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Chemical fractionation of zinc and its relationship with important properties of rice grown soils

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Abstract
GPS based 90 representative surface soil samples were collected randomly from rice growing farmers' fields to understand the distribution of Zn fractions. Five mechanistic Zn fraction *i.e.* Extractable Zn, carbonate Zn, organic Zn, amorphous Zn and residual Zn were determined and Total Zn was calculated as a sum of these five pools which ranged from 14.28 to 138.41 mg kg^{-1} with an average of 34.47 mg kg^{-1}. Fractional distribution of Zn in these rice soils showed the order: RES-Zn > Org-Zn > WSEx-Zn > CO_3-Zn > Ox-Zn. Correlation analysis showed that WSEx-Zn increased with SOC (r = 0.788) and silt+clay (r = 0.237).The fact that the chemistry of Zn in this set of soils appears to be dominated by the most stable fractions offers an explanation for the common notion held that majority of rice grown Navsari soils have low soil Zn test levels which accounts for low Zn bio-availability.

Keywords: Chemical Zn fractionation, Soil Zn, rice soils, correlation coefficients, regression

1. Introduction

Zinc (Zn) is a vital essential element which is required only in limited amounts by plants, animals and humans for various physiological and reproductive functions. It influences the quality and yield of crops (Chidanandappa *et al.*, 2008) [3] and in humans, it is a necessary co-factor in more than 300 enzymes and numerous transcription factors (Haug *et al.*, 2010) [7]. It is found in nearly 100 specific enzymes, serves as structural ions in transcription factors and is stored and transferred in metallothioneins. It is 'typically the second most abundant transition metal in organisms' after iron (Fe) and it is the only metal which appears in all enzyme classes. In proteins, Zn ions are often coordinated to the amino acid side chains of aspartic acid, glutamic acid cysteine and histidine. The theoretical and computational description of this Zn binding in proteins (as well as that of other transition metals) is difficult.

Rice (*Oryza sativa* L.) is the most widely consumed staple food for a large part of the worlds' human population, especially in Asia. In Navsari district of Gujarat state, rice is a major food staple and a mainstay for the rural population and their food security. In rice plant, Zn is a crucial nutrient required for several biochemical processes in the rice plant, and it plays an important role in auxin metabolism, preferential accumulation of chlorophyll, protein synthesis, starch metabolism and membrane integrity. Thus, Zn deficiencies affect plant color and turgor. In plant, Zn is slightly mobile, but that is quite immobile in rice fields. Zn deficiency is the most common nutritional disorder of Asia's rice paddy fields immediately after N and P constraints. Tillering decreased or could stop completely and prolonged crop maturity (Anon., 2007). [1] Anon Zn deficiencies could also increase spikelet sterility in rice. Zn deficiency continues to be one of the key factors in determining production in several parts of the country (Chaudhary *et al.* 2007). It is now recognized as the fifth leading risk factor in developing Asian countries (Anon., 2007). [1] and efforts are being made to reduce Zn deficiency in soils as it is not only a barrier to achieving crop yield goals but also results in low Zn content in grains and straw leading to poor Zn nutrition of humans and animals, a subject which recently received considerable attention (Schardt, 2006).[15]

Content of total soil Zn provides only limited information about its transformations and bioavailability. The distribution of Zn fractions among soil particles play a vital in supplying adequate amounts of Zn needed for crop growth. The most important forms of Zn are water extractable (WSEx-Zn), organically bound (Org-Zn), sesqueoxide bound Zn (Ox-Zn), carbonate bound Zn (CO_3-Zn) and residual (Res-Zn), while the WSEx-Zn and CO_3-Zn are the phyto-available forms of Zn for crop growth. It has been widely reported that the residual Zn and oxide bound Zn are the more stable fractions while the exchangeable Zn and water soluble Zn fractions are rather more soluble (Saffari *et al.*, 2009).[14]

Zn availability is reported to be associated with its transformation in soils and plant continuum through various mechanisms, such as adsorption by clay surfaces, hydrous oxide minerals, organic matter and so forth, which affect crop Zn uptake. Understanding the distribution of Zn among various fractions of soils will help to characterize the chemistry of Zn in soils and possibly its availability for plant uptake. Zn availability to rice is strongly related to Zn fractions in the soil. The Zn requirement of crops is largely met from soluble portions released through chemical transformations of native soil-Zn (Shuman, 1991). In addition, Zn may be supplied to plants from soluble forms in synthetic or organic sources, as well as anthropogenic atmospheric inputs (Iyengar *et al.*, 1981; Johnson and Petras, 1998) [8, 10].

The present study has been undertaken to determine the chemical fractionation of Zn, its distribution and their relationship with important soil properties of rice growing soils of Navsari district.

Materials and methods:

An overview of study area

Rice growing soils of Navsari district of Gujarat state was been taken under the present study which consists of six *talukas viz.*, Navsari, Jalalpore, Gandevi, Chikhli, Khergam and Vansda. The is situated in the southern part of the Gujarat state (between $20^0$45'-$21^0$00' N latitude and $72^0$45' - $73^0$15' E longitude) and the present physiographic set-up is combined result of diversified lithology (Deccan tap and Alluvium). This district comes under Agro-ecological situation (AES) III of South Gujarat heavy rain fall zone.

Soils

Soils of this district belong to *Inceptisols* having *Vertic* as characteristics horizon with predominance of smectite silicate clay mineral.

Cropping pattern and history

Conversation with farmers revealed that more than 50 per cent of the farmers of Navsari and Jalalpore *talukas* preferred rice after rice cultivation continuously, while farmers of Gandevi, Chikhli, Khergam and Vansda *talukas* preferred diversified cultivation inclusive of rice as intercrop cultivation between mango /sapota (chiku) plantation or rotation with non-cereal crops (*viz.*, vegetables or pulses). All rice growing farmers of this district reported that they used to burn the crop residue (rice straw) after harvest of the crop. However, such burning might prove dangerous towards sustaining environmental health as well as soil health too, as it would accentuates depletion of organic carbon rapidly from the soil causing deterioration of soil quality and crop productivity. Researchers of Navsari Agricultural University, Navsari (Gujarat) recommended for rice growing farmers that an addition of zinc sulphate @ 25 kg ha^{-1} once in a three years would be essential to maintain Zn status in these soils as well as to sustain rice yield. But, hardly any farmer was found in this district to incorporate zinc sulphate into the rice soil. This fact might lead to increase deficiency of Zn in soil more severely in the upcoming future. The lengths and intensities of cultivation and management practices for rice crop at the various locations were different spatially.

Fig 1

Collection of Soil samples

Surface soil samples collected as per the identified location with the help of GPS (Latitude, Longitude with elevation). One representative surface sample was collected from each field up to a depth of 0-22.5 cm following zig-zag method of sampling and the centre of the field was designated as geo-referenced point of sampling. From each *taluka* of Navsari district, 15 nos. of surface (0-22.5 cm) samples were collected from farmers' rice field of 15 villages after harvest of crop at proper condition. Total 90 representative surface soil samples were collected from the entire district. All the samples was properly labeled, brought and kept to the laboratory in safe place for further processing.

Soil analyses

All samples were air dried and crushed to pass through a 2 mm sieve. Soil analysis was done using standard procedures. All the samples brought in laboratory will be first air-dried and passed through 2 mm sieve. The samples will be processed properly as per requirement for analysis of all the parameters below.

1) **Soil pH and EC:** Measured in 1:2.5 soils: water suspension by using glass electrode electric pH-meter and EC-meter, respectively (Gupta, 2007). [6]
2) **Soil organic carbon:** Determined following Walkley and Black rapid titration method (Walkley and Black, 1934).
3) **Percent of $CaCO_3$:** Percent $CaCO_3$ was determined by acid neutralization method using standard hydrochloric acid (1 N HCl) destroying carbonates and amount of excess acid was determined by titration with standard sodium hydroxides (0.2 N NaOH) after separation from the soil by filtration or centrifugation (Dewis and Freitas, 1970). [5]
4) **Exchangeable cations:**
   a) Exchangeable Na^+ and K^+: Determined flame photometrically by using neutral normal ammonium acetate extractant (Jackson, 1973). [9]
   b) Exchangeable Ca^{++} and Mg^{++}**:** Determined using neutral normal ammonium acetate exctractant by EDTA- titration- Versenate method (Jackson, 1973). [9]
5) **Mechanical Analysis:** Determined by following International pipette method (piper, 1950). [12]

Zinc fractionation

A modified version of the batch or single extraction scheme (Johnson and Petras, 1998) [10] was used to define the various Zn fractions in the soils. Rather than using the same soil residue in the next extraction step, fresh sample was weighed into the next reagent, as follows:

1. **Extractable Zn (WSEx-Zn):** Representing the water soluble and exchangeable fraction: Twenty grams of soil was extracted in 40 mL 0.005 M DTPA for 2 h
2. **Carbonate bound Zn (CO_3-Zn):** Representing the inorganically bound fraction: One gram soil was extracted in 20 mL 1 M CH_3COONH_4/CH_3COOH mixture at pH 5 for 5 h
3. **Organic bound Zn (Org-Zn):** Representing the fraction complexed, chelated or adsorbed to Organic ligands: One gram soil extracted in 40 mL 0.1 M $K_2P_4O_7$ for 17 h
4. **Sesquioxide Zn (Ox-Zn):** Representing the amorphous bound fraction: one gram soil was extracted in 50 mL acid Oxalate at pH 3 (four parts 0.2 M ammonium oxalate and three parts 0.23 M oxalic acid) for 17 h
5. **Residual Zn (Res-Zn):** One gram soil sample was digested in 25 mL aqua regia (one part HNO3 to three parts HCl) for twenty minutes on a hot plate and then allowed to cool
6. **Total Zn (Tot-Zn):** Total Zn was calculated as a sum of all the fractions determined

Each soil suspension was filtered after shaking or digestion. The concentration of Zn in the extracts was determined using the AAS (atomic absorption spectrophotometer.

Statistical analysis
The simple correlations among different parameters as per requirement were workout by following standard method given by Panse and Sukhatme (1967) and results were interpreted and discussed accordingly. Regression analyses were carried out using the 'Statistical Data Analysis Tool-pack' of Microsoft Excel.

Results and discussion
Soil Properties
Rice grown soils of Navsari district were 'clayey' in texture, neutral in reaction and normal in salinity, except soils of few villages with slightly salinity and moderately alkaline in reaction. Soil pH varied widely from 5.70 to 8.20 *i.e.* Medium acidic to moderately alkaline. Soil EC varied from low (0.02 dS m^{-1}) to medium 1.82 dS m^{-1}. SOC, as reported by Zang *et al.* (2003). [18] and Andrews *et al.* (2004) to be a good indicator of soil productivity potential, ranged from 2.1 to as high as 19.10 g kg^{-1} (low to high) with soils of one, nine, ten, seven, two and three villages respectively from Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *taluka* low SOC status. As fields where farmers mainly practicing rice after rice cultivation continuously or burning post-harvest-crop residue, were found to be low in plant-available Zn status as compared to those of others, it is suggested that farmers should follow diversified cultivation / crop rotation with non-cereal crop / intercropping, *etc*. and incorporate crop residue to elevate SOC.$CaCO_3$ content varied from 0.32 to 6.5 per cent *i.e.* low to high. CEC varied appreciably *i.e.* from 32.28 cmol (p+) kg^{-1} to 70.32 cmol (p+) kg^{-1} with the mean CEC of 48.36 cmol (p+) kg^{-1}. Exchangeable cations followed the trend as Ca^{++} >Mg^{++} >Na^{+} >K^{+} in all the rice grown surface soils of the district (Table 1).

Fractionation and distribution of Zn
a) Extractable Zn (WSEx-Zn)

Water soluble plus exchangeable Zn (WSEx-Zn) *i.e.* DAPA-Zn, in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* varied from 0.25 to 1.51, 0.24 to 0.85, 0.31 to 1.05, 0.20 to 1.06, 0.15 to 1.83 and 0.36 to 1.69 ppm, respectively (deficient to adequate status of available Zn in all the *talukas*) with mean values of 0.82, 0.47, 0.65, 0.57, 0.80 and 0.88 ppm. WSEx-Zn in soils of Navsari district varied widely from 0.15 to 1.83 ppm (deficient to adequate) with mean value of 0.67 ppm. Mean WSEx-Zn in soils of these *talukas* showed the following descending order: Chikhli > Vansda > Khergam > Navsari > Gandevi > Jalalpore indicating soils of Jalalpore *taluka* were most inferior in plant-available Zn pool. Soils from thirty two villages (35.56 %) of Navsari district were found deficient in available Zn as of today.

Table 1: Physico-chemcial properties of rice growing soils of different *talukas* of Navsari district and the district as a whole

	Soil pH	Soil EC (dS m^{-1})	SOC (g kg^{-1})	$CaCO_3$ content (%)	Exchangeable cations cmol (p+) kg^{-1}				CEC cmol (p+) kg^{-1}	Particle size distribution			Silt +clay (%)
					Ca^{++}	Mg^{++}	Na^{+}	K^{+}		Sand %	Silt %	Clay %	
Vansda *taluka*													
Range	6.40-7.40	0.10-0.84	2.10-14.40	0.32-5.87	21.38-43.65	10.55-21.34	0.19-1.15	1.78-5.19	34.56-63.76	6-40	4- 46	44- 58	60-94
Mean	6.79	0.32	8.90	1.91	29.90	15.98	0.42	3.35	49.66	16.27	31.73	52.00	83.73
Jalalpore *taluka*													
Range	6.40-7.40	0.02-1.66	2.90-19.10	0.62-6.50	22.80-40.26	10.11-29.10	0.18-0.90	3.41-11.15	45.38-70.32	4-18	18- 42	48-70	82-96
Mean	6.94	0.91	5.90	2.90	30.87	18.77	0.44	6.57	56.65	10.93	34.00	55.07	89.07
Navsari *taluka*													
Range	6.50-7.90	0.17-1.82	2.10-9.80	1.25-6.50	23.68-39.52	10.19-20.86	0.17-0.79	2.07-7.62	43.71-60.13	6-16	26-38	48-58	84-94
Mean	7.18	0.56	5.40	3.95	32.01	13.71	0.42	4.52	50.66	13.07	33.60	53.33	86.93
Gandevi *taluka*													
Range	6.40-8.10	0.20-1.05	3.50-16.10	0.50-5.25	25.17-39.47	10.19-17.46	0.18-0.72	2.68-9.36	39.19-57.66	6-28	16-54	32-58	72-94
Mean	7.38	0.40	6.00	3.37	34.08	12.60	0.42	4.10	51.20	14.67	31.87	53.47	85.33
Khergam *taluka*													
Range	5.70-7.70	0.13-0.81	2.7-0-14.90	0.50-6.25	20.64-27.65	10.55-25.22	0.15-0.88	1.25-2.08	32.28-50.78	8-20	22-40	48-58	80-92
Mean	6.73	0.34	9.60	3.77	24.41	14.71	0.40	1.61	41.13	14.80	31.47	53.73	85.20
Chikhli *taluka*													
Range	6.10-8.20	0.15-1.77	4.40-16.70	1.50-5.50	21.83-35.89	10.19-24.68	0.18-1.15	1.35-2.45	34.72-50.61	6-22	26-44	48-58	78-94
Mean	7.05	0.52	8.50	3.86	26.69	15.20	0.48	1.80	44.18	13.47	32.00	54.53	86.53
Navsari district as a whole													
Range	5.70-8.20	0.02-1.82	2.10-19.10	0.32-6.50	20.64-43.65	10.05-29.10	0.15-1.15	1.25-11.2	32.28-70.32	4-40	4-54	32-70	60-96
Mean	7.01	0.51	7.40	3.29	29.44	15.12	0.42	3.74	48.36	13.84	32.53	53.69	86.13

Table 2: Categorization of rice grown soils of different talukas and Navsari district as a whole based on soil EC, soil pH, SOC and $CaCO_3$ content depending upon their degree /extent

Parameters	Category	Talukas of Navsari district						
		Vansda	**Jalalpore**	**Navsari**	**Gandevi**	**Khergam**	**Chikhli**	**Navsari district**
Soil EC	Normal	15 (100)	08 (53.33)	14 (93.33)	14 (93.33)	15 (100.0)	14 (93.33)	80 (88.88)
	Slightly saline	00 (00.00)	07 (46.67)	01 (06.67)	01 (06.67)	00 (00.00)	01 (06.67)	10 (11.11)
Soil pH	Medium acidic	00 (00.00)	00 (00.00)	00 (00.00)	00 (00.00)	03 (20.00)	00 (00.00)	03 (03.33)
	Slightly acidic	05 (33.33)	02 (13.33)	01 (06.67)	01 (06.67)	02 (13.33)	04 (26.67)	15 (16.67)
	Neutral	09 (60.00)	12 (80.00)	09 (60.00)	06 (40.00)	08 (53.33)	06 (40.00)	50 (55.56)
	Mildly alkaline	01 (06.67)	01 (06.67)	05 (33.33)	05 (33.33)	02 (13.33)	04 (26.67)	18 (20.00)
	Moderately Alkaline	00 (00.00)	00 (00.00)	00 (00.00)	03 (20.00)	00 (00.00)	01 (06.67)	04 (04.44)
SOC content	Low	01 (06.67)	09 (60.00)	07 (46.67)	10 (66.67)	02 (13.33)	03 (20.00)	32 (35.55)
	Medium	05 (33.33)	04 (26.67)	06 (40.00)	02 (13.33)	02 (13.33)	06 (40.00)	25 (27.78)
	High	09 (60.00)	02 (13.33)	02 (13.33)	03 (20.00)	11 (73.33)	06 (40.00)	33 (36.67)
$CaCO_3$ content	Low	03 (20.00)	02 (13.33)	00 (00.00)	02 (13.33)	01(06.67)	00 (0.00)	08 (08.88)
	Medium	11 (73.33)	11 (73.33)	10 (66.67)	11 (73.33)	10 (66.67)	11 (73.33)	64 (71.11)
	High	01(06.67)	02 (13.33)	05 (33.33)	02 (13.33)	04 (26.67)	04 (26.67)	18 (20.00)

*Values in parenthesis shows percentage of samples

Out of thirty two villages, one (Vadichaudha), nine (Sarav, Vedccha, Manekpore, Tavdi, Mahuvar, Simalgam, Sagra, Hansapore and Enthan), six (Sisodara, Nagdhara, Itavala, Ambada, Onchi and Munsad), eight (Gandeva, Khaparia, Rahej, Deshad, Pati, Ambeta, Dhanori and Pathri), four (Peladi Bhairavi, Wadpada, Jamanpada and Chinampada) and four villages (Soldhara, Mogarvadi, Agashi and Kanbhai) respectively from Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *taluka* came under deficient category of available Zn. Thus, farmers of these soils must take intensive care to enhance Zn availability for sustainable rice production through application of Zn containing fertilizers (basal or foliar spray as per University recommendation), organic manures and also by avoidance of cultivating rice after rice crop to arrest further available Zn depletion from soil. This apart, sixteen other villages (Vansda *taluka*: Bhinar, Kavdej and Mindhabari, Jalalpore *taluka*: Abrama, Kadoli and Chinam, Navsari *taluka*: Khergam and Partapore, Gandevi *taluka*: Sarikhurd and Ancheli, Khergam *taluka*: Bhervi, Panaj and Panikhadak, Chikhli *taluka*: Godthal, Vankal and Thala) were found to marginally cross deficiency limit of available Zn for which farmers should also pay attention in order to sustain rice yield and maintain plant available Zn status. Rice growing soils from thirty two villages (9, 8, 6, 4, 4 and 1 village from Jalalpore, Gandevi, Navsari, Khergam, Chikhli and Vansda *taluka*, respectively) recording clearly deficient (< 0.5 ppm) in plant-available Zn indicated that application of Zn (village-specific) either in soil or through foliar spray (in sulphate form or as Zn-Chelates / Na-Zn-EDTA) would be highly needed to overcome Zn deficiency in soil and also to sustain rice yield. This apart, sixteen villages which came under marginally medium (< 0.6 ppm) available Zn status also call for special attention to maintain soil available Zn status in order to sustain rice yield. The present results are in good agreement with the findings of Hazra *et al.* (1987) for acid alluvial rice grown soils of West Bengal, Wijebandra *et al.* (2011) for rice soils of northern dry and hill zones in Karnataka and Kandali *et al.* (2016) for rice grown soils of Assam.

b) Carbonate bound Zn (CO_3-Zn):

CO_3-Zn in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* was in the range from 0.17 to 0.98, 0.10 to 1.07, 0.37 to 0.64, 0.50 to 0.92, 0.23 to 4.52 and 0.16 to 4.60 ppm respectively. However, the same for soils of Navsari district ranged from 0.10 to 4.6 ppm with mean of 0.70 ppm. Barring two villages (Jamanpada and Kukeri respectively in Khergam and Chikhli *taluka* showing exceptionally high CO_3-Zn), CO_3-Zn did not differ appreciably in soils of one *taluka* to another. In case of mean CO_3-Zn at *taluka*-level, the following order was obtained: Jalalpore (0.50 ppm) < Navsari (0.52 ppm) < Vansda (0.53 ppm) < Gandevi (0.72 ppm) < Chikhli (0.93 ppm) < Khergam (0.97 ppm) which indicated that soils of Khergam *taluka* overall possessed the highest CO_3-Zn and Jalalpore exhibited the least one. Kumar *et al.* (2010) reported quite nearer concentrations of CO_3-Zn in some rice soils of Kollegal and Range *talukas* of Chamarajanagar district (Karnataka).

c) Organic bound Zn (Org-Zn):

Org-Zn in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* was recorded to vary from 2.28 to 5.25, 1.10 to 5.98, 1.18 to 5.95, 1.66 to 5.34, 2.28 to 6.68 and 1.83 to 5.88 ppm, respectively with corresponding mean values of 3.41, 3.04, 2.91, 2.92, 4.02 and 3.61 ppm indicating range of Org-Zn differing slightly from one *taluka* to another. However, variation in mean Org-Zn from one *taluka* to another due to inconsistent variation of Org-Zn from one village to another and the mean Org-Zn of different *talukas* were in order: Khergam > Chikhli > Vansda > Jalalpore > Gandevi > Navsari. This fact indicated that soils of Khergam *taluka* with higher Org-Zn pool was enable to provide more plant-available Zn via WSEx-Zn in due course of time, followed by Chikhli, Vansda, Jalalpore, Gandevi and Navsari. However, for entire rice grown soils of Navsari district, Org-Zn varied from 1.1 to as high as 6.68 ppm with the mean of 3.32 ppm. Mean SOC of Khergam, Vansda, Chikhli, Gandevi, Jalalpore and Navsari *taluka* was 9.65, 8.86, 8.49, 5.99, 5.89 and 5.36 g kg^{-1}, respectively and keeping in abeyance to this, Org-Zn in rice soils of Jalalpore, Navsari and Gandevi *taluka* was recorded low over others. Thus, addition of more organic manures (FYM, VC, bio-compost, *etc*.) in these soils would be advantageous to boost Org-Zn status which in turn would release more plant-available Zn in due course of time. Quite similar results were reported by Hazra *et al.* (1987) for acid alluvial rice grown surface soils of Assam, Wijebandra *et al.* (2011) for paddy soil of hill zone (Karnataka), Selvaraj *et al.* (2012) for paddy growing surface soils in of Gangavati *taluka* (Karnataka), Wani *et al.* (2013) for alluvial rice growing soils of Kashmir and Kandali *et al.* (2016) for acid alluvial rice growing surface soils of Assam.

d) Sesqueoxide bound Zn (Ox-Zn):

Ox-Zn in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* was in the range from 0.40 to 1.01, 0.35 to 94, 0.37 to 1.32, 0.19 to 1.02, 0.13 to 0.96 and 0.05 to 0.96 ppm, respectively with corresponding mean values of 0.72, 0.65, 0.71, 0.57, 0.54 and 0.61 ppm, while corresponding values in soils of Navsari district were 0.05 to 1.32 ppm with the mean of 0.63 ppm. All the *talukas* recorded similar range of value. However due to inconsistent variations in Ox-Zn from one village to another within these *talukas,* mean Ox-Zn differed to certain extent from *taluka* to *taluka* with the following order: Khergam <Gandevi < Chikhli < Jalalpore < Navsari < Vansda. The higher quantum of mean Ox-Zn for soils of Navsari and Vansda might be due to more Fe-Al oxides in soils of these *talukas.* In case of Ox-Zn, the mean value of *talukas* followed the reverse trend as that of mean value of Org-Zn which might be due to higher complexation by organic ligands in soils of sufficient organic carbon content under prevailing pH condition and as a result might reduce occlusion of Zn by soil sesquioxides. Results were in good agreement in earlier findings of Selvaraj *et al.* (2012) for rice grown soils of Gandavati *taluka* of Karnataka. In addition, wider range of Ox-Zn was also reported by many scientists such as Kumar *et al.* (2010) for rice soils of Chamarajanagar district (Karnataka), Wijebandra *et al.* (2011) for paddy soil of northern dry and hill zones in Karnataka, Chirwa and Yerokun (2012), Wani *et al.* (2013) and Ramzan *et al.* (2014) for rice fields in Kashmir and well as Kandali *et al.* (2016) for rice growing areas of Assam.

e) Residual Zn (RES-Zn)

RES-Zn otherwise can be looked as a primary Zn storage capacity in primary minerals of soil. RES-Zn in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* was in the range from 12.80 to 27.70, 10.70 to 23.50, 12.00 to 47.50, 10.70 to 56.00, 22.50 to 128.40 and 10.40 to 73.50 ppm, respectively with mean values of 19.27, 18.65, 21.45, 27.47, 55.25 and 32.68 ppm, respectively. Mean RES-Zn in soils of all *talukas* was in following order: Jalalpore < Vansda < Navsari < Gandevi < Chikhli < Khergam indicating higher quantum of Zn held in primary minerals in soils of Khergam *taluka*. Though, RES-Zn would not available in nearer future, yet it has been predicted to be available for remobilization under very drastic conditions after several years. Hence, major soils of Khergam, Chikhli and Gandevi exhibited higher storage capacity of Zn with possible availability in soil for future generations as compared to rest of the *talukas*. Similar results regarding RES-Zn in soils were reported by Chirwa and Yerokun (2012) for soils of Mazabuka, Lusaka and Mpongwe of Zambia.

f) Total Zn (Tot-Zn)

Tot-Zn reflects the total capacity of soils to reserve Zn including a small portion as readily available form (WSEx-Zn), some portion as replenishing source (CO_3-Zn, Org-Zn and Ox-Zn) of readily available in due course of time and major portion as residual form (RES-Zn) is otherwise in most stable form. Tot-Zn in rice grown soils of Vansda, Jalalpore, Navsari, Gandevi, Khergam and Chikhli *talukas* varied from 17.82 to 33.39, 14.41 to 30.43, 14.88 to 51.15, 14.56 to 60.561, 29.52 to 138.41 and 14.28 to 78.72 ppm, respectively with mean values of 24.75, 23.31, 26.25, 32.26, 61.57 and 38.71 ppm, respectively showing the order at *taluka*-level: Jalalpore < Vansda < Navsari < Gandevi < Chikhli < Khergam. In case of Navsari district as a whole, Tot-Zn varied widely from 14.28 to 138.41 ppm with the mean of 34.47 ppm. Amongst *talukas,* Khergam was rich in reserved Zn source and thus possessed higher capacity to release Zn as plant available form in due course of time as compared to others. Similar results were reported by Chirwa and Yerokun (2012) for soils of Mazabuka, Lusaka and Mpongwe of Zambia.

Table 3: Different Zinc fractions in rice growing soils of different *talukas* of Navsari district and the district as a whole

	WSEX-Zn (ppm)	CO_3-Zn (ppm)	Org-Zn (ppm)	Ox-Zn (ppm)	Res-Zn (ppm)	Tot-Zn (ppm)
Vansda *taluka*						
Range	0.25-1.51	0.17-0.98	2.28-5.25	0.40-1.01	12.80-27.70	17.82-33.39
Mean	0.82	0.53	3.41	0.72	19.27	24.75
Jalalpore *taluka*						
Range	0.24-0.85	0.10-1.07	1.10-5.98	0.35-0.94	10.70-23.50	16.71-28.80
Mean	0.47	0.50	3.04	0.65	18.65	23.30
Navsari *taluka*						
Range	0.31-1.05	0.37-0.64	1.18-5.95	0.37-1.32	12.00-47.50	14.8--51.15
Mean	0.65	0.52	2.91	0.71	21.45	26.25
Gandevi *taluka*						
Range	0.20-1.06	0.50-0.92	1.66-5.34	0.19-1.02	10.70-56.00	13.25-64.34
Mean	0.56	0.72	2.92	0.57	27.47	32.24
Khergam *taluka*						
Range	0.15-1.83	0.23-4.52	2.28-6.68	0.13-0.96	22.50-128.40	29.53-138.41
Mean	0.80	0.97	4.02	0.54	55.25	61.57
Chikhli *taluka*						
Range	0.36-1.69	0.16-4.60	1.83-5.88	0.05-0.96	1-0.40-73.50	14.28-78.72
Mean	0.88	0.93	3.61	0.61	32.68	38.71
Navsari district as a whole						
Range	0.15-1.83	0.10-4.60	1.10-6.68	0.05-1.32	10.40-128.40	14.28-138.41
Mean	0.70	0.70	3.32	0.63	29.13	34.47

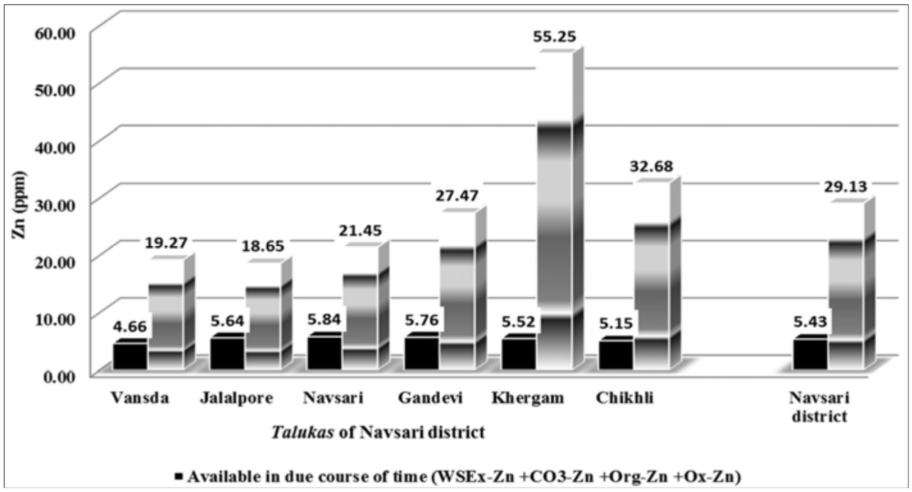

Fig 2: Distribution of potential available Zn in due course of time and non-available Zn in rice grown soils of different *talukas* and Navsari district as a whole

Here, available in due course of time portion included WSEx-Zn, CO_3-Zn. Org-Zn and Ox-Zn, while non-available were the residual fraction of Zn (Fig. 2).

Simple correlations relating different fractions of Zn with some important soil properties in rice growing soils of Navsari district

WSEx-Zn was positively and significantly correlated with SOC and silt +clay, while negatively and significantly correlated with soil EC, soil pH and $CaCO_3$ as depicted in Table 4. A positive and significant correlation was obtained between Org-Zn and WSEx-Zn. Both RES-Zn and Tot-Zn were correlated negatively and significantly with CEC. Tot-Zn was found to increase with the increase in RES-Zn in soils of district level as was evidenced by high correlation coefficient between them. Similar type of correlations between different Zn fractions with soil properties were reported by Wijebandara *et al.* (2011), Ramzan *et al.* (2014) [13] and Kandali *et al.* (2016). [11]

Table 4: Simples correlation relating different fractions of Zn with some important soil properties in rice growing soils of Navsari district (n=90)

	Soil EC	Soil pH	SOC	$CaCO_3$	CEC	Clay	Silt +Clay
WSEx-Zn	-0.355**	-0.447**	0.788***	-0.319**	-0.124	-0.011	0.237*
CO_3-Zn	0.036	0.154	0.121	0.082	-0.097	0.162	0.103
Org-Zn	-0.169	-0.106	0.209	-0.132	-0.163	-0.008	0.005
Ox-Zn	0.126	0.102	-0.195	0.121	0.074	-0.029	-0.090
RES-Zn	-0.168	-0.190	0.059	0.166	-0.252*	0.036	-0.049
Tot-Zn	-0.170	-0.201	0.082	0.154	-0.257*	0.043	-0.037
* & ** indicates correlation is significant at the 0.05 and 0.01 level, respectively (2-tailed).							

Step down multiple regressions relating WSEx-Zn with some important soil properties

As soluble portion of Zn (WSEx-Zn/ DTPA-Zn) is the most important fraction from which requirement of crops is largely satisfied, step-down multiple regression equations relating WSEx-Zn with physico-chemical properties worked to find out factors that contributed to Zn availability to plants. It was indicated that single parameter (soil EC) had 12.62 per cent predictability of available Zn (WSEx-Zn). However, other soil properties (soil pH, SOC, $CaCO_3$, CEC, clay and silt +clay in chronological order) increased that contribution up to 64.61 per cent in predicting available Zn. SOC had the greater effect on the predictability of available Zn as it increased the contribution from 22.62 to 62.63 per cent. Wijebandara *et al.* (2011), Ramzan *et al.* (2014) [13] and Kandali *et al.* (2016) [11] obtained respectively 59.8, 43.6 and 38.80 per cent variation of WSEx-Zn due to soil pH, SOC, $CaCO_3$ content, Fe_2O_3content, clay content collectively, soil pH, SOC, $CaCO_3$, CEC, clay content together and soil properties, respectively.

Table 5: Multiple regression equations relating WSEx-Zn with physico-chemical properties in rice growing soils of Navsari district

Step-down multiple regression	R^2 X 100
Y_1= -0.6577 -0.0911X_1 +0.0087X_2 + 0.6975X_3 +0.0049X_4 -0.0035X_5 +0.0057X_6 +0.0078X_7	64.61
Y_1= 0.1679 -0.0668X_1 -0.0141X_2 + 0.7072X_3 +0.0016X_4 -0.0028X_5 +0.0051X_6	63.29
Y_1= 0.4476 -0.0561X_1 -0.0227X_2 + 0.7081X_3 +0.0039X_4 -0.0020X_5	62.95
Y_1= 0.3711 -0.0687X_1 -0.0260X_2 + 0.7088X_3 + 0.0061X_4	62.69
Y_1= 0.3380 -0.0627X_1 -0.0184X_2 + 0.7049X_3	62.63
Y_1= 2.5941 -0.1691X_1 -0.2584X_2	22.54
Y_1= 0.8649 -0.3310X_1	12.62

Y_1=WSEx-Zn, X_1 =soil EC, X_2 =soil pH, X_3= SOC, X_4= $CaCO_3$ content, X_5 =CEC, X_6= clay content, X_7 =silt +clay content

Conclusion

Fractional distribution of Zn in ninety rice growing soils of Navsari district depicted that on an average 2.02, 13.48 and 84.50 per cent of total Zn were under the category of readily available (WSEx-Zn / DTPA-Zn), available in due course of time (CO_3-Zn, Org-Zn and Ox-Zn) and non-available (RES-Zn) to plant, respectively showing the following order for different fractions: residual Zn (RES-Zn) > organically bound Zn (Org-Zn) > extractable Zn (WSEx-Zn) > carbonate bound Zn (CO_3-Zn) > sesquioxides bound Zn (Ox-Zn). However, the order in soils of four *talukas* (Vansda, Jalalpore, Navsari and Gandevi) differed slightl*y.* The overall results clearly indicated that application of Zn (village-specific) either in soil or through foliar spray would be highly needed to overcome Zn deficiency in soil and also to sustain rice yield. Further, farmers should avoid practice of rice-rice sequence continuously to avert more depletion of soil available Zn.

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