), CEC (r = 0.116) and clay (r = 0.084) of soil suggesting that clay and organic matter provides more exchange sites for adsorption of zinc. Similar results were reported by many workers (Iyengar and Deb 1977; Pal *et al*., 1997) [9, 14].

Organically bound zinc fractions (OC-Zn)

This fraction varied from 2.40-6.12 mg kg^{-1} and mean value was 4.65 mg kg^{-1} (Table 3). This fraction contributed highest per cent (5.06%) of total zinc in soil next to residual form of zinc. Organically bound zinc fraction showed significant positive relationship with organic carbon (r = 0.467*), positive correlation with EC (r = 0.165), CEC (r = 0.116) and clay (r = 0.317) of soil suggesting that clay and organic matter provides more exchange sites for adsorption of zinc. Similar results were observed by Mandal and Mandal (1986) [12]. Organically bound zinc negatively correlated with pH (r = -0.350). Same results were observed by Pal *et al.*, (1997) [14].

Manganese oxide bound zinc (Mn-Zn)
This fraction varied from 0.98-4.69 mg kg^{-1} and mean value was 2.30 mg kg^{-1} (Table 3). On an average it constituted 2.50 per cent of total zinc in soil. Manganese oxide bound zinc had a significant positive relationship with organic carbon (r = 0.463*), positive relationship with pH (r = 0.056), EC (r = 0.208) and clay (r = 0.200) of the soils. Manganese oxide bound zinc had negative relationship with CEC (r = -0.318) of the soils. Similar results were observed by Singh *et al.*, (1988) [17].

Amorphous sesquioxide bound zinc (AMOX-Zn)
This fraction varied from 2.82-4.70 mg kg^{-1} and mean value was 3.69 mg kg^{-1} (Table 3). This fraction contributed 4.01 per cent of total zinc in soil next to organically bound zinc fraction. Higher content of amorphous sesquioxide bound zinc than crystalline sesquioxide bound zinc in soils could be attributed to the greater ability of amorphous sesquioxide to adsorb zinc because of their high specific surface area (Devis and Leckie 1978; Wijebandara *et al.*, 2011) [4, 19]. Higher amount of amorphous Fe oxides compared to crystalline Fe oxide in acidic environment (Mandal *et al.*, 1986) [13] and hence the extractants used namely in acidified ammonium oxalate (pH 3) might have extracted less quantity of highly stable nature of the crystalline sesquioxide (Hazra *et al.*, 1987) [8] may also be the reason for higher amount of amorphous sesquioxide bound zinc than the crystalline sesquioxide bound zinc in these soils. Amorphous sesquioxide oxide bound zinc fraction correlated negatively with pH (r = -0.152), OC (r = -0.103) and CEC (r = -0.277) of the soils. Amorphous sesquioxide bound zinc showed positively correlated with EC (r = 0.288) and significant positive relationship with clay (r = 0.494*) of soils due to zinc was adsorbed by clay (Shuman, 1985) [16].

Crystalline sesquioxide bound zinc (CRYOX-Zn)
This fraction varied from 1.08-2.20 mg kg^{-1} and mean value was 1.52 mg kg^{-1} (Table 3). On an average it constituted 1.65 per cent of total zinc in soil. Crystalline sesquioxide bound zinc showed a significant positive relationship with EC (r = 0.454*), positive relationship pH (r = 0.199), OC (r = 0.234) and clay (r = 0.358) of the soils. Crystalline sesquioxide bound zinc showed a negative relationship with CEC (r = -0.310) of the soils. The results are in confirmation with the findings of Shuman, (1985) [16].

Residual form of zinc (RES-Zn)
This fraction varied from 58.91-100.32 mg $kg^{-1}$and mean value was78.99 mg kg^{-1} (Table 3). This fraction was the dominant fraction among all the zinc fractions studied and is in agreement with the findings of Raja and Iyengar (1986) [6] and Iyengar and Deb (1977) [9]. On an average it constituted 85.95 per cent of total zinc in soil. This fraction was positively related to OC (r = 0.244), CEC (r = 0.092) and clay (r = 0.289) content of the soils. Residual zinc was negatively related with pH (r = -0.267) and EC (r = -0.008) of the soils. The results are in confirmation with the findings of Pal *et al.*, (1997) [14].

Total zinc
This fraction varied from 71.94-112.62 mg kg^{-1} and the mean value was 91.90 mg kg^{-1} (Table 3).Total zinc was correlated negatively with pH (r = -0.291) and correlated positively with EC (r = 0.041), OC (r = 0.305), CEC (r = 0.065) and clay (r = 0.289) content of the soils. Similar results were observed by Katyal and Sharma, (1991) [10].

Conclusion
Among the zinc fractions, WSEX-Zn form contributed lowest and RES-Zn form contributed highest concentration to the total zinc of the soils. OC-Zn form contributed highest concentration next to residual form, followed by AMOX-Zn, MN-Zn and CRYOX-Zn to the total zinc of the soils. WSEX-Zn correlated negatively with pH and EC and positively correlated with organic carbon, CEC and clay of soils. OC-Zn showed significant positive relationship with organic carbon, positive correlation with EC, CEC and clay and negatively correlated with pH of soils. MN-Zn significant positive relationship with organic carbon, positive relationship with pH, EC and clay and negative relationship with CEC of soils. AMOX-Zn correlated negatively with pH, OC and CEC and significant positive relationship with clay of soils. CRYOX-Zn significant positive relationship with EC, positive relationship pH, OC and clay and negative relationship with CEC of soils. RES-Zn positively related to OC, CEC and clay and negatively related with pH and EC of soils. Total Zn correlated negatively with pH and positively with EC, OC, CEC and clay of the soils.

Table 2: Some physico-chemical properties of soils

District & Block	villages	Sl. No.	pH	EC (dS m^{-1})	OC %	CEC [cmol(P^+) kg^{-1}]	DTPA-Zn (mg kg^{-1})	Sand (%)	Silt (%)	Clay (%)	Textural class
Saikul block of Kangpokpi district	Saikul	1	4.45	0.11	1.20	23.60	0.94	15.40	37.70	46.90	Clay
		2	4.47	0.08	1.05	19.40	0.85	4.50	42.70	52.80	Silt Clay
		3	4.58	0.12	1.20	11.00	0.94	24.50	25.20	50.30	Clay
		4	5.32	0.09	1.59	17.00	1.24	17.00	35.20	47.80	Clay
		5	4.55	0.14	0.57	13.00	1.20	10.40	35.20	54.40	Clay
		6	4.45	0.13	0.99	20.80	1.24	15.40	32.70	51.90	Clay
	Sadu koireng	7	5.16	0.10	1.26	14.00	1.36	16.30	37.70	46.00	Clay
		8	5.69	0.07	1.20	12.00	0.86	26.30	35.20	38.50	Clay Loam
		9	4.94	0.11	0.30	16.60	0.90	19.50	37.70	42.80	Clay
		10	4.96	0.06	0.93	20.80	1.17	17.00	40.20	42.80	Clay

		11	4.75	0.07	1.17	18.40	0.95	13.80	37.70	48.50	Clay
		12	5.20	0.10	1.05	16.00	0.80	7.00	40.20	52.80	Clay
	Utonglok	13	6.06	0.12	0.30	11.00	0.80	46.30	14.30	39.40	Sandy Clay
		14	5.66	0.09	0.60	13.00	0.74	37.00	22.00	41.00	Clay
		15	5.53	0.08	0.45	20.00	0.80	41.30	24.30	34.40	Clay Loam
		16	5.24	0.13	0.30	16.40	0.85	32.00	34.50	33.50	Clay Loam
		17	5.67	0.11	1.35	20.40	0.90	40.40	21.80	37.80	Clay Loam
		18	5.30	0.06	0.90	18.40	0.85	31.40	26.80	42.80	Clay
	Saijang	19	5.56	0.08	0.63	13.00	0.74	17.90	35.20	46.90	Clay
		20	5.79	0.11	0.87	10.80	0.30	8.60	41.10	50.30	Silt Clay
		21	5.49	0.12	0.57	15.00	0.48	13.80	40.20	46.00	Clay
		22	5.23	0.20	1.41	9.20	0.59	3.60	43.60	52.80	Silt Clay
		23	5.18	0.11	1.14	11.00	1.00	7.90	47.70	44.40	Silt Clay
		24	5.50	0.09	0.90	13.60	0.52	12.90	37.70	49.40	Clay
	Mean		5.20	0.10	0.91	15.60	0.88	0.88	34.44	45.59	
	Range		4.45 6.06	0.06-0.20	0.30 1.59	9.20- 23.60	0.30-1.36	0.30- 1.36	14.3047.70	33.50 54.40	

Table 3: Different zinc fractions (mg kg^{-1}) in soils

District & Block	villages	S. No	WSEX-Zn	OC-Zn	MN-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	Total-Zn
Kangpokpi district, Saikul block	Gamdeiphai	1	0.64	5.10	1.70	3.44	1.63	68.88	81.39
		2	0.92	4.41	0.98	4.28	1.55	98.78	110.92
		3	0.78	5.48	3.12	3.74	1.52	69.06	83.70
		4	0.89	5.02	4.69	3.89	1.78	89.28	105.54
		5	0.89	5.74	3.03	4.70	1.64	90.51	106.51
		6	0.70	5.70	2.42	3.36	1.53	80.82	94.53
	Sadu koireng	7	0.93	4.98	1.82	3.11	1.47	100.32	112.62
		8	0.81	4.06	3.00	3.18	1.41	76.88	89.34
		9	0.82	2.40	1.47	3.93	1.10	82.86	92.58
		10	0.64	4.37	2.46	3.97	1.08	92.24	104.76
		11	0.81	4.95	2.10	2.82	1.49	78.88	91.05
		12	0.78	4.88	2.47	4.03	1.52	70.92	84.60
	Utonglok	13	0.45	2.50	1.91	3.89	2.18	76.57	87.50
		14	0.73	3.40	2.93	3.85	1.56	63.20	75.67
		15	0.76	4.94	1.34	3.21	1.32	69.01	80.58
		16	0.83	2.60	2.17	3.11	1.08	84.91	94.69
		17	0.85	5.16	2.24	3.02	1.57	79.21	92.05
		18	0.81	5.70	2.05	3.98	1.50	75.31	89.34
	Saijang	19	0.71	5.69	2.09	3.01	1.53	58.91	71.94
		20	0.89	4.94	2.21	3.86	1.55	91.31	104.76
		21	0.64	6.12	1.68	4.07	1.53	61.80	75.85
		22	0.54	5.31	3.22	4.20	2.20	78.31	93.78
		23	0.81	4.38	2.19	3.89	1.08	77.00	89.34
		24	0.71	3.70	1.96	3.97	1.55	80.69	92.58
	Mean		0.76	4.65	2.30	3.69	1.52	78.99	91.90
	Range		0.45-0.93	2.40-6.12	0.98-4.69	2.82-4.70	1.08-2.20	58.91-100.32	71.94-112.62

Table 4: Correlation coefficients (r) between zinc fractions and soil properties of soils

Soil properties	WSEX-Zn	OC-Zn	MNOX-Zn	AMOX-Zn	CRYOX-Zn	RES-Zn	Total-Zn
pH	-0.222	-0.350	0.056	-0.152	0.199	-0.267	-0.291
EC	-0.309	0.165	0.208	0.288	0.454*	-0.008	0.041
OC	0.223	0.467*	0.463*	-0.103	0.234	0.244	0.305
CEC	0.116	0.169	-0.318	-0.277	-0.310	0.092	0.065
Clay	0.084	0.317	0.200	0.494*	0.358	0.289	0.289

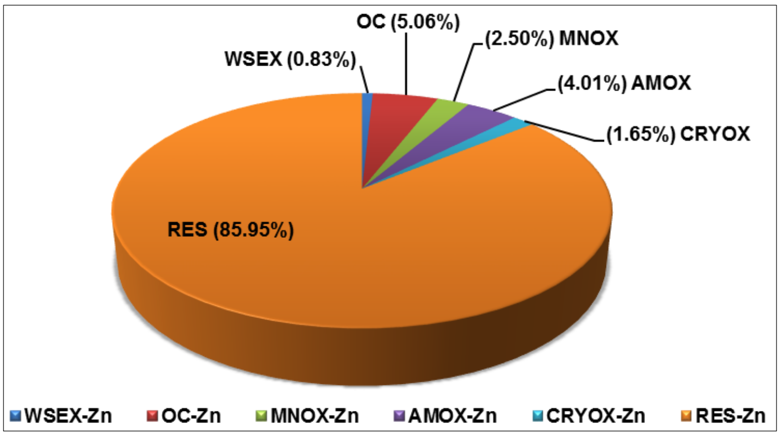

Fig 1: Contribution of different forms zinc to the total zinc in soils of Saikul block of Kangpokpi district

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