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Cu, Pb and Zn Fractionation
in a Savannah Type Grassland Soil

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1. Introduction

Heavy metal contamination in soil has received much attention and extensive research has been conducted on estimation of metals in soils. Several heavy metals are known to accumulate in water, soil, sediments and tissues of organisms (Chaphekar, 1991; Lambou & Williams, 1980; Ramadan, 2003) and cause chronic to acute toxicity in due course of time. For evaluation of the heavy metal burden in the environment, it is not sufficient to measure only total metal concentrations, it is also very important to establish the proportions of heavy metals present in various soil solid phase forms their bioavailability and toxicity. Quantifying the geochemical phases of metals associated with soil is an important step in predicting the ultimate fate, bioavailability, and toxicity of metals (Azeez et al., 2006; Lu et al., 2005; Prusty et al., 1994). Easily soluble fractions that are bioavailable and most mobile in the environment are commonly investigated by single extraction procedures such as that of Deely et al. (1992), while the partitioning of heavy metals between easily and sparingly soluble fractions in soils and sediments is investigated by sequential extraction procedures.

Sequential extractions, although operationally defined, give information about the association of heavy metals with geochemical phases of soil, and hence helps to reveal the distribution of heavy metals in fractions and to assess the mobility and toxicity of metals in soils (Ahnstrom & Parker, 1999; Quevauiller et al., 1993). Several sequential chemical extraction procedures are in practice in speciation studies to assess metals in different environmental matrices (Badri & Aston, 1983; Kersten & Förstner, 1986; Pickering, 1981; Tessier et al., 1979; Young et al., 1992). Element specific methods have also been developed as that of Poulton & Canfield (2005) for iron partitioning. Of these, the five step extraction method by Tessier et al. (1979) is a widely used one, although the disadvantages of this extraction scheme, e.g., non-specificity of extraction (Nirel & Morel, 1990; Reuther, 1999) and re-sorption (Howard & Shu, 1996; Howard & Vandenbrink, 1999) have been well recognized. According to this protocol, metals in soil are fractionated into five geochemical pools, *viz.*, exchangeable (EXC), carbonate- (CA), multiple hydroxide (Fe-Mn oxide), organic matter and sulphide (oxidizable, OM-S), and lithogenic or residual

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(RES). The mobility and bioavailability of metals decrease approximately in the order of extraction sequence (Prusty et al., 1994) and hence the strength of the chemical reagents used in extraction increases with the sequence. Generally, exchangeable form is considered readily mobile and easily bioavailable, while lithogenic or residual form is considered as incorporated into crystalline lattice of soil minerals and the most inactive. The carbonate, Fe-Mn oxide and organic matter- bound fractions could be relatively active depending on the physical and chemical properties of the medium. Metals bound to sulphides and organic matter are more stable and hard to take part in the geochemical cycle and generally act as a sink and reservoir for pollutants (Prusty et al., 1994; Yuan et al., 2004).

Heavy metal partitioning in soil has become imperative as this acts as a potential environmental indicator and soils enriched in metals may eventually become sources of metal contamination during oxidative weathering and be available for plant uptake. Metal speciation studies have been extensively undertaken in aquatic systems (Fan et al., 2002; Jagadeesh et al., 2006; Li et al., 2000, 2001; Mathew et al., 2003; Prusty et al., 2007a; Shanthi et al., 2003) for assessment of metal mobility and bioavailability. However, less progress has been made in terrestrial environments, mainly owing 1) to the difficulties in measuring metal activities in soil systems, and 2) to the heterogeneous nature of the soil environment, where exposure of organisms to metals occurs through solid, liquid, and gaseous pathways (Nolan et al., 2003). The Keoladeo National Park (KNP), India inspite of being one of the early Ramsar sites in the country is lacking studies on soil characterization and assessment of metal distribution in the soil. The impetus behind the research presented here was to investigate the chemical partitioning of Cu, Pb and Zn in the soil profile of the grassland system in the park. The particular objectives were to 1) examine the distribution of the metals amongst different operationally defined geochemical pools, and 2) assess the variation of metal distribution among years and soil layers.

2. Study area

Field investigations were carried out in the Keoladeo National Park (KNP, Figure 1), Bharatpur, India in summer of 2003, 2004 and 2005. It was declared as a protected area and bird sanctuary in 1956 and later upgraded to a National Park in 1981 (Sharma & Praveen, 2002). This 29 Km^2 park (27°7.6' to 27°12.2'N and 77°29.5' to 77°33.9'E, almost equidistant about 180 km from Delhi and Jaipur), exixting for more than 250 years (Azeez et al., 1992) is one of the early Ramsar sites (Mathur et al., 2005). The park is segmented into 15 blocks or compartments, named alphabetically from A to O, separated by earthen dykes or mud trails, for the ease of management and tourism. The large number of migratory water fowls, the range of habitats (Prusty et al., 2006) clearly distinguished by vegetation types (Davis & van der Valk, 1988) and hydrological parameters (Azeez et al., 2007) available in the area are the distinctive features of the park. About 8.5 km^2 large central depression of the park is (Figure 1) wetland, while the rest is covered by grassland and woodland (Azeez et al., 2000). The grassland is comprised of *Vetiveria zizanioides*, *Desmostachya bipinnata* and *Cynodon dactylon* as characteristic vegetation (Sharma & Praveen, 2002). While the study was conducted in all the habitats, for the scope of this chapter only the results from the grassland habitat were synthesized and presented here.

The area is a part of the Aravalli Supergroup and falls under semi-arid hot dry zone of India (Pal et al., 2000) and experiences four distinct seasons; summer / pre-monsoon (April to June), rainy / monsoon (July to Mid-September), post monsoon (mid-September to mid-November) and winter (mid-November to March, Prusty & Azeez, 2004). Usually the temperature in the Park varies from 1°C to 49°C, showing strong diurnal and seasonal fluctuations. The soil type of the park is clay loam (terrestrial areas) to clayey (aquatic areas) with scattered saline patches in the terrestrial areas.
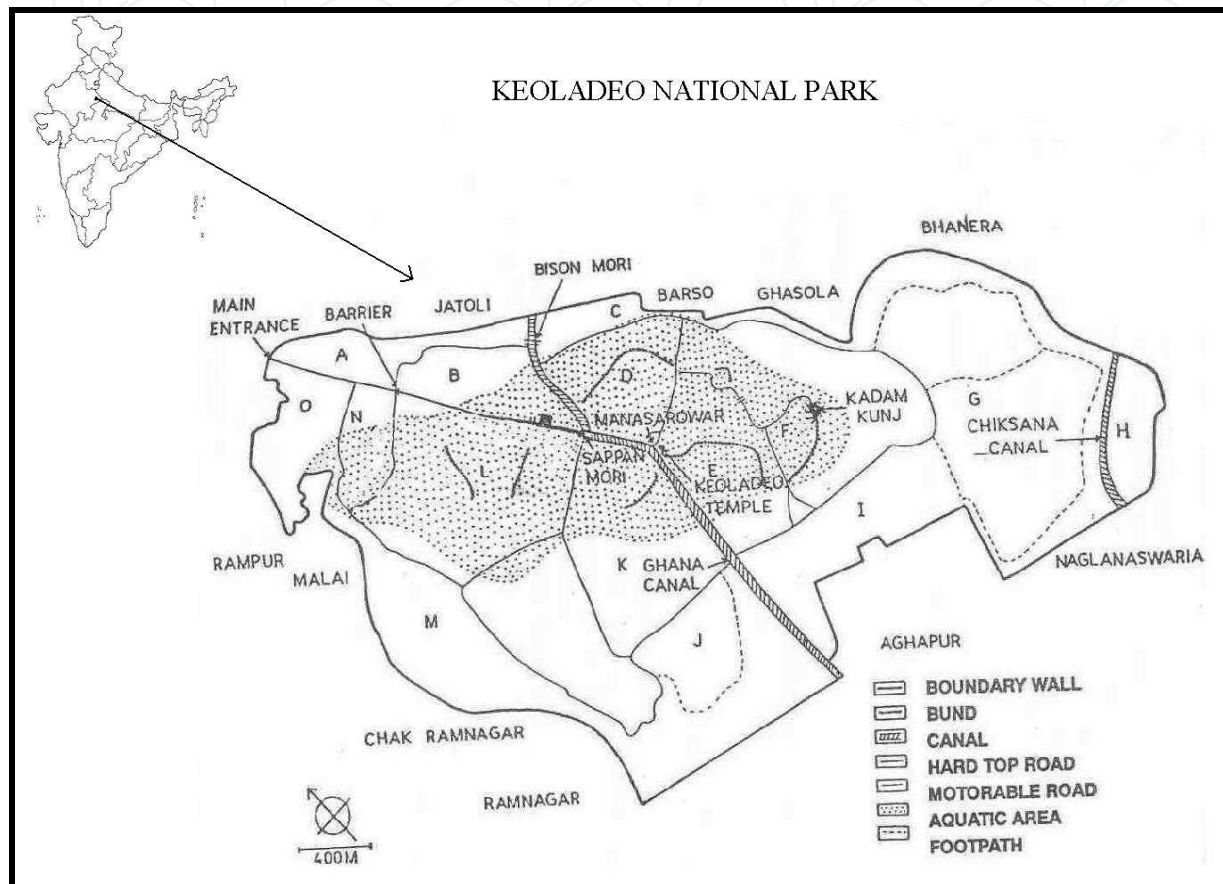

Fig. 1. Study Area Map

3. Methods

3.1 Soil sampling, processing and analyses

Of the total grassland area, three blocks were considered for the present study and the samples were collected in mid June of the year. A trench of 1 m³ was dug up in three locations in each block and the uppermost litter layer was removed by scrapping with a plastic scrapper. Subsequent soil layers from 0, 25, 50, 75 and 100 cm depths were removed using a plastic scoop. The soil samples were packed in pre-cleaned, acid treated and airtight plastic bags and transferred to the laboratory for further processing and analyses. In the laboratory, the soil samples were air-dried at room temperature (Jackson, 1958), homogenized / gently crushed using an agate mortar and pestle and sieved through a standard sieve of 2 mm mesh size (Tandon, 2001). The soil samples with particle size of <2 mm were stored in acid washed plastic containers. Equal proportion of samples from all the

three points from each block were thoroughly mixed to get a representative sample per block.

Total Organic Carbon (TOC, %) in soil was estimated following the wet digestion method of Walkley & Black (1934) and the values were converted to the Total Organic Matter (TOM) empirically assuming that TOC comprises 58% of TOM. The Carbonate Carbon (CO_3-C, %) content in soil was estimated following the rapid titration method of Allen (1989). The chemical fractionation of metals was assessed following Sequential Extraction Procedure based on Tessier et al. (1979). It was carried out progressively on an initial weight of 1.0 g of homogenized material using the following extractions:

Step 1.   0.5 M Magnesium chloride adjusted to pH 7.0 with 10% ammonia solution.
Step 2.   1 M Sodium acetate adjusted to pH 5.0 with Acetic acid.
Step 3.   0.04 M Hydroxylamine hydrochloride in 25% Acetic acid.
Step 4.   30% Hydogen peroxide in 0.02 M Nitric acid.
Step 5.   Aquaregia digestion.

Of the five steps mentioned above, step 1 to step 4 were performed following Tessier et al. (1979) and   step 5 was performed following Ure (1990). The method is intended to distinguish five fractions representing the following phases; Exchangeable (EXC – step 1), Carbonate and specifically adsorbed (CA – step 2), Fe-Mn oxide (Fe-Mn – step 3), Organic matter and sulphide (OM-S – step 4) and Residual / lithogenic (Res – step 5). Aquaregia digestion was performed to estimate the total metal (pseudototal level) content which was compared with the sum of all the five fractions. The geochemical phases at each extraction step are largely operationally defined and indicate relative rather than absolute chemical speciation. The main interpretations are based on the solubility of metals.

Simultaneously blanks and internal standards were also run to verify the precision of the method and accuracy. The precision and bias was generally <10%. The estimated detection limits of the metals in the soil ($\mu g/g$) and the recovery rate for all the metals are given in Table 1. Analysis of standardised soil samples showed an average recovery rate of 94.6 ± 1.9%. Values for constituents lower than the method detection limits (< DL) were substituted with DL/2 prior to statistical analysis (Farnham et al., 1998; Ryu et al., 2006). For quality assurance throughout the experiments and analyses, all extracting reagents were prepared using metal free, AnalaR grade chemicals procured from Qualigens Fine Chemicals Division of GlaxoSmithKline Pharmaceuticals Limited, Mumbai and double distilled water prepared using quartz double distillation assembly was used for the reagent preparations. Room temperature was 30ºC, while extractions were carried out. Polypropylene centrifuge tubes and bottles were subjected to cleaning procedures prescribed by Laxen & Harrison (1981). The metals in the extracts were analyzed using an AAS (Perkin Elmer AAnalyst 800).

Metal	Cu	Pb	Zn
Detection level in soil ($\mu g/g$)	0.01	0.01	0.1
Recovery rate (%)	94.3	92.9	96.7

Table 1. Detection limits for metals

3.2 Statistical analyses

Basic descriptive statistics and two-tail Correlation matrix were performed on the analytical data using "MEGASTAT" to infer the range, distribution and association of different metal fractions among themselves and with TOM and CO_3-C. Univariate tests were performed following the General Linear Model (GLM) to assess variations of the distribution of the metals among fractions, soil layers and years. Post-hoc analysis, i.e. One Way Analysis of Variance (ANOVA) was performed coupled with a test of Least Significant Difference (LSD), only in the cases with significant differences. The statistical tests were performed using SPSS 11.0 (Norušis, 1986).

4. Results and discussions

4.1 Distribution of heavy metals in soil profile

Of the metals studied, Zn was seen highest in soil while Pb was seen the least. The total concentration of Cu in soil ranged from 23.6mg/Kg to 46.4 mg/Kg. The range for Zn was 35.9 mg/Kg to 63.2 mg/Kg and Pb was 8.7 mg/Kg to 13.1 mg/Kg. Cu was seen least at a depth of 25 cm during 2003 and was seen highest in the surface layer during 2004. Pb was found minimum at the depth of 100 cm duing 2005, while maximum was seen at a depth of 50 cm during 2005. The lowest concentration of Zn was at a depth of 25 cm during 2003 and the highest at the bottom of the profile. Two-Way ANOVA test results show that the variation of Cu and Zn was highly significant among the years (Table 2). Of the three metals studied, Cu and Zn had an increasing pattern along the soil profile during all the years (Figure 2). However, a sustained pattern of increase throughout the depth profile was observed duirng 2005 only. Irrespective of the year and metal, the metal level decreased from surface layer to the immediate next layer, i.e. to a depth of 25 cm and then gradually increased till the bottom of the soil profile. The depthwise trend of increase in metals concentration could be associated with their lithogenic nature. The extent of their lithogenic nature is discussed in the subsequent paragraphs. The higher metal levels in the surface layers compared to the subsequent layer might be because of the two reasons, of which the first being the contribution from the plant litters during the process of decomposition. The results of the earlier works by the authors in the KNP reports several species of plants showing notable uptake rates for elements such as Cu, Pb and Zn from the soil (Azeez et al., 2007; Prusty et al., 2007b). The second reason may be the automobile exhausts, they being one of the substantial sources for metals such as Pb (Baker, 1990). KNP has one of the major and busy National High-way (Delhi-Jaipur) traversing beside its immediate boundary. Moreover, its proximity to Bharatpur city might add substantially to the cause.

Metal	Source of variation	F actual	F critical	P value
Cu	Years	6.169	4.459	*0.024
	Soil Layers	0.228	3.838	0.915
Pb	Years	0.666	4.459	0.54
	Soil Layers	2.139	3.838	0.167
Zn	Years	20.432	4.459	*7.18-04
	Soil Layers	1.253	3.838	0.363
* Significant at p<0.05				

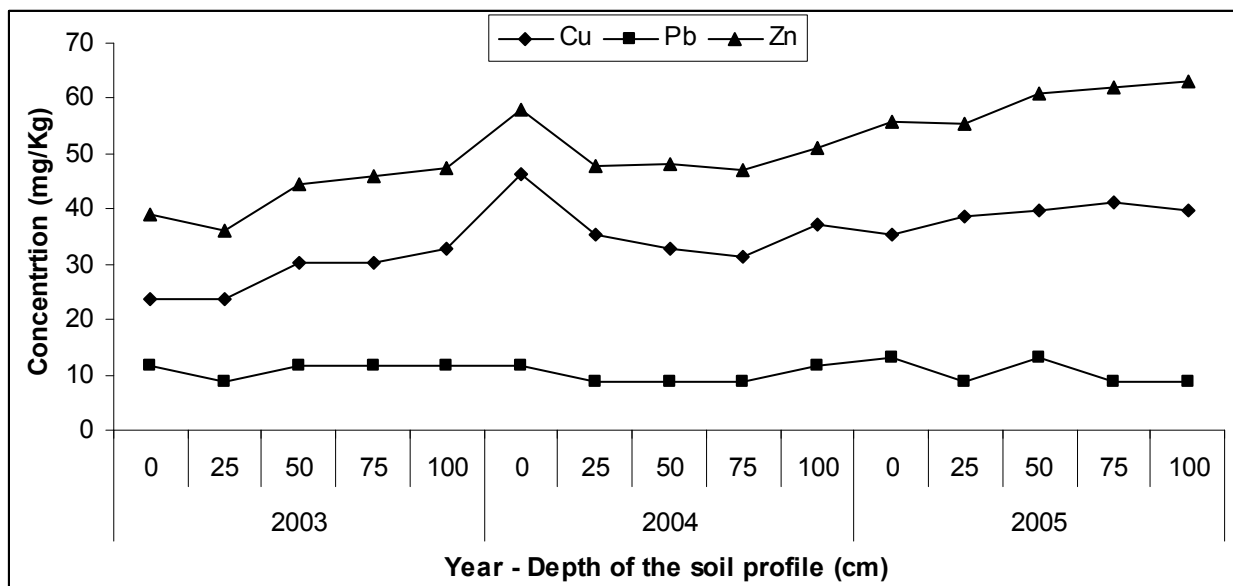Table 2. ANOVA of total metal content in soil

Fig. 2. Variation of total metal content in the soil profile

4.2 Fractionation of heavy metals in soil profile

The association of the three metals to various geochemical phases is presented in Figure 3 to Figure 5. Of the three metals studied, Cu was mainly associated with RES phase while it showed least preferences to the EXC phase (Figure 3). Cu was seen in the range of 30.4% to 76.2% in the residual phase and 0.01% to 0.7% in the EXC phase and the order of the fractions in terms of Cu concentration was Res > Fe-Mn > OM-S > CA > EXC. In contrast, Pb was mostly contained in the multiple hydroxides fraction and least attached with the EXC phase (Figure 4). Pb was seen in the range of 36.6% to 74.0% in the Fe-Mn oxide phase and 0.02% to 7.5% in the EXC phase and the order of fraction in terms of Pb concentration was Fe-Mn > Res > OM-S > CA > EXC. Zn, similar to Cu, had preference towards RES phase and least preference towards EXC phase (Figure 5). Zn was seen in the range of 60.7% to 88.9% in the RES phase, while 0.1% to 1.6% was seen in the EXC phase. The fractions in terms of Zn levels was in the order Res > Fe-Mn > OM-S > CA > EXC. The results indicate two major points: (1) RES phase is the major binding site for Cu and Zn, indicating that the major proportion of the metal is incorporated in the silicate mineral matrix. This may indicate that this element was derived from natural geological sources. (2) Fe-Mn phase is the important binding site for Pb and the reducible Fe and Mn plays a major role in binding these metals. Fe-Mn phase represents the second most significant sink for Cu and Zn after RES phase. It has been shown that in Saline - alkaline soils, as in the case of KNP, the second extraction step (CA phase) may not be effective in removing all the carbonate minerals into solution. Metals extracted in step 3 (Fe-Mn phase) therefore may contain a proportion of the carbonate forms in addition to those bound to Fe-Mn oxides (Maskall & Thornton 1998). The observed higher attachment of Cu and Zn to the RES phase is consistent with observations of Li et al. (2001). The highest affinity of Zn towards RES phase was also reported by Svete et al. (2001) in a study on the chemical partitioning of Zn from a mine area.
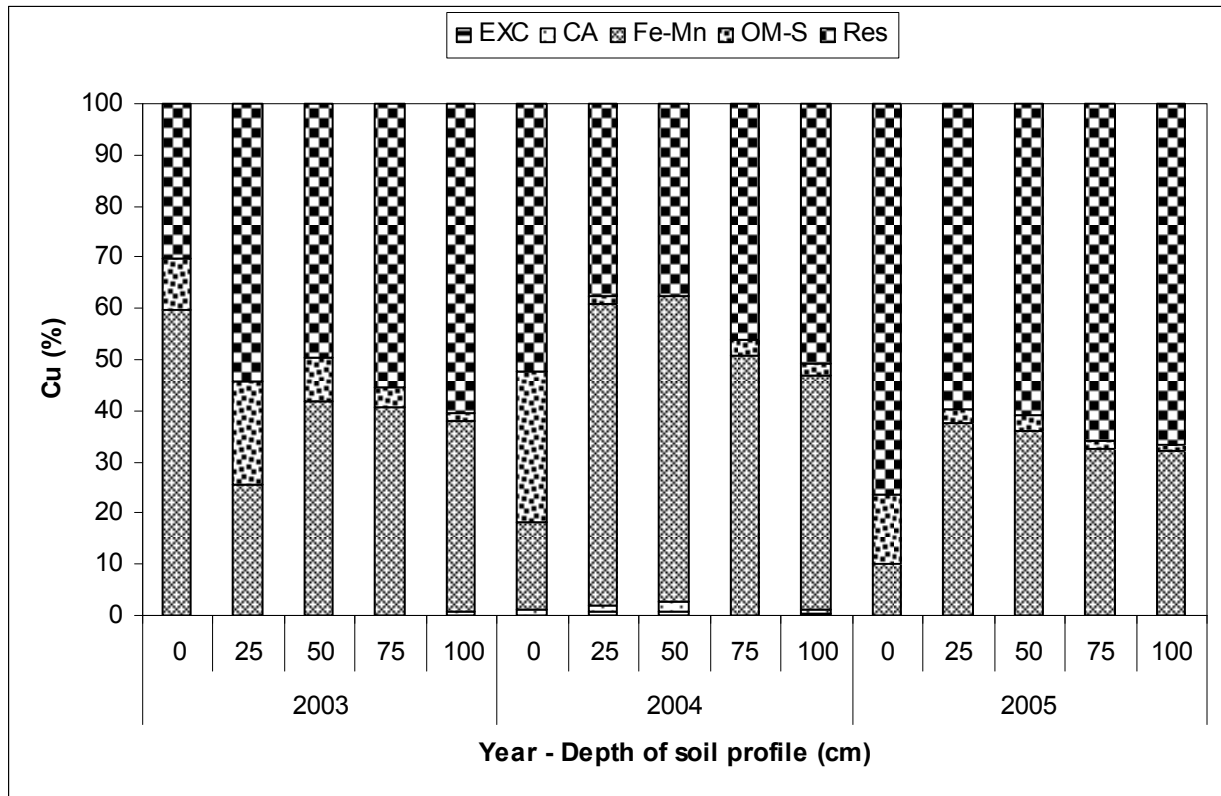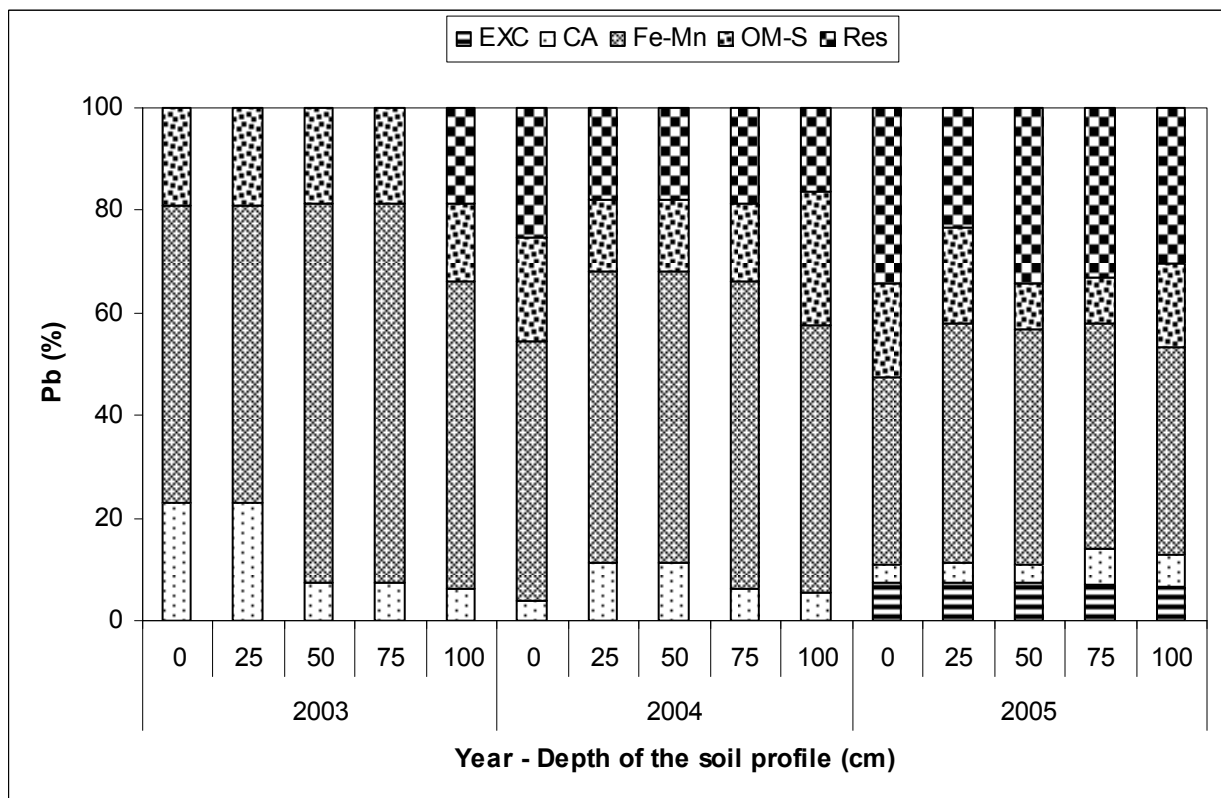
Fig. 3. Cu fractionation in grassland

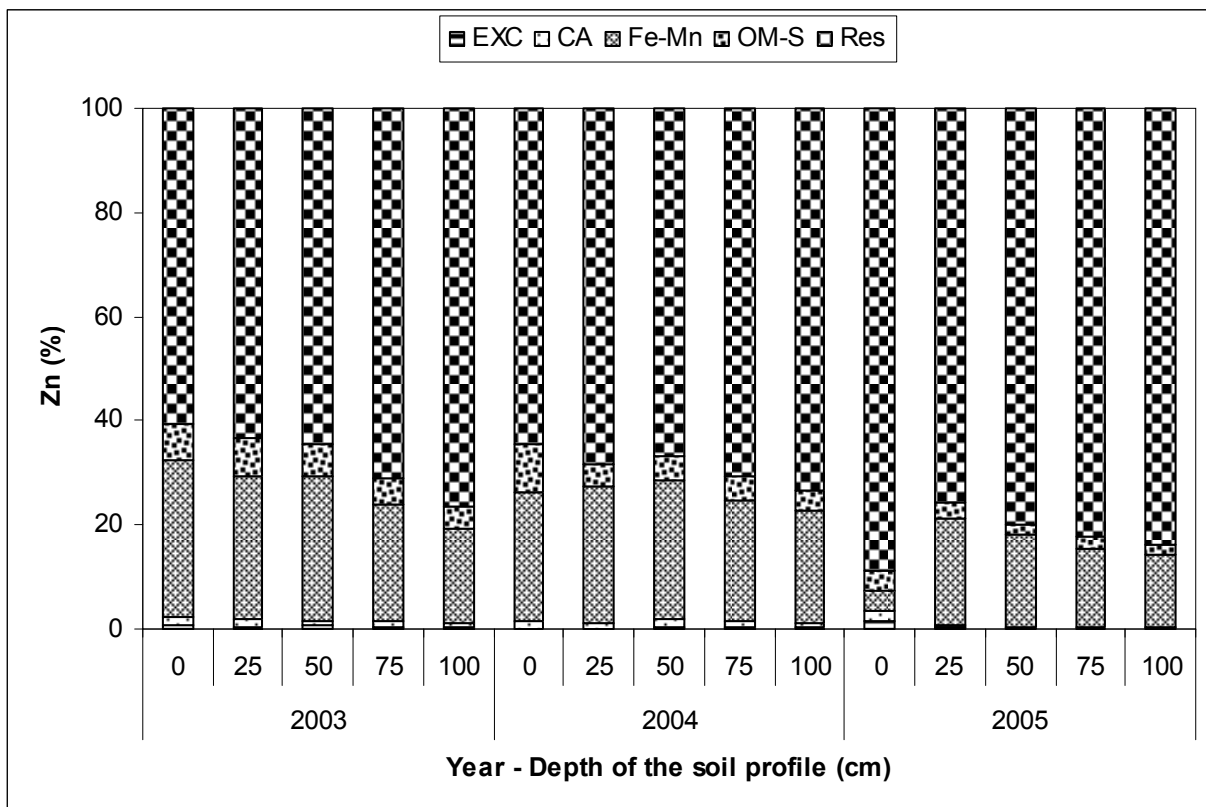Fig. 4. Pb fractionation in grassland

Fig. 5. Zn fractionation in grassland

Although all the metals showed least preference to the exchangeable pool, the order of the metals with average percentage bound to the EXC pool in parenthesis was Cu $(0.1 \pm 0.2\%)$ < Zn $(0.4 \pm 0.3\%)$ < Pb $(2.4 \pm 3.4\%)$. This indicates that the anthropogenic input of Pb is comparatively higher than those of Cu and Zn. As the sampling was done in summer months that have less organic matter in soil as evidenced by our earlier reports, the metals mostly remain attached either with the RES phase and/or with the Fe-Mn oxides phase, and the attachment to organic matter (OM-S) phase is comparatively less. Fan et al. (2002) & Li et al. (2000) also reported similar findings. The apparently greater contribution made by the hydroxylamine hydrochloride-extractable (Fe-Mn) fraction to the Pb compared to Cu and Zn was also reported from other environments (Jones, 1987).

The extent of association among different fractions, and with TOM (%) and CO_3-C (%) is shown in Table 3. Among the non residual fractions only Fe-Mn was negatively correlated with the RES fraction in the case of all the metals. However, in specific cases such as Zn, OM-S was also negatively correlated with RES fraction. The OM-S was positively correlated with the TOM (%) only in the case of Cu (r = 0.673, $P<0.05$). Similar results were also reported by the authors in their study on heavy metal fractionation in woodland soil (Prusty et al., 2009). However, the negative correlation of CA with CO_3-C (%) needs further investigation. The contribution of RES fraction to the total metal content in soil was supported by their poisitive correlation, which was significant only in the case of Zn (r = 0.743, $P<0.05$) indicating the contribution of the lithogenic fraction to the total concentration. The proportion of the metals in the RES phase increased and that in the Fe-Mn oxide fraction decreased along the soil profile in case of all the metals.

Cu

	EXC	CA	Fe-Mn	OM-S	Res	SP-PT	TOM (%)	CO₃-C (%)
EXC	1.000							
CA	.787*	1.000						
Fe-Mn	.570*	.366	1.000					
OM-S	-.344	-.055	-.592*	1.000				
Res	-.509	-.466	-.826*	.038	1.000			
Total metal	.021	.166	-.396	.018	.455	1.000		
TOM (%)	-.275	-.069	-.617*	.673*	.289	.176	1.000	
CO₃-C (%)	-.393	-.110	-.107	-.250	.312	.157	-.070	1.000

Pb

	EXC	CA	Fe-Mn	OM-S	Res	SP - PT	TOM (%)	CO₃-C (%)
EXC	1.000							
CA	-.435	1.000						
Fe-Mn	-.773*	.281	1.000					
OM-S	-.423	.126	.204	1.000				
Res	.744*	-.659*	-.847*	-.461	1.000			
Total metal	.017	-.247	.037	.218	.012	1.000		
TOM (%)	.228	-.070	-.445	.219	.276	.490	1.000	
CO₃-C (%)	.446	-.160	-.203	-.780*	.396	-.359	-.070	1.000

Zn

	EXC	CA	Fe-Mn	OM-S	Res	SP - PT	TOM (%)	CO₃-C (%)
EXC	1.000							
CA	.593*	1.000						
Fe-Mn	-.395	.238	1.000					
OM-S	.098	.650*	.612*	1.000				
Res	.218	-.441	-.964*	-.791*	1.000			
Total metal	-.216	-.538*	-.683*	-.583*	.743*	1.000		
TOM (%)	.664*	.594*	-.408	.352	.180	.160	1.000	
CO₃-C (%)	-.129	-.250	-.326	-.382	.381	.362	-.070	1.000

45 Sample size, ± .514 critical value, P < 0.05 (two-tail), * Significant

EXC = Exchangeable metal, CA = Carbonate bound metal, Fe-Mn = Iron – Manganese bound metal, OM-S = Bound to organic matter and sulphur, Total metal = Pseudototal metal, TOM = Total Organic Matter, CaCO₃ = Carbonate carbon

Table 3. Correlation matrix of metal fractions in the soil

The Univariate test performed following the GLM showed that the distribution of metals was significant only among fractions ($P<0.05$) and hence the Post-hoc analysis (One-Way ANOVA - LSD) was performed on the fractions and the results are shown in Table 4 to Table 6. Fe-Mn phase was found to contribute significantly to the reported variability in the case of all the metals studied. However, there are other additional phases in case of specific metals, for e.g., in the case of Cu, RES was also a significant contributor to the cause (Table 4). In the case of Pb, it was EXC and CA (Table 5), and in the case of Zn, the significant contributor was OM-S and RES (Table 6). As indicated earlier, the findings in the case of Cu and Zn indicate the lithogenic nature of the metals, while in the case of Pb it indicates to the anthorpogenic influences. The significant contribution of CA in the case of Pb may be due to the relatively high pH values in soil at the study site, which have been elevated due to the release of Ca and Carbonate compounds from the soil. Previous study undertaken by the authors report saline and alkaline patches throughout the terrestrial area in the park wherein, the CO_3-C content in grassland soil in KNP ranged from 5.4% to 27.5%. The highest pH in the grassland system in KNP was reported to be 9.97. Maskall & Thornton (1998) reported similar observations and ascribe these to the release of Ca from soil. It can be explained by specific adsorption, which is more important for Pb than other two metals (Borůvka et al., 1997).

Multiple Comparisons

Dependent Variable: CU

LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.2417	3.42211	.944	-7.0669	6.5835
	Fe-Mn	-38.8850*	3.42211	.000	-45.7102	-32.0598
	OM-S	-6.7867	3.42211	.051	-13.6119	.0385
	RES	-53.4141*	3.42211	.000	-60.2393	-46.5889
CA	EXC	.2417	3.42211	.944	-6.5835	7.0669
	Fe-Mn	-38.6433*	3.42211	.000	-45.4685	-31.8181
	OM-S	-6.5450	3.42211	.060	-13.3702	.2802
	RES	-53.1724*	3.42211	.000	-59.9976	-46.3472
Fe-Mn	EXC	38.8850*	3.42211	.000	32.0598	45.7102
	CA	38.6433*	3.42211	.000	31.8181	45.4685
	OM-S	32.0983*	3.42211	.000	25.2731	38.9235
	RES	-14.5291*	3.42211	.000	-21.3543	-7.7039
OM-S	EXC	6.7867	3.42211	.051	-.0385	13.6119
	CA	6.5450	3.42211	.060	-.2802	13.3702
	Fe-Mn	-32.0983*	3.42211	.000	-38.9235	-25.2731
	RES	-46.6274*	3.42211	.000	-53.4526	-39.8022
RES	EXC	53.4141*	3.42211	.000	46.5889	60.2393
	CA	53.1724*	3.42211	.000	46.3472	59.9976
	Fe-Mn	14.5291*	3.42211	.000	7.7039	21.3543
	OM-S	46.6274*	3.42211	.000	39.8022	53.4526

*. The mean difference is significant at the .05 level.

Table 4. LSD of Cu – fractions

Multiple Comparisons

Dependent Variable: PB

LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-6.2347*	3.06070	.045	-12.3390	-.1303
	Fe-Mn	-51.8199*	3.06070	.000	-57.9242	-45.7155
	OM-S	-14.3561*	3.06070	.000	-20.4604	-8.2517
	RES	-15.6058*	3.06070	.000	-21.7102	-9.5014
CA	EXC	6.2347*	3.06070	.045	.1303	12.3390
	Fe-Mn	-45.5852*	3.06070	.000	-51.6896	-39.4808
	OM-S	-8.1214*	3.06070	.010	-14.2258	-2.0170
	RES	-9.3711*	3.06070	.003	-15.4755	-3.2668
Fe-Mn	EXC	51.8199*	3.06070	.000	45.7155	57.9242
	CA	45.5852*	3.06070	.000	39.4808	51.6896
	OM-S	37.4638*	3.06070	.000	31.3594	43.5682
	RES	36.2141*	3.06070	.000	30.1097	42.3184
OM-S	EXC	14.3561*	3.06070	.000	8.2517	20.4604
	CA	8.1214*	3.06070	.010	2.0170	14.2258
	Fe-Mn	-37.4638*	3.06070	.000	-43.5682	-31.3594
	RES	-1.2497	3.06070	.684	-7.3541	4.8546
RES	EXC	15.6058*	3.06070	.000	9.5014	21.7102
	CA	9.3711*	3.06070	.003	3.2668	15.4755
	Fe-Mn	-36.2141*	3.06070	.000	-42.3184	-30.1097
	OM-S	1.2497	3.06070	.684	-4.8546	7.3541

*. The mean difference is significant at the .05 level.

Table 5. LSD of Pb – Fractions

Multiple Comparisons

Dependent Variable: ZN

LSD

(I) FRACTION	(J) FRACTION	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
EXC	CA	-.5969	1.80145	.741	-4.1898	2.9959
	Fe-Mn	-20.8475*	1.80145	.000	-24.4403	-17.2546
	OM-S	-4.2336*	1.80145	.022	-7.8265	-.6407
	RES	-72.2304*	1.80145	.000	-75.8233	-68.6375
CA	EXC	.5969	1.80145	.741	-2.9959	4.1898
	Fe-Mn	-20.2505*	1.80145	.000	-23.8434	-16.6577
	OM-S	-3.6367*	1.80145	.047	-7.2295	-.0438
	RES	-71.6335*	1.80145	.000	-75.2263	-68.0406
Fe-Mn	EXC	20.8475*	1.80145	.000	17.2546	24.4403
	CA	20.2505*	1.80145	.000	16.6577	23.8434
	OM-S	16.6139*	1.80145	.000	13.0210	20.2067
	RES	-51.3829*	1.80145	.000	-54.9758	-47.7901
OM-S	EXC	4.2336*	1.80145	.022	.6407	7.8265
	CA	3.6367*	1.80145	.047	.0438	7.2295
	Fe-Mn	-16.6139*	1.80145	.000	-20.2067	-13.0210
	RES	-67.9968*	1.80145	.000	-71.5897	-64.4039
RES	EXC	72.2304*	1.80145	.000	68.6375	75.8233
	CA	71.6335*	1.80145	.000	68.0406	75.2263
	Fe-Mn	51.3829*	1.80145	.000	47.7901	54.9758
	OM-S	67.9968*	1.80145	.000	64.4039	71.5897

*. The mean difference is significant at the .05 level.

Table 6. LSD of Zn – Fractions

The heavy metal partitioning in soil could be used to determine its mobility and possible sources. Fractionation of total metal contents might give indications about the origin of the metals. The levels in the EXC, CA and Fe-Mn fraction may indicate pollution from anthropogenic origin, and those in OM-S and RES fraction are relatively immobile. Hence, the Fe-Mn phase being the common factor in all the metals, needs further attention from the point of view of metal mobility and bioavailability. Due to their high scavenging capacity, Fe and Mn oxides has been recorded as significant heavy metal sink in soil. Although the dynamics of metal scavenging by Fe and Mn oxides is still poorly understood, assuming that the extraction using Hydroxylamine hydrochloride with acetic acid is an appropriate indicator of metals associated with amorphous iron and manganese oxides, this process seems to exert a significant control on the metals studied in this grassland system. Although the attachment of metals to Fe-Mn oxides indicates that metals are relatively immobilized, slight chemical changes in the ambient conditions could result in their likely mobility and easy absorption by plants. pH and redox changes are the two crucial factors in this regard.

5. Conclusions

The analysis of the extracts produced by a sequential extraction procedure allowed the determination of metals in different fractions of the soil samples. Of all the metals studied the proportion of Pb was maximum in EXC phase and the order of metals in this fraction was Cu < Zn < Pb indicating their relative anthropogenic input. Fe-Mn oxide phase was found to be the common sink for all the metals under study and a significant contributor to the reported variability of each of these metals. However, to confirm this more detailed investigations of the mechanisms controlling the distribution and mobility of different metal species are required.

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7. References

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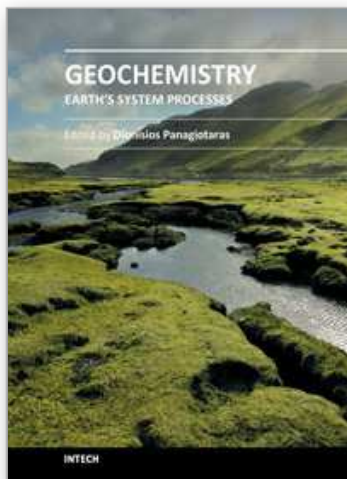
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