Journal of Pharmacognosy and Phytochemistry

Available online at www.phytojournal.com

E-ISSN: 2278-4136
P-ISSN: 2349-8234
JPP 2019; 8(5): 1342-1347
Received: 13-07-2019
Accepted: 15-08-2019

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Distribution of zinc fractions and their relationship with soil properties in different soil series of Haryana

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Abstract
A laboratory experiment was conducted to determine the distribution of Zinc fractions and their relationship with soil properties in different soil series of Haryana. Surface soil samples (0-15 cm) were collected from each soil series using Global Positioning System (GPS). The soil samples were processed and analyzed for the determination of total Zn and zinc fractions (exchangeable, organic bound, calcium carbonate bound and residual). Zinc fractions were analyzed by sequential extraction procedure. Results showed that total amount of the Zn ranged from 36.02 to 72.45 mg kg^{-1} in all the soil series. The amount Ex- Zn, OM- Zn and $CaCO_3$- Zn, comprised 0.4-1.9, 2.1-7.7 and 3.5-17.6% of total Zn, respectively. The highest fraction of the total Zn (74.0-90.4%) was present in the residual fraction. The residual fraction varied from 30.68 to 50.02 mg kg^{-1} with a mean value of 39.30 mg kg^{-1} in soil series of Aeolian Plain while it ranged from 27.23 to 59.75 mg kg^{-1} with a mean value of 42.48 mg kg^{-1} in soil series of Alluvium Plain. The Sohna soil series of Aravali Hills had 39.60 mg kg^{-1} residual Zn. Different Zn fractions followed the order: Res- > $CaCO_3$- >OM- > Ex- in Aeolian Plain and Alluvial Plain while in Aravali Hills soils order: Res- > $CaCO_3$- ~ OM- > Ex- was followed. Results reflected that soil properties influence the distribution of different Zn fractions in soils.

Keywords: Sequential extraction, organic bound, calcium carbonate bound, residual

Introduction

Zinc is required by crop plants in very small amounts. It is required as a structural component of a large number of proteins such as transcription factors and metallo-enzymes (Figueiredo *et al.*, 2012) [4]. It influences the quality and yield of crops (Chidanandappa *et al.*, 2008) [3] and plays an important role in auxin metabolism, preferential accumulation of chlorophyll, protein synthesis and starch metabolism.

Zinc bioavailability 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 Zn uptake by crops (Soltani *et al*., 2015) [13]. For a better understanding, total soil Zn can be broadly classified into five mechanistic fractions using sequential or batch fractionation schemes (Saffari *et al.*, 2009) [10]. These fractions include water soluble pool, exchangeable pool with ions bound to soil particles by electrical charges, organically bound pool consisting of ions adsorbed, chelated or complexed with organic ligands, pool of zinc sorbed non-exchangeably onto clay minerals and insoluble metallic oxides and pool of weathering primary minerals (Alloway, 2008) [1]. These fractions provide broad information on the biological, geological and chemical processes occurring in a soil and are useful for predicting the availability of Zn for plant uptake. Zinc in water-soluble and exchangeable fractions is readily bio-available, whereas in the residual fraction it is tightly bound and unlikely to be released easily under normal conditions. The extent to which each fraction is present and transformation between fractions is influenced by soil properties such as pH, cation exchange capacity, texture and soil organic matter (Ramzan *et al*., 2014) [9], Thus, chemistry and effect of aforementioned properties appear to be of major importance in determining the concentration of Zn fractions (Naik and Das, 2007) [5].

The available Zn status in soils of Haryana has been reported by many workers. However, the data available are hardly sufficient to bring out the variability inherent in soils, it is only possible to draw conclusion if the sampling with soil series as the basis is considered. The study of various fractions of Zn present in surface soils of different series of Haryana and conditions under which they become available to plants is pre-requisite in assessing its availability to plants. Knowledge on distribution of zinc fractions in soils and various soil properties influencing its availability might prove to be the best approach for obtaining reliable information about the need of zinc.

Therefore, the major objective of this study was to determine zinc fractionation of soils from different soil series and their relationships with some soil properties.

Material and Methods

Location

The study area under different soil series of Haryana state is located between 27° 39' to 30º 35' N latitudes and between 74º 28' to 77 º 36' E longitudes with an altitude ranging between 200 meters to 1200 meters above sea level covering a total geographical area of 4.42 million hectare. The area under various soil series in Haryana is characterized by light in texture, moderate to high in pH and low to medium in organic content. These soils were also studied in the field in detailed description and classified using soil taxonomical classification procedure. Majority of the soils of eighteen soil series fall under alluvial plain followed by Aeolian plain and only one type of soil series falls under Aravali hills soil. These soil series were selected based on the physical and chemical properties of the soils. The details on location of soil samples collected from different soil series of Haryana are given in Table 1.

Table 1: Details of location of soil samples collected from different soil series of Haryana

S. No.	Name of Soil Series	Latitude	Longitude	Details
Soils of Aeolian Plain				
1.	Balsamand	29°05'293" N	74°44'560" E	Near Rajasthan border on Balsamand-Bhadra road, district Hisar
2.	Isarwal	29°06'393" N	75°46'436" E	CCS HAU Dry Land Research Farm, Balsamand, district Hisar
3.	Rawalwas	29°08'716" N	75°58'162" E	1 km before village Rawalwas on Hisar-Balsamand road, district Hisar
4.	Nimriwali	28°89'029" N	75°89'545" E	Near Tosham by pass, district Bhiwani
5.	Atela	28°59'239" N	76°11'575" E	1 km from Barsana towards Loharu on Dadri-Loharu road, district Bhiwani
6.	Khoh	28°35'453" N	76°89'525" E	After crossing Manesar village, left towards Kasan village, district Gurugaon
Soils of Alluvial Plain				
7.	Barwala	29°33'389" N	75°90'884" E	3 km from Barwala towards south on Barwala-Hansi road, district Hisar
8.	Ladwa	29°15'036" N	75°67'844" E	Field No.63/16, CCS HAU Research Farm, district Hisar
9.	Lukhi	28°32'010" N	76°79'572" E	East of Pataudi-Gurgaon road, village Uncha Majra, district Gurugaon
10.	Nai	27°84'770" N	77°26'318" E	2 km from village Singar near Punhana block, district Mewat
11.	Uchani	29°72'991" N	76°98'333" E	Field No. 67, CCS HAU Research Farm, Uchani, district Karnal
12.	Kaul	29°85'756" N	76°65'667" E	Field No. 3, Block-B, CCS HAU Research Farm, Kaul, district Kaithal
13.	Ujina	28°04'991" N	77°08'187" E	Nuh to Hodal road, village Ujina, district Gurugaon
14.	Narnaund	29°20'993" N	76°10'750" E	4 km from Narnaund on Narnaund-Hansi road, district Hisar
15.	Berpura	30°43'978" N	76°98'413" E	Shahzadpur-Ambala road, left towards Berpura village, district Ambala
16.	ZarifaViran	29°70'926" N	76°94'584" E	After crossing CSSRI, about 1.5 km from village Gudha, district Karnal
17.	Shahzadpur	30°49'729" N	77°14'342" E	After crossing village Kularpur, 0.5 km towards Tokkas-Gurudawara road, district Ambala
Soils of Aravali Hills				
18.	Sohna	28°22'823" N	77°01'715" E	About 10 km from Sohna town on Sohna–Rewari road, district Gurugaon

Soil series and characteristics: It was found that there are 18 soil series in Haryana. The name of the 18 soil series and their characteristics are mentioned below:

1. **Balsamand Series**

The Balsamand series is a member of mixed, hyperthermic family of Typic Torripsamments. Balsamand soils have yellowish brown, mildly alkaline sandy A horizon and dark yellowish brown to brown, mildly alkaline sandy C horizon.

2. **Isarwal Series**

The Isarwal series is a member of mixed, hyperthermic family of Typic Torripsamments. Isarawal soils have yellowish brown, loamy sand, moderately alkaline A horizon and brown, loamy fine sand, moderately alkaline C horizon.

3. **Rawalwas Series**

The Rawalwas series is a member of coarse loamy, mixed, hyperthermic family of Typic Paleorthids. Rawalwas soils have brown, mildly alkaline, loamy sand A horizon; dark yellowish brown to yellowish brown, mildly alkaline; loamy sand to sandy loam B horizon and yellowish brown to light olive brown loamy C horizon. The B2 horizon has hard calcic layer.

4. **Nimriwali Series**

The Nimriwali series is a member of coarse loamy, mixed, hyperthermic family of Typic Camborthids. Soils have yellowish brown mildly alkaline, loamy sand A horizon, brown to dark brown, moderately alkaline, sandy loam, B horizon, 'C' horizon are dark yellowish brown, moderately alkaline, sandy loam and calcareous.

5. **Atela Series**

The Atela series is a member of mixed, hyperthermic family of Aridic Ustipsamments. Atela soils have dark yellowish brown to yellowish brown, loamy sand and mildly alkaline A horizon and dark yellowish brown, loamy sand and mildly alkaline C horizon.

6. **Khoh Series**

The Khoh series is a member of mixed, hyperthermic family of Typic Ustipsamments. Typically, Khoh soils have brownish yellow to yellowish brown, moderately alkaline, loamy sand A horizon and brownish yellow to yellowish brown, moderately alkaline, loamy sand C horizon.

7. **Barwala Series**

The Barwala series is a member of mixed, hyperthermic, coarse loamy, non-calcareous family of Aridic Ustochrepts. These soils have yellowish brown, loamy fine sand, moderately alkaline A horizon and dark yellowish brown, sandy loam to loam moderately alkaline B horizon.

8. **Ladwa Series**

The Ladwa series is a member of fine loamy, mixed, hyperthermic family of Aridic Ustochrepts. Ladwa soils have yellowish brown, mildly alkaline, sandy loam to loam A horizon, yellowish brown to dark yellowish brown, mildly alkaline clay loam B horizon.

9. Lukhi Series

The Lukhi series is a member of coarse loamy, mixed, hyperthermic, family of Typic Ustochrepts. Typically, Lukhi soils have dark yellowish brown to dark brown, moderately alkaline, sandy loam A horizon and dark brown, moderately to strongly alkaline, sandy loam B horizon.

10. Nai Series

The Nai series is a member of coarse loamy, mixed, hyperthermic, family of Typic Ustorthents. Typically, Nai soils are brown to yellowish brown, moderately alkaline, loamy fine sand A horizon and grayish brown to light yellowish brown, moderately alkaline, sandy loam C horizon.

11. Uchani Series

The Uchani series is a member of fine loamy, mixed, hyperthermic, and family of Typic Ustochrepts. These soils have dark brown, mildly alkaline, loam A horizon, dark brown, mildly alkaline, loam to clay loam B horizon and dark yellowish brown, mildly alkaline, silty clay loam C horizon.

12. Kaul Series

The Kaul series is a member of fine, mixed, hyperthermic, family of Aquic-Vertic Ustochrepts. These soils have dark brown, loam, moderately alkaline A horizon and dark gray brown to very dark gray brown, clay loam, moderately alkaline B horizon.

13. Ujina Series

The Ujina series is a member of fine, calcareous, mixed, hyperthermic, family of Aeric Haplaquepts. These soils have grayish brown to dark grayish brown, moderately alkaline, clay loam A horizon and dark gray to very dark gray with dark brown mottles, alkaline, clay loam B horizon. The lithlogically separate C horizon is light yellowish brown with dark brown mottles, strongly alkaline, loam and soft Fe-Mn concretions.

14. Narnaund Series

The Narnaund series is a member of coarse loamy (saline-alkali), mixed, hyperthermic, family of Natric Ustochrepts. Narnaund soils have light olive brown to light yellowish brown, very strongly saline-alkali, sandy loam A horizon and yellowish brown, very strongly alkali and moderately saline, loam to silt loam B horizon. The C horizon is brown, strongly alkali, silt loam.

15. Berpura Series

The Berpura series is a member of fine loamy, mixed, hyperthermic, family of Udic Ustochrepts. Typically, Berpura soils have pale brown to dark yellowish brown, moderately alkaline, loam A horizon and dark yellowish brown to brown, mildly to moderately alkaline, clay loam B horizon.

16. Zarifa Viran series

The Zarifa Viran series is a member of fine silty, mixed, hyperthermic, family of Typic Natrustalfs. Typically, Zarifa Viran soils have pale yellow to yellowish brown, very strongly alkaline, loam to clay loam A horizon, olive brown to light olive brown, very strongly alkaline, loam to clay loam B horizon and light olive brown, very strongly alkaline, loam C horizon.

17. Shahzadapur Series

The Shahzadapur series is a member of fine loamy, mixed, hyperthermic, family of Udic Ustochrepts. Typically, Shahzadpur soils have yellowish brown to dark yellowish brown, neutral, loamy fine sand A horizon and yellowish brown to dark brown, slightly acidic to neutral, sandy loam to sandy clay loam B horizon underlain by brown to dark brown, slightly acidic, sandy loan C horizon.

18. Sohna Series

The Sohna series is a member of loamy skeletal, mixed, hyperthermic, cancerous family of Ruptic-Lithic Ustorthents. Sohna soils have known to yellowish brown, mildly alkaline, loamy sand A horizon; brown to dark brown, mildly alkaline loam AC horizon and dark brown bed rock (Aravali hill) C horizon.

Collection and processing of soil samples

In order to assess the Zinc fractions, surface soil samples (0-15 cm) representing all the eighteen soil series of Haryana were collected using Global Positioning System (GPS). Location of the soil sample sites (X, Y coordinates) was recorded. In the laboratory, the soils were processed by drying at ambient temperature and sieving through 2mm aperture stainless sieve. Air-dried samples <2 mm were stored in polythene bags for subsequent analysis.

Soil analysis

These processed soil samples were used for the determination of total Zn and zinc fractions (exchangeable, organic bound, calcium carbonate bound and residual) in the soil. Zinc fractions were analyzed by sequential extraction procedure out lined by Tessier *et al.* (1979) [15]. Total Zn (%) was analyzed by Hydrofluoric-perchloric acid mixture as prescribed by Page *et al.* (1982) [7]. Zn content in the extract was estimated using Atomic Absorption Spectrophotometer (Varian-Spectra AA-240 FS).

Statistical analysis

Data obtained from all the observation were statistically analyzed. The relationship between relevant soil properties and Zn fractions was carried out and the correlation coefficients were computed as per Snedecor and Cochran (1967) [12] by using the formula:

$$r = \sqrt{\frac{SP(xy)}{SS(x),SS(y)}}$$

Where,
r = Correlation coefficient
SP (xy) = Sum product of x, y variables
SS (x) = Sum of square of x variable
SS (y) = Sum of square of y variable.

Result and Discussion

In the studied soil profiles (Aeolian, Alluvial and Aravali Hills), the results of the fractions of zinc in the surface soils (0-15 cm) is presented in Table 2 and their mean percent distribution is shown in Fig. 1.

Distribution of zinc fractions

Amounts of Zn in soil fractions and percent distribution of 18 soils are summarized in Table 2. Total Zn content varied from 36.02-72.45 mg kg^{-1} among various soil series of Haryana.

The total Zn content varied from 36.02-57.15 mg kg^{-1} with a mean value of 45.55 mg kg^{-1} in soil series of Aeolian Plain while it ranged from 36.78-72.45 mg kg^{-1} with an average value of 50.68 mg kg^{-1} in Alluvial Plain soil series. In soil series of Aravali Hills, the total Zn content was 48.25 mg kg^{-1}. Total zinc content of soils depends on the parent material. Although, total Zn content is considered as a poor indicator of zinc supplying capacity of soil for long term management practices in crop cultivation. Most of the total Zn (74.0-90.4%) was present in the residual fraction. The residual fraction varied from 30.68 to 50.02 mg kg^{-1} with a mean value of 39.30 mg kg^{-1} in soil series of Aeolian Plain while it ranged from 27.23 to 59.75 mg kg^{-1} with a mean value of 42.48 mg kg^{-1} in soil series of Alluvium Plain. The Sohna soil series of Aravali Hills had 39.60 mg kg^{-1} residual fraction. The amount and percent distribution of the different fractions also varied widely in the 18 soil series. The content of Zn in Ex-, OM- and $CaCO_3$-, comprised 0.4-1.9, 2.1-7.7 and 3.5-17.6% of total Zn, respectively. Zinc fractions as percentage of total soil Zn followed the order: Res- > $CaCO_3$- >OM- > Ex- in Aeolian Plain and Alluvial Plain while in Aravali Hills soils order: Res- > $CaCO_3$- ~ OM- > Ex- was followed. The results are in agreement with the findings of Selvaraj *et al.* (2012) [11] who also reported that more than 79.4% in Herura village and 99.3% in Maralanahalli village of total zinc occurred as residual zinc, whereas water soluble + exchangeable Zn occurred only in 0.11% in Maralanahalli village and 6.71% in Sanapura village soil samples while studying distribution of different forms of zinc in paddy growing soils in selected villages of Gangavati taluk, north Karnataka. Extractable Zn concentrations of these soils are generally low because the stable fraction is the dominant form in soils. Spalbar *et al.* (2017) [14] concluded that distribution of Zn in the soils on the basis of average concentrations was in the order Res Zn (78%)> 4.82 mg kg^{-1} OCx (11%) > 3.39 mg kg^{-1} AMOX (8%)> 0.89 mg kg^{-1}CRYoX (2%)> 0.52 mg kg^{-1} WSEX (1%).

Relationship between Zn fractions and soil properties

The distribution of different fractions may vary significantly in response to changing soil properties. The optimum plant growth and crop yield depends on the bioavailability of metal present in the soil at a particular time which in turn is controlled by physico-chemical properties like soil texture, organic carbon, calcium carbonate, cation exchange capacity and pH (Wijebandara *et al*. 2011) [16]. The relationship between forms of Zn and some relevant soil properties (Table 4.12) revealed that the total-Zn was positively and non-significantly correlated with soil properties. Ex-Zn fraction was positively and significantly correlated with OC (r=0.550*) and clay (r=0.484*), whereas, positively and non-significantly correlated with EC (r=0.180) and CEC (r=0.365) and a negative and non-significant correlation was obtained with pH (r=-0.124) and $CaCO_3$ (r=-0.300). Priyanka *et al.* (2017) [8] also found similar correlations for Ex-Zn fraction with OC and pH. A significant positive correlation between the exchangeable fractions with organic carbon indicates that increase in organic carbon content would increase the sorbed metal content of soil. Similar observations by and large were reported by Chahal *et al.* (2005) [2] while studying distribution of forms of Zinc and their association with soil properties, they reported that organic matter and size fractions (clay and silt) had a strong influence on the distribution of different forms of Zn. The results are also in conformity with the observations of Ramzan *et al.* (2014) [9]. OM-Zn fraction was positively and non-significantly correlated with EC (r=0.124), OC (r=0.148) and $CaCO_3$ (r=0.349) while it was negatively and non-significantly correlated with pH (r=-0.274), CEC (r=-0.067) and clay (r=-0.036). $CaCO_3$-Zn fraction was positively and significantly correlated with EC (r=0.573*). It was positively and non-significantly correlated with most of the soil properties whereas Res-Zn had no significant correlation with any of the soil properties. Similar findings were observed by Okoli *et al.* (2016) [6] for Res-Zn. Spalbar *et al.* (2017) [14] studied distribution of Zinc fractions in some rice-wheat growing soils of Jammu Region, India and concluded that all the fractions of Zn were significantly negatively correlated with pH except for OCx, while as a positive relation with electrical conductivity (EC), organic carbon (OC) and clay content.

Conclusion

The results revealed that soil properties influence the distribution of different Zn fractions in soils.Most of the total Zn was present in the residual fraction. Zinc fractions as % of total soil Zn followed the order: Res- > $CaCO_3$- >OM- > Ex- in Aeolian Plain and Alluvial Plain while in Aravali Hills soils order: Res- > $CaCO_3$- ~ OM- > Ex- was followed. Extractable Zn contents of these soils are generally low because the stable fraction is the dominant form in soils. Ex-Zn was positively and significantly correlated with OC and clay while OM-Zn was positively and non-significantly correlated with EC, OC & $CaCO_3$. $CaCO_3$-Zn was positively & significantly correlated with EC. Res-Zn had no significant correlation with any of the soil properties.

Table 1: Zinc fractions expressed as amount extracted and percentage of total Zn for Aeolian Plain, Alluvial Plain and Aravali soils

Location/Soil series	Total-Zn	Ex-Zn*		OM-Zn		$CaCO_3$-Zn		Res-Zn	
	(mg kg^{-1})	(mg kg^{-1})	(%)**	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)
Soil of Aeolian Plain									
1. Balsamand	53.25	0.29	0.54	2.12	3.98	1.88	3.53	47.98	90.10
2. Isarwal	36.02	0.36	1.00	1.04	2.89	1.68	4.66	32.09	89.09
3. Rawalwas	41.32	0.41	0.99	1.32	3.19	3.52	8.52	35.05	84.83
4. Nimriwali	44.21	0.36	0.81	1.22	2.76	2.02	4.57	39.98	90.43
5. Atela	57.15	0.38	0.66	3.25	5.69	3.22	5.63	50.02	87.52
6. Khoh	41.35	0.43	1.04	2.60	6.29	6.51	15.74	30.68	74.20
Range	36.02-57.15	0.29-0.43	0.54-1.04	1.04-3.25	2.76-6.29	1.68-6.51	3.53-15.74	30.68-50.02	74.20-90.43
Mean	45.55	0.37	0.84	1.93	4.13	3.14	7.11	39.30	86.03
Soil of Alluvial Plain									
7. Barwala	44.26	0.45	1.02	1.54	3.48	2.83	6.39	39.16	88.48
8. Ladwa	46.13	0.87	1.89	2.06	4.47	2.99	6.48	39.97	86.65
9. Lukhi	45.14	0.41	0.91	2.36	5.23	2.66	5.89	39.34	87.15
10. Nai	44.02	0.42	0.95	2.66	6.04	5.12	11.63	35.12	79.78

Location/Soil series	Total-Zn	Ex-Zn*		OM-Zn		$CaCO_3$-Zn		Res-Zn	
	(mg kg^{-1})	(mg kg^{-1})	(%)**	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)
11. Uchani	36.78	0.42	1.14	1.83	4.98	6.48	17.62	27.23	74.03
12. Kaul	72.45	0.97	1.34	4.25	5.87	6.38	8.81	59.75	82.47
13. Ujina	59.64	0.44	0.74	1.26	2.11	3.19	5.35	53.24	89.27
14. Narnaund	60.32	0.35	0.58	3.01	4.99	5.34	8.85	50.32	83.42
15. Berpura	54.38	0.45	0.83	2.12	3.90	6.78	12.47	43.84	80.62
16. Zarifa Viran	46.89	0.36	0.77	2.36	5.03	3.47	7.40	39.56	84.37
17. Shahzadpur	47.56	0.79	1.66	2.68	5.63	3.43	7.21	39.80	83.68
Range	36.78-72.45	0.35-0.97	0.58-1.89	1.26-4.25	2.11-6.04	2.66-6.78	5.35-17.62	27.23-59.75	74.03-89.27
Mean	50.69	0.54	1.08	2.38	4.70	4.42	8.92	42.48	83.63
Soil of Aravali Hills									
18. Sohna	48.25	0.18	0.37	3.72	7.71	3.68	7.63	39.60	82.07

*Ex-Zn: Exchangeable + water soluble; OM-Zn: Organically bound; $CaCO_3$-Zn: Calcium carbonated bound; Res-Zn: Residual
**Expressed as a percentage of total

Table 2: Simple linear correlation coefficient (r) between forms of Zn and soil properties

Zn	pH	EC	OC	$CaCO_3$	CEC	Clay
Total-Zn	0.135^{NS}	0.295^{NS}	0.392^{NS}	0.268^{NS}	0.462^{NS}	0.379^{NS}
Ex-Zn	-0.124^{NS}	0.180^{NS}	0.550*	-0.300^{NS}	0.365^{NS}	0.484*
OM-Zn	-0.274^{NS}	0.124^{NS}	0.148^{NS}	0.349^{NS}	-0.067^{NS}	-0.036^{NS}
$CaCO_3$-Zn	0.294^{NS}	0.573*	0.412^{NS}	0.154^{NS}	0.164^{NS}	0.286^{NS}
Res-Zn	0.096^{NS}	0.174^{NS}	0.311^{NS}	0.218^{NS}	0.455^{NS}	0.334^{NS}

* Significant at $p<0.05$; NS- Non-significant

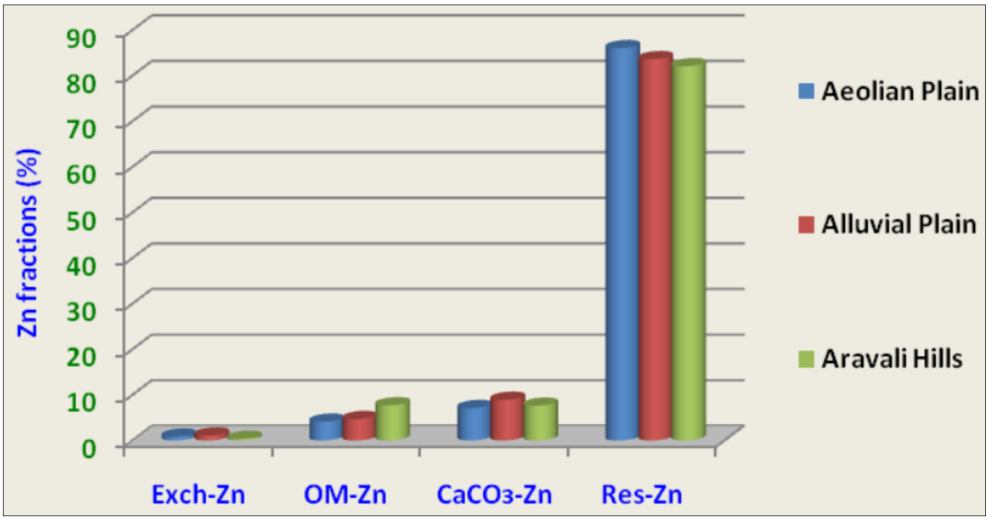

Fig 1: Average percent Zn fractions in the surface soils

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