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Pawan Kumar
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Nandini Chongtham
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Herojit Singh Athokpam
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Naorem Brajendra Singh
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Athokpam Sanatomba
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Naorem Gopimohan Singh
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Corresponding Author:
Pawan Kumar
Department of Soil Science and Agricultural Chemistry, College of Agriculture, Central Agricultural University, Imphal, Manipur, India

Forms and status of zinc in the acidic soils of Imphal East District, Manipur (India)

Pawan Kumar, Nandini Chongtham, Herojit Singh Athokpam, Naorem Brajendra Singh, Athokpam Sanatomba and Naorem Gopimohan Singh

Abstract
A total of 20 soil samples (0-15 cm depth) were collected from different cultivated paddy fields of Imphal-East district of Manipur using Stratified Random Sampling with the objectives to evaluate the status and different forms of zinc in the soils and also to evaluate the relationship between some Physico-chemical properties of the soils with the various fractions of zinc. The soils were acidic in nature with pH varied from 5.01 to 6.08, electrical conductivity 0.04 to 0.18 dSm^{-1}, organic carbon 8.28 to 23.77 g kg^{-1}, cation exchange capacity 12.59 to 23.75 [cmol(p+)kg^{-1}]. All the studied soils were clay in textural class. Sand content varied from 8.61% to 25.35%, silt content 22.73% to 38.95%, and clay content ranged from 43.50% to 66.92%. The DTPA available zinc content ranged from 0.66-1.70 mg kg^{-1}. The DTPA extractable zinc showed a positive and significant correlation with EC, OC, CEC and available nitrogen; positive but non-significant with available potassium and clay. A negative and significant correlation was also found of available zinc with soil pH and available phosphorous. The distribution of Zn fractions present in the soil with average concentration were in the following order: WSEX-Zn (0.43mg kg^{-1}) < CRYOX-Zn (1.43 mg kg^{-1}) < MnOX-Zn (2.08 mg kg^{-1}) < AMOX-Zn (3.14mg kg^{-1}) < OCx-Zn (3.18 mg kg^{-1}) < Res-Zn (91.36 mg kg^{-1}). The correlation study of fractions of zinc with soil properties, a positive correlation was found with EC, OC, CEC, available N, available K and clay content and a negative correlation was found with pH, available P and sand content. Different zinc fractions of soil were found to be significantly correlated amongst themselves. An application of zinc enhances the total dry matter, zinc content and zinc uptake by the maize crop plant.

Keywords: Zinc fractions, paddy fields, acidic, clay, correlation, dry matter, zinc uptake, maize

Introduction

Zinc (Zn) is an indispensable element for both plants, animals and humans for various reproductive and physiological processes. Zinc deficiency is more pronounced among the micro-nutrients. In the world, half of the cultivated soils are deficient in zinc. On a global scenario, dietary deficiency of Zn in foods is a severe health problem distressing over two billion peoples resulting in 63 million life-years loss per annum (Myers *et al*. 2014) [27]. In India, the zinc deficiency was the first time was observed on field-scale was in rice crop in *tarai* soils by Nene in 1966. The zinc deficiency is more severe in North-East Indian soils (Kumar *et al.* 2016) [22]. At the present time, 49% of the cultivated Indian soils are deficient in zinc (Singh, 2000) [33]. In India the extent of zinc deficiency in different agro-ecological zones, this ranged from 20% to 77% (Singh, 2000 and 2001b) [33, 34].

Zinc is one of the important micronutrients for many crop plants such as rice, maize, wheat, and soybean, which all are worldwide cultivated. Zn influences quality and yields of crops (Alloway, 2003) [2]. It is a trace element needed in small but in critical concentrations, if the amount of zinc is not adequate in soils, plants will agonize from a physiological stress resulting from the dysfunction of several enzyme systems and other plant metabolic activities because it plays a vital role in several plant metabolic processes; it acts as a enzymes activator and also involved in the protein synthesis process and carbohydrate, lipid metabolism and nucleic acid (Marschner, 1986; Pahlsson, 1989) [25, 30]. Nevertheless, like other all heavy metals (Doncheva, 1997 and 1998) [13, 14] when Zn is stored in additional in plant tissues, it results in alterations in vital growth processes like chlorophyll biosynthesis and (Doncheva *et al.*, 2001) [15] and membrane integrity also (De Vos *et al.*, 1991) [11]. According to (Chaoui *et al.*, 1997) [10] an additional quantity of Zn also has been stated to have an undesirable effect on mineral nutrition.

Maize belongs to Maideas tribe and grass family of Poaceae /Gramineae is categorized as the most sensitive cereal crop to Zn deficiency. However, Zn deficiency mainly occurs in maize crop plants as Zn plays so many important structural and functional roles in plant growth and development and a lack of Zn resulted to decreased seed formation (Bell and Dell, 2008) [4]. Zinc deficiency in human being also looks to be a critical nutritional and health hazards in the whole world. The severe challenge is being looked to enhance grain Zn concentration in agricultural crops to overawed widespread malnutrition problem especially in under developing and economically poor countries (Bouis and Welch, 2010) [6]. Therefore, with the increasing levels of Zn content in grain is results in providing more Zn to people, who belief directly or indirectly on pea-derived food. Zinc is also essential for the transportation of calcium throughout the corn plant.

Maize *(Zea mays* L.) is the third most important cereal crop of the world as well as India after wheat and rice. Maize has the highest production among all the cereals world with 11,34,747 thousand tonnes (1.13 billion metric tons) in year 2017 (FAOSTAT, 2019) [17] as compared to 10,60,107 thousand tonnes produced in year 2016 (FAOSTAT, 2018) [16]. In India, maize is cultivated in 9.47 million hectares with an annual production of 28.72 million tonnes with the average productivity of 3,032 kg ha^{-1} (Directorate of Economics & Statistics, DAC&FW, 2018) [12]. Over 85% of maize produced in the country grown throughout the year as three seasons as *kharif, rabi and jayad* season.

Materials and Methods

Twenty soil samples (0-15 cm depth) were collected from various cultivated paddy fields of Imphal East district in 100 kg capacity polythene clean bags. The soil samples were thoroughly dried in shade, ground with wooden pestle and mortar and passed through 2 mm sieve separately without any mixture of foreign material. The soil samples were stored in separate clean polythene bags with using proper labels and used for further the various physico-chemical analyses of the soils.

Mechanical analysis were carried out by hydrometer method (Bouyoucos, 1951; 1962) [7, 8]. These samples were analysed for soil pH, and EC using standard procedures as described by Jackson, (1973) [19] and CEC as described by Borah *et al.* (1987) [5]. Available nitrogen, P_2O_5 and K_2O were determined by Subbiah and Asija (1956) [36], Bray and Kurtz No.1 method (1945) [9] and Jackson (1973) [19], respectively. Organic carbon was determined by wet oxidation method (Walkley and Black, 1934) [37].

Soil available zinc was determined by using Atomic Adsorption Spectrophotometer (ASS) as described by Lindsay and Norvell (1978) [23]. Different forms of zinc *viz*., water-soluble plus exchangeable (WSEX-Zn), organically complexed (OC_X-Zn), amorphous sesquioxide bound form (AMOX-Zn), crystalline sesquioxide bound form (CRYOX-Zn), and manganese oxide bound form (MnOX-Zn) were determined by sequential fractionation procedure outlined by Murthy (1982) [26] modified by Mandal and Mandal (1986) [24]. After each extraction, the suspension was centrifuged at 4000 rpm for 20 minutes. The solution was filtered with Whatman No. 42 Filter paper and the residue were washed with distilled water and used for the subsequent extractions.

All data obtained from the present experiment were computed as per method described by Gomez and Gomez (1984) [18] to obtain the mean and standard deviation of zinc concentration in the different pools. In addition correlation analysis was done to obtain the relationship among zinc concentration in various pools and various soil properties. The significance of various effects was tested at 5% level of probability.

Results and Discussion

The results shows that soil pH values were ranged from 5.01 to 6.08 (mean 5.42), EC varied from 0.04 dSm^{-1} to 0.18 dSm^{-1}at 25 ^{0}C (mean 0.10), CEC from 12.59 [cmol(P^+)kg^{-1}] to 23.75 [cmol($p^{+)}$ kg^{-1}]. (mean 16.36 [cmol($p^{+)}$ kg^{-1}]), organic carbon content from 8.28 to 23.77 g kg^{-1} (mean 17.71 g kg^{-1}). The available nitrogen, P_2O_5 and K_2O content were ranged from 214.12 kg ha^{-1} to 425.83 kg ha^{-1} (mean 299.74 kg ha^{-1}), 21.21 kg ha^{-1} to 39.49 kg ha^{-1} (mean 30.36 kg ha^{-1}) and 226.44 kg ha^{-1} to 322.94 Kg ha^{-1} (mean 271.51 Kg ha^{-1}.), respectively. The soils were clay in textural class. Similar observation was also reported by Athokpam *et al.* (2018) [3].

Soil Available Zinc

The available zinc content soils varied from 0.66 mg kg^{-1} to 1.70 mg kg^{-1} and the mean value was 1.06 mg kg^{-1}. The DTPA extractable zinc shows positive and significant correlation with EC (r=0.444 *) organic carbon (r=0.515 *) CEC (r=0.623 **) available nitrogen (r=0.652 **). Very closer results was supported by Kumar and Babel (2010); Athokpam *et al.* (2018) [21, 3]. A negative and significant correlation was observed with pH (r=-0.461*) available phosphorous (r=-0.849**). Similar result was supported by Prasad (1991) [31], Nayak *et al.* (2000) [28], Athokpam *et al.* (2018) [3] and Akter *et al.* (2019) [1].

Water soluble + exchangeable zinc (WSEX-Zn)

The WSEX-Zn fraction ranged from 0.11 to 1.10 mg kg^{-1} and the mean value was 0.43 mg kg^{-1}. The WSEX-Zn fraction was positively and significantly correlated with EC (r=0.598 **) organic carbon (r=0.468 *) CEC (r=500 *) available nitrogen (r=0.771 **). Similar results was supported by Kandali *et al.* (2016); Athokpam *et al.* (2018) [20, 3]. It was negatively and significantly correlated with pH (r=-0.467 *) and available phosphorous (r=-0.855 **). Similar result was supported by Athokpam *et al.* (2018) [3]

Organically complexed zinc (OCx-Zn): The OCx-Zn fraction ranged from 2.58 to 4.66 mg kg^{-1} and the mean value was 3.18 mg kg^{-1}. The OCx-Zn fraction was positively and significantly correlated with EC (r=0.625 **), organic carbon (r=0.492 *) CEC (r=0.588 *) available nitrogen (r=0.703 **) and available potassium (r=453 *). A negative and significant correlation was observed with pH (r=-0.474 *), available phosphorous (r=-0.843 **).Similar results were supported by Athokpam *et al.* (2018) [3] in acidic soils of Manipur valley.

Amorphous sesquioxide bound zinc (AMOX-Zn)

The AMOX-Zn fraction ranged from 2.40 to 4.30 mg kg^{-1} and the mean value was 3.14 mg kg^{-1}. The AMOX-Zn fraction was positively and significantly correlated with EC (r=0.582 **), CEC (r=0.561 **), available nitrogen (r=0.693 **).The similar finding was reported by Kandali *et al.* (2016) [20]. A negative and significant correlation was observed with pH (r=-0.475 *) available phosphorous (r=-0.826 **).These were in the line with the findings reported by Spalbar *et al.* (2017) and Athokpam *et al.* (2018) [35, 3].

Crystalline sesquioxide bound zinc (CRYOX-Zn): The CRYOX-Zn fraction ranged from 0.36 to 2.17 mg kg^{-1} and the mean value was 1.43 mg kg^{-1}. The CRYOX-Zn fraction was positively and significantly correlated with EC (r=0.484 *), CEC (r=0.601 **). It was negatively and significantly correlated with pH (r=-0.557 *) and available phosphorous (r=-0.609 **). The similar findings were reported by Spalbar *et al.* (2017) and Athokpam *et al.* (2018) [35, 3].

Table 1: Some Physico-chemical properties of soil

Soil samples	pH (mol/lit.)	EC (dSm^{-1})	Org. C (g kg^{-1})	Av. N (kg ha^{-1})	Av. P_2O_5 (kg ha^{-1})	Av. K_2O (kg ha^{-1})	CEC [cmol (P^+) kg^{-1}]	Sand (%)	Silt (%)	Clay (%)	Textural Class
1.	5.25	0.04	17.09	253.64	37.66	257.85	15.41	17.63	32.15	50.22	Clay
2.	5.58	0.09	8.96	272.66	38.75	236.59	13.82	10.12	26.43	63.45	Clay
3.	6.05	0.10	22.10	274.88	28.46	291.06	16.14	9.80	23.28	66.92	Clay
4.	5.85	0.09	21.67	286.46	26.70	285.33	15.58	10.50	31.80	57.70	Clay
5.	5.90	0.07	16.32	301.62	37.38	270.19	12.59	16.39	36.03	47.58	Clay
6.	5.28	0.06	15.75	292.67	36.20	250.23	15.84	19.84	34.46	45.70	Clay
7.	5.69	0.13	8.28	221.45	39.49	226.44	18.72	10.15	30.50	59.35	Clay
8.	6.08	0.11	19.60	268.70	32.91	306.52	15.62	8.61	27.85	63.54	Clay
9.	5.02	0.06	15.68	214.12	31.88	242.09	17.44	23.94	32.56	43.50	Clay
10.	5.95	0.09	20.17	287.37	28.44	322.75	16.60	9.90	34.03	56.07	Clay
11.	5.01	0.08	20.07	402.69	23.15	265.56	14.40	11.40	31.50	57.10	Clay
12.	5.05	0.16	19.63	407.09	22.49	296.08	15.07	11.86	27.64	60.50	Clay
13.	5.03	0.18	23.77	341.45	21.21	322.94	23.75	10.00	23.54	66.46	Clay
14.	5.35	0.05	19.10	348.48	25.41	253.71	16.00	12.50	27.63	59.87	Clay
15.	5.60	0.15	18.11	425.83	22.02	253.78	16.12	12.20	38.95	48.85	Clay
16.	5.40	0.10	17.66	249.76	37.20	282.70	16.28	10.34	36.10	53.56	Clay
17.	5.07	0.06	17.51	238.85	32.49	270.56	18.65	18.49	29.50	52.01	Clay
18.	5.03	0.11	15.70	289.21	27.17	267.76	16.48	25.35	27.34	47.31	Clay
19.	5.02	0.13	16.96	247.42	36.27	236.38	14.01	17.78	22.73	59.49	Clay
20.	5.10	0.15	20.12	370.40	21.84	291.73	18.75	10.65	31.50	57.85	Clay
Mean	5.42	0.10	17.71	299.74	30.36	271.51	16.36	13.87	30.28	55.85	

Table 2: Amount of different zinc fractions (mg kg^{-1}) in soils

Soil samples	DTPA Extractant Available Zn	Fractions						
		WSEX- Zn	OCx-Zn	AMOX-Zn	CRYOX-Zn	MnOX-Zn	Res-Zn	Total-Zn
1.	0.94	0.26	2.92	2.89	1.41	2.43	82.50	92.10
2.	0.75	0.16	2.74	2.71	1.22	0.94	76.50	85.50
3.	0.92	0.24	2.88	2.78	1.20	2.13	74.44	80.10
4.	0.88	0.22	2.79	2.55	1.17	0.78	78.44	84.33
5.	0.66	0.11	2.58	2.40	0.36	0.62	72.50	77.71
6.	0.87	0.22	2.78	2.68	1.22	2.09	77.50	86.30
7.	0.82	0.15	2.60	2.78	1.30	1.68	86.32	92.50
8.	0.81	0.12	2.66	2.94	1.17	1.95	84.32	90.10
9.	1.10	0.48	3.12	3.05	1.48	2.19	88.44	96.20
10.	1.15	0.45	3.25	3.28	1.60	2.24	92.32	101.20
11.	1.26	0.64	3.40	3.55	1.64	2.52	98.50	107.50
12.	1.24	0.96	3.95	3.86	1.77	2.96	110.50	120.50
13.	1.70	1.10	4.66	4.30	2.17	3.46	122.50	132.50
14.	1.35	0.51	3.28	3.34	1.52	2.10	90.50	92.10
15.	1.40	0.95	3.90	3.88	1.90	2.96	112.10	118.20
16.	0.98	0.25	2.80	2.78	1.43	2.12	92.10	96.30
17.	0.99	0.29	2.95	3.12	1.59	2.76	94.50	102.50
18.	1.23	0.49	3.56	3.62	1.54	2.21	99.33	105.50
19.	0.74	0.14	2.68	2.65	1.51	0.68	88.44	98.50
20.	1.37	0.83	4.10	3.68	1.48	2.68	105.40	115.10
Mean	1.06	0.43	3.18	3.14	1.43	2.08	91.36	98.74

(WSEX-Zn = Water soluble + Exchangeable zinc; OCx-Zn = Organically complexed zinc; AMOX-Zn = Amorphous sesquioxide bound zinc; CRYOX-Zn = Crystalline sesquioxide bound zinc; MnOX-Zn = Manganese oxide bound zinc; Res-Zn = Residual zinc; Total-Zn = Total zinc)

Table 3: Simple correlation coefficient of different forms of zinc and soil Physico-chemical properties

	Soil properties	DTPA extractant Zn	Fractions						
			WSEX- Zn	OCx-Zn	AMOX-Zn	CRYOX-Zn	MnOX-Zn	Res-Zn	Total-Zn
1.	PH	-0.461 *	-0.467 *	-0.474 *	-0.475 *	-0.557 *	-0.417	-0.545 *	-0.585**
2.	EC	0.444 *	0.598 **	0.625 **	0.582 **	0.484 *	0.316	0.687 **	0.693 **
3.	OC	0.515 *	0.468 *	0.492 *	0.424	0.326	0.418	0.380	0.362
4.	CEC	0.623 **	0.500 *	0.588 **	0.561 **	0.601 **	0.636 **	0.597 **	0.589 **
5.	AV. N	0.652 **	0.771 **	0.703 **	0.693 **	0.394	0.459 *	0.609 **	0.588 **

6.	AV. P	-0.849 **	-0.855 **	-0.843 **	-0.826 **	-0.609 **	-0.611 **	-0.728 **	-0.697 **
7.	AV. K	0.403	0.380	0.453 *	0.409	0.221	0.411	0.362	0.357
8.	Sand	-0.102	-0.135	-0.110	-0.100	-0.075	-0.051	-0.106	-0.083
9.	Silt	-0.039	0.004	-0.104	-0.114	-0.211	0.038	-0.057	-0.086
10.	Clay	0.099	0.095	0.146	0.146	0.190	0.012	0.113	0.116

Table 4: Simple correlation coefficient among the different forms of zinc fractions

		DTPA- Zn	WSEX- Zn	OCX-Zn	AMOX-Zn	CRYOX-Zn	MNOX-Zn	RES-Zn	TOTAL-Zn
1.	DTPA-Zn	1	0.929 **	0.939 **	0.942 **	0.801 **	0.808 **	0.877 **	0.843 **
2.	WSEX-Zn		1	0.973 **	0.949 **	0.760 **	0.772 **	0.914 **	0.905 **
3.	OCx-Zn			1	0.956 **	0.749 **	0.761 **	0.910 **	0.908 **
4.	AMOX-Zn				1	0.821 **	0.830 **	0.943 **	0.929 **
5.	CRYOX-Zn					1	0.760 **	0.852 **	0.857 **
6.	MnOX-Zn						1	0.770 **	0.761 **
7.	Res-Zn							1	0.988 **
8.	Total-Zn								1

* Significant at 5 per cent level
** Significant at 1 per cent level

Manganese oxide bound zinc (MnOX-Zn)

The MnOX-Zn fraction ranged from 0.62 to 3.46 mg kg^{-1} and the mean value was 2.08 mg kg^{-1}.The MnOX-Zn fraction was positively and significantly correlated with CEC (r=0.636 **), available nitrogen (r=0.459 *). It was negatively and significantly correlated with available phosphorous (r=-0.611 **). There is a negative relationship among zinc content and available manganese contents in soils was revealed by many scientists.

Residual zinc (Res-Zn)

The Res-Zn fraction ranged from 72.50 to 122.50 mg kg^{-1} and the mean value was 91.36 mg kg^{-1}. The Res-Zn fraction was positively and significantly correlated with EC (r=0.687 **), CEC (r=0.597 **), available nitrogen (r=0.609 **) and organic carbon (r=0.380).A positive relationship among Res-Zn fraction and OC (organic carbon) indicates that residual zinc contents some portion which is derived from resistant organic matter and ferrous oxides, which is earliest reported by Singh *et al.* (1988). It was negatively and significantly correlated with pH (r=-0.545 *) and available phosphorous (r=-0.728 **) Similar findings were also reported by Spalbar *et al.* (2017) and Athokpam *et al.* (2018) [35, 3].

Total zinc (Total-Zn)

The Total-Zn fraction ranged from 77.71 to 132.50 mg kg^{-1} and the mean value was 98.74 mg kg^{-1}. The Total-Zn fraction was positively and significantly correlated with EC (r=0.693**), CEC (r=0.589 **) and available nitrogen (r=0.588 *). A negative and significant correlation was observed with pH (r=-0.585*), available phosphorous (r=-0.697 **). The similar finding was reported by Athokpam *et al.* (2018) [3].

Correlation between various zinc Fraction

The result showed that there was a positive and significant correlation was found among the different zinc fractions with varying degrees. The highest significant correlation was found between Residual zinc (Res-Zn) and Total-Zn (r=0.988 **) and the least significant correlation was found between Crystalline sesquioxide bound zinc (CRYOX-Zn) and organically complexes zinc (OCx-Zn) (r=0.749 **).This indicating the dependence of these forms on each other. The similar finding was reported by Sharma *et al.* (1996) [32] and Athokpam *et al.* (2018) [32, 3].

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