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# Distribution of different fractions of zinc and their relation to soil properties in paddy growing soils of Panchkula district in Haryana, India

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**Abstract**
Fifteen surface (0-20 cm) soil samples from the farmer's field were collected from different selected sites of Panchkula district in the year 2017-2018. The soil samples were handled for laboratory analysis. Fractionation of zinc in soil samples was carried out with standard procedure. The results showed that the distribution of zinc in soils under paddy land use in Panchkula district. The exchangeable zinc fractions in these soils were in the range of 0.13 to 0.96 mg $kg^{-1}$. Organic matter bound (OM-Zn), carbonate bound (CA-Zn), iron and aluminium oxides bound (Fe&MnOX-Zn) and residual (RES-Zn) zinc fractions were in the range of 0.81 to 3.17, 0.59 to 3.01, 7.95 to 13.35 and 32.82 to 57.17 mg $kg^{-1}$, respectively. Among various fractions studied, exchangeable zinc was low in all the soils when compared to other fractions; still it is very important from the plant availability point of view. Residual form of zinc dominated when compared to exchangeable zinc, organic bound zinc, carbonate bound zinc and crystalline iron-manganese oxide bound zinc fractions. However, the order of preponderance of zinc fractions remained same viz., exchangeable zinc < organic zinc < carbonate zinc < crystalline iron and manganese oxide bound zinc < residual zinc in selected samples.

**Keywords:** Crystalline iron-manganese oxide bound zinc, exchangeable iron, zinc fractions, residual bound zinc, organic bound zinc and carbonate bound zinc

## Introduction
Micronutrients are essential minerals that are needed in small amounts for various physiological functions of the human body. Because the body itself cannot make the micronutrients or synthesize it in adequate quantities, humans need to obtain micronutrients from foods. Cereal grains are the most important dietary source of micronutrients in many developing countries. Micronutrients concentration and bioavailability in cereal grains is generally low. Cereal crops play an important role in satisfying daily calorie intake in developing world, but are inherently very low in Zn concentrations in grain, particularly when grown on Zn- deficient soils. The rice-wheat cropping system (RWCS) may be age-old practice but its present worth was triggered by the development of high yielding varieties of both the crops.
The transformation of Zn from one chemical form to another with changing soil properties can be studied by using fractionation techniques. The understanding of the distribution of micronutrients in different fractions is imperative to appreciate their retention in soils and release to plants. Therefore, speciation analysis is very important to separate and to identify specific or binding forms of metals and allows assessing the availability and mobility of metals in order to understand their chemical behavior. The mobility, transport and partitioning of micronutrient cations in soil are dependent upon various soil chemical properties like soil pH, the type and content of clay minerals, contents of aluminum (Al) and iron (Fe) oxides and (oxy) hydroxides carbonates and organic matter (OM) (Keren and Bingham, 1985) [1]. Therefore, an attempt was made to study the distribution of different fractions of Zinc and their relation to soil properties in paddy growing soils in selected sites of Panchkula district in Haryana, India.

## Materials and Methods
**Location of the experimental site:** Fifteen surface (0-20 cm) soil samples each from the farmers paddy field collected from different selected site of Panchkula district in Haryana in the year 2017-2018. The latitude and longitude of soil sampling sites are given the Table 1.

**Collection and analysis of soil samples:** The surface (0-20 cm) soil samples from each selected site were taken using a 5 cm diameter auger, after harvest of paddy crop these soil samples mixed thoroughly, air dried in shade and crushed to pass through 2 mm sieve and stored in sealed polythene covers for analysis.

The soil samples were used for zinc and their fractions study in paddy ecosystem. The soils were analyzed for pH, EC, CEC, texture and Organic carbon, $CaCO_3$, Available NPK with standard methods. Fractionation of soil zinc was carried out with standard procedure. DTPA-extractable Zn was determined from 1:2 soil-extractant ratio using DTPA-TEA buffer (0.005 M DTPA+ 0.001 M $CaCl_2$ + 0.1M TEA, pH 7.3) and concentration of Zn was measured on an atomic absorption spectrophotometer Varian AA 240FS by Lindsay and Norvell, (1978) [2].

**Table 1**: Latitude and longitude of various soil sampling sites

| Site No. | Latitude | Longitude |
|---|---|---|
| 1. | 30.60958 | 76.96627 |
| 2. | 30.61785 | 76.97347 |
| 3. | 30.63872 | 76.99732 |
| 4. | 30.64084 | 77.01711 |
| 5. | 30.61471 | 77.01571 |
| 6. | 30.61442 | 77.02427 |
| 7. | 30.61816 | 77.04106 |
| 8. | 30.6328 | 77.0405 |
| 9. | 30.622 | 77.03058 |
| 10. | 30.59536 | 77.00478 |
| 11. | 30.5993 | 77.9887 |
| 12. | 30.59295 | 76.97767 |
| 13. | 30.58714 | 76.96891 |
| 14. | 30.56665 | 76.96181 |
| 15. | 30.56048 | 76.94811 |

**Sequential extraction of soil samples for different fractions:** The processed soil samples were used to fractionate Zn into following chemical fractions as per sequential procedure described below.

| | | |
|---|---|---|
| | | Soil (1 g) |
| | | ↓ |
| Exchangeable Zn | ←――――――― | 8 ml 1 M NaOAc (Shake 1 hrs.) |
| | | ↓ |
| | | Soil |
| | | ↓ |
| Carbonate bounded Zn | ←――――――― | 8 ml 1 M NaOAc (pH 5.0, $CH_3COOH$) |
| | | (Shake 5 hrs.) |
| | | ↓ |
| | | Soil |
| | | ↓ |
| | | 3 ml 0.02 M $HNO_3$ + 5 ml $H_2O_2$ (pH 2) |
| Organically bounded Zn | ←――――――― | (3 hrs in boiling water bath. Stir occasionally, |
| | | Repeat extraction) |
| | | ↓ |
| | | Soil |
| | | ↓ |
| Fe-Mn bounded Zn | ←――――――― | 20 ml 0.04 M $NH_2OH.HCl$ (25 % HOAc) |
| | | (Shake 30 min.) |
| | | ↓ |
| | | Soil |
| Residual bounded Zn | ←――――――― | Conc., HF, conc. $HClO_4$ and conc. HCl in sequence |

**Fig: 1** Sequential fractionation scheme for partitioning Zn in soils (Tessier *et al.*, 1979)

## Results and Discussion
### Physico-chemical properties of soils
### Particle size distribution
Fifteen soil samples (0–20 cm), one each collected from Panchkula (North district of Haryana) under well established rice wheat cropping system were used in the present investigation. The data presented in Table 3 indicates the relative proportion of sand, silt and clay content in Panchkula of Haryana. The texture of Panchkula is loamy to loamy sand. The soil texture is governed more by the type of parent material from which the soils have developed.

### Chemical properties of soil
The chemical properties such as soil pH, electrical conductivity, CEC, $CaCO_3$ content, organic carbon content and available NPK of soils are presented in Table 2,3.

The results revealed that Panchkula soils were alkaline in nature with pH values ranging from 7.6 to 8.1, suggesting soils are neutral in soil reaction, which may be due to difference in annual rainfall which caused differential movement of salts to lower layers. The electrical conductivity of Panchkula soils ranged from 0.10 to 0.65 $dSm^{-1}$ at 25°C, respectively and was in normal range with respect to soluble salt concentration. The higher values in surface soils are indicative of the accumulation of salts in the root zone due to fertigation of the crop continuously. The cation exchange capacity (CEC) of Panchkula soils ranged from 5.11 to 14.95 $cmol(p^+)kg^{-1}$. Singhal and Rattan, (1995) [5] reported a higher range of cation exchange capacity in some soils, relating it with their corresponding high levels of organic matter and clay. The $CaCO_3$ content varied traces to 1.9. Organic carbon content in Panchkula soils ranged from 0.22 to 0.52 per cent and was low to medium in organic carbon content. The available nitrogen in Panchkula soils ranged from 96.6 to 273.0 kg $ha^{-1}$ and was low in available nitrogen in soil. The low levels of N may be due to the cultivation of high nutrient requirement crops. The available phosphorus in Panchkula soils ranged from 4.0 to 19.0 kg $ha^{-1}$and was low to medium in available phosphorus in soil. The available potassium in Panchkula soils ranged from 94.38 to 320.6 kg $ha^{-1}$and was medium to high in available potassium in soil. Similar results were also reported by Sharma *et al.* (2013) [3].

**Table 2**: Chemical properties of soils of sampling sites under rice wheat cropping system

| Site No. | Soil : Solution (1:2) | | CEC [$cmol(p^+)kg^{-1}$] | $CaCO_3$ (%) | OC (%) |
|---|---|---|---|---|---|
| | pH | EC (ds $m^{-1}$) | | | |
| 1. | 7.6 | 0.24 | 13.26 | Tr | 0.34 |
| 2. | 7.8 | 0.18 | 14.40 | Tr | 0.36 |
| 3. | 7.8 | 0.10 | 14.95 | Tr | 0.33 |
| 4. | 7.7 | 0.31 | 7.34 | 1.6 | 0.52 |
| 5. | 7.9 | 0.12 | 5.11 | Tr | 0.43 |
| 6. | 7.8 | 0.15 | 9.02 | Tr | 0.25 |
| 7. | 8.0 | 0.14 | 9.29 | Tr | 0.27 |
| 8. | 7.8 | 0.15 | 4.29 | Tr | 0.31 |
| 9. | 7.9 | 0.19 | 9.46 | Tr | 0.43 |
| 10. | 7.6 | 0.13 | 10.11 | Tr | 0.22 |
| 11. | 7.6 | 0.14 | 10.49 | Tr | 0.34 |
| 12. | 7.9 | 0.46 | 12.07 | 1.9 | 0.42 |
| 13. | 7.8 | 0.65 | 11.09 | 1.4 | 0.36 |
| 14. | 8.0 | 0.14 | 11.63 | Tr | 0.37 |
| 15. | 8.1 | 0.13 | 11.58 | Tr | 0.30 |

**Table 3**: Physico-chemical properties of soils of sampling under rice wheat cropping system

| Site No. | Particle size (%) | | | Texture | Available nutrient (kg $ha^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | Sand | Silt | Clay | | N | P | K |
| 1. | 49.5 | 25.3 | 25.2 | L | 197.4 | 17.4 | 94.38 |
| 2. | 39.2 | 34.5 | 26.3 | L | 225.4 | 16.4 | 141.5 |
| 3. | 37.3 | 33.4 | 29.3 | L | 126.0 | 19.0 | 225.0 |
| 4. | 80.3 | 15.2 | 4.5 | LS | 134.4 | 13.0 | 225.0 |
| 5. | 85.4 | 11.3 | 3.3 | LS | 128.8 | 13.4 | 185.1 |
| 6. | 84.1 | 11.5 | 4.4 | LS | 124.6 | 13.0 | 225.0 |
| 7. | 83.2 | 11.5 | 5.3 | LS | 96.6 | 13.6 | 258.9 |
| 8. | 81.4 | 15.1 | 3.5 | LS | 203.0 | 9.6 | 296.4 |
| 9. | 81.6 | 13.2 | 5.2 | LS | 273.0 | 13.4 | 309.7 |
| 10. | 83.3 | 11.3 | 5.4 | LS | 215.6 | 9.6 | 317.0 |
| 11. | 80.2 | 10.3 | 9.5 | LS | 231.0 | 11.6 | 294.0 |
| 12. | 63.4 | 21.2 | 15.4 | SL | 246.4 | 13.8 | 320.6 |
| 13. | 66.5 | 21.2 | 12.3 | SL | 226.8 | 9.6 | 212.9 |
| 14. | 66.3 | 20.3 | 13.4 | SL | 231.0 | 13.6 | 202.0 |
| 15. | 66.2 | 21.3 | 12.5 | SL | 247.8 | 4.0 | 237.1 |

Tr = Traces; SL = Sandy loam; L = Loamy; CL = Clay loam; LS = Loamy sand

### Distribution of DTPA-extractable zinc status and zinc fractions in soil
The results of available (DTPA-extractable) zinc content of soils under paddy land use Panchkula are presented in Table 3. The results indicate that available (DTPA-extractable) zinc content in the soils of Panchkula ranged from 0.30 to 1.71mg $kg^{-1}$, respectively. A critical level of DTPA-extractable Zn 0.60 mg $kg^{-1}$ used for delineating the Zn deficient soils from the non deficient ones.

Results presented in Table 3 indicate the distribution of zinc in soils under paddy land use in Panchkula district. The exchangeable zinc fractions in these soils were in the range of 0.13 to 0.96 mg $kg^{-1}$. Organic matter bound (OM-Zn), carbonate bound (CA-Zn), iron and manganese oxides bound (Fe&MnOX-Zn) and residual (RES-Zn) zinc fractions were in the range of 0.81 to 3.17, 0.59 to 3.01, 7.95 to 13.35 and 32.82 to 57.17 mg $kg^{-1}$, respectively. The medium to high amounts of zinc in exchangeable forms may be due to application of $ZnSO_4$ of the soils which ultimately affects the solubility of zinc (Wijebandara *et al.*, 2011 and Singh *et al.*, 1997) [7, 4].

**Table 3**: DTPA extractable Zn and Zn fractions (mg kg$^{-1}$) in paddy growing soils under rice wheat cropping system

| Site No. | DTPA- Zn (mg kg$^{-1}$) | Fractions (mg kg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ex-Zn | OM-Zn | $CaCO_3$-Zn | Fe MnOX- Zn | Res- Zn | Sum |
| 1. | 0.69 | 0.34 | 2.07 | 1.35 | 10.04 | 47.37 | 63.25 |
| 2. | 0.65 | 0.38 | 2.24 | 1.40 | 8.02 | 46.09 | 60.21 |
| 3. | 0.31 | 0.14 | 1.81 | 0.67 | 9.21 | 38.28 | 52.19 |
| 4. | 1.71 | 0.96 | 3.17 | 2.03 | 7.95 | 57.17 | 73.36 |
| 5. | 1.08 | 0.64 | 2.80 | 1.50 | 11.85 | 34.28 | 53.15 |
| 6. | 0.46 | 0.21 | 1.02 | 0.84 | 12.05 | 36.16 | 52.36 |
| 7. | 0.30 | 0.13 | 1.17 | 0.59 | 9.80 | 33.21 | 46.98 |
| 8. | 0.87 | 0.40 | 1.60 | 1.36 | 9.55 | 42.64 | 57.63 |
| 9. | 1.28 | 0.76 | 2.68 | 1.46 | 10.52 | 52.61 | 70.11 |
| 10. | 0.33 | 0.15 | 0.81 | 0.65 | 8.35 | 34.28 | 46.32 |
| 11. | 1.31 | 0.72 | 1.99 | 1.55 | 12.25 | 38.27 | 56.86 |
| 12. | 1.29 | 0.70 | 2.52 | 2.51 | 13.35 | 39.72 | 60.88 |
| 13. | 1.28 | 0.66 | 2.29 | 3.01 | 8.06 | 48.30 | 64.40 |
| 14. | 1.39 | 0.74 | 2.37 | 1.70 | 11.96 | 46.81 | 65.66 |
| 15. | 0.71 | 0.41 | 1.39 | 1.52 | 12.48 | 32.82 | 50.70 |

**Relationship between zinc fractions and soil properties**

The results of correlation between different zinc fractions and soil properties in soils under paddy land use in north district of Haryana are presented in Table 4.

Exchangable zinc correlated significantly and positively with OC (r=0.524**) and CEC (r=0.217$^{**}$). Non-significant and negatively with clay, EC and pH of soil. Organic matter bound zinc correlated significantly and positively with organic carbon (r=-0.873**), clay (r=-0.278$^{**}$) and CEC (r=-0.282$^{**}$) and non-significant and positive correlation was recorded with pH, EC and $CaCO_3$.

Significant and positive correlation was recorded between carbonate bound zinc and $CaCO_3$ content (r=0.952$^{**}$) and EC (r=0.512$^{**}$), whereas non-significant and positive correlation was noticed with organic carbon, pH and negative with CEC.

Iron and manganese oxides bound zinc correlated significantly and positively with organic carbon (r=0.171$^{*}$) and CEC (r=0.180$^{*}$).

**Table 4**: Simple linear correlation coefficient (r) between Zn fractions and soil properties

| Zn fractions | pH | EC | CEC | Clay | $CaCO_3$ | OC |
|---|---|---|---|---|---|---|
| Ex-Zn | -0.091$^{NS}$ | -0.014$^{NS}$ | 0.217$^{**}$ | -0.150$^{NS}$ | 0.169$^{*}$ | 0.524$^{**}$ |
| OM- Zn | 0.029$^{NS}$ | 0.148$^{NS}$ | 0.282$^{**}$ | 0.278$^{**}$ | 0.166$^{*}$ | 0.873$^{**}$ |
| $CaCO_3$-Zn | 0.125$^{NS}$ | 0.512$^{**}$ | -0.017$^{NS}$ | 0.092$^{NS}$ | 0.952$^{**}$ | 0.116$^{NS}$ |
| Fe MnOX- Zn | 0.042$^{NS}$ | -0.028$^{NS}$ | 0.180$^{*}$ | 0.139$^{NS}$ | -0.066$^{NS}$ | 0.171$^{*}$ |
| Res- Zn | -0.102$^{NS}$ | 0.125$^{NS}$ | 0.227$^{**}$ | 0.255$^{**}$ | 0.107$^{NS}$ | 0.544$^{**}$ |

## Conclusion

Based on the present study it is concluded that different fractions of soil zinc are in dynamic equilibrium with each other. The content of different zinc fractions differed between soils of selected site in Panchkula. However, the order of preponderance of zinc fractions remained same viz., exchangeable zinc < organic zinc < carbonate zinc < crystalline iron and manganese oxide bound zinc < residual zinc in selected samples. Depletion of exchangeable iron and complexed forms of zinc occurred with a build-up of residual zinc, crystalline iron and manganese oxide bound zinc occurred.

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