

Study of Metal Speciation in Soils of a Tropical Region of India

Mayank Pandey¹, Ashutosh Kumar Pandey² and B.D. Tripathi^{3*}

^{1,2}*Institute of Environment and Sustainable Development,
Banaras Hindu University, Varanasi-221005, India.*

^{3*}*Department of Botany, Centre of Advanced Study,
Banaras Hindu University, Varanasi-221005, India.*

Abstract

Present study deals with metal speciation of Cr, Cu, Zn and Cd in the soils of a tropical region of India, using Sequential Extraction Process (SEP). The order of metal concentration at all the sites was Zn (896.7 mgkg^{-1}) > Cr (601.36 mgkg^{-1}) > Cu (223.2 mgkg^{-1}) > Cd (74.08 mgkg^{-1}). Cr, Cu and Zn present predominantly in residual form followed by bound to organic form. However Cd is predominant in exchangeable and bound to carbonate form at SB and SC. Strong positive correlation was seen between Cu-Zn (0.989) and Cr-Zn (0.842) for different soil samples. The main reason for metal concentrations in the study region may be anthropogenic. Study also revealed the significance of sequential extraction process over total acid digestion process to understand metal composition and effect of their contamination.

Keyword: Metal speciation, Sequential Extraction Process, leaching, toxicity, mobility.

1. Introduction

Soils are the ultimate and endless sink of pollutants in terrestrial environment. Trace metals finally join soil compartment by weathering (bio-geochemical cycle), polluted water (irrigation), atmospheric fall down (total particulate matter) and other anthropogenic activities (industries, solid waste and e-waste landfill etc.). Anthropogenic activities (rapid urbanization, high population growth rate, mining, metallurgy, smelting, electroplating, solid waste etc.) have worsened the metal pollution scenario (D'Amore et al. 2005). Analyzing different forms and species of a

particular metal gives clear idea about its accumulation, bioavailability and mobility (Passos et.al. 2010). Speciation can be defined as “specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.” Multistep Sequential Extraction Procedure (SEP), given by Tessier and co-workers, and provides information about the interaction of metal species with solid and liquid phases in environment in the presence of different external factors like pH, temperature, oxidation-reduction potential etc. Modified BCR-SEP protocol was used in the present study (Table 1). Toxicity, mobility, bio-availability and leachability of metals depend upon the species in which they are present in different compartments of environment and influenced by the physical and chemical factors of the environment (Tessier et al. 1979). Reaction of various species of metal in soil depends upon the physical and chemical factors around the reaction sphere (Zhang 2008). Metal speciation works have been done in many parts of world but negligible information is available on metal speciation and related topics in India especially in tropical region. The aim of this work was to fill the information and data gap for the metal speciation study in the region.

Table 1: Sequential Extraction Procedure (Tessier Protocol)

Extraction Step	Reagents and Reaction Conditions	Phase
1	40 ml, 1 M MgCl ₂ , pH 7.5, 4 hrs stirring	Exchangeable form
2	40 ml, 1M CH ₃ COONa, pH 5 adjusted with CH ₃ COOH, 4 hrs stirring	Bound to carbonate
3	40 ml of 0.06M NH ₂ OH.HCl in 25% acetic acid, 96 ± 4 °C for nearly 45 minutes	Bound to Fe-Mn oxides
4	15ml 0.02 M HNO ₃ + 25ml 30% H ₂ O ₂ (pH 2), heated at 95 ± 5 °C for 3 hrs. After 3 hrs, 15ml 30% H ₂ O ₂ (pH 2) + heat at 65-75 °C for next 3 hrs. After cooling at room temperature, 25ml of 3.2 M CH ₃ COONH ₄ in 20% (v/v) and make up to 100ml	Bound to organic matter
5	4ml aqua regia (3HCl:1HNO ₃) and 5ml concentrated HF 100-110 °C for 90-120 minutes. Add 5.6 g Boric Acid and make volume up to 100 ml	Residual, not extractable in above 4 steps
6	4ml aqua regia (3HCl:1HNO ₃) and 5ml concentrated HF 100-110 °C for 90-120 minutes. Add 5.6 g Boric Acid and make volume up to 100 ml	Total digestion

2. Materials and Method

2.1 Study region

Varanasi (25°16'55"N, 82°57'23"E, 76m amsl), situated at the bank of River Ganga is the oldest living city of the globe and religious, cultural & knowledge city of India

and is known for its high population density (2399 person km⁻²), numerous temples and narrow lanes. Samples (Table 2) transported to lab in airtight packets and were dried (110 °C), crushed (agate pestle mortar) and sieved (75 µm) for further analysis. Metal speciation analysis was carried out by SEP (Tessier et al. 1979; Rauret et al. 2001; Sutherland 2010) and total acid digestion was done with the help of Teflon vessels (USEPA 3050B).

Table 2: Sampling Stations.

Sample	Station Name	Station Co-ordinates
SA	Jakkhini	25°11'6.4" N 82°47'7.14" E
SB	Pandeypur	25°20'57.51" N 82°59'37.93" E
SC	Chandpur Industrial Estate	25°17'58.24" N 82°57'16.80" E
SD	Sigra	25°18'59.33" N 82°59'24.07" E
SE	DLW	25°17'6.24" N 82°57'35.80" E
SF	BHU	25°16'1.4" N, 082°59'27.4" E

Table 3: Recovery percentage, Enrichment Factor and Contamination Factor

Sites	Recovery Percentage [(Σ/TAD)x100]				Contamination Factor				Geo Accumulation Index			
	Cr	Cu	Zn	Cd	Cr	Cu	Zn	Cd	Cr	Cu	Zn	Cd
SA	93.87%	101.83%	89.51%	103%	2.0	0.61	0.43	48.53	1.33	0.40	0.29	32.36
SB	101.22%	91.6%	104.2%	97.62%	0.90	0.85	1.93	8.00	0.60	0.57	1.29	5.33
SC	107.41%	112.5%	95.32%	103.7%	1.35	3.15	0.34	26.07	0.90	2.10	0.23	17.38
SD	96.1%	104.75%	117.11%	109.08%	1.06	1.03	1.48	17.33	0.70	0.69	0.99	11.56
SE	101.3%	97.2%	103.36%	95.7%	1.00	1.18	1.47	10.33	0.67	0.78	0.98	6.89
SF	104.72	88.53%	99.31%	104.26%	0.86	1.76	9.30	13.20	0.57	1.17	6.20	8.80

TAD-Total Acid Digestion

3. Results and Discussion

Highest concentration of Cr was found at SA (167.08 mgkg⁻¹) predominant in fraction 4 (32.68%) and 5 (33.04%). Fig.1 shows that fractional distribution of Cr at SC was nearly equal. However least concentration of Cr was found at SF predominant in exchangeable (20.56%) and residual form (26.39%). Cr concentration at other sites was found as follows: SB (75.6 mgkg⁻¹), SD (88.7 mgkg⁻¹), SE (84.2 mgkg⁻¹). The significant percentage of available fraction (exchangeable + carbonate) of Cr at SB, SC, SE and SF indicates alarming condition in the near future. Contamination Factor (CF) and Geo accumulation index (I_{geo}) was found highest for SA (Table 3). Cr³⁺ species are biologically important and have complex coordination biochemistry. Although Cr³⁺ is present in ultra-low concentration in tissue and fluid of human body, it significantly takes part in lipid and carbohydrate metabolism.

Results reveal that highest concentration of Cu was found at SC (81.94 mgkg⁻¹) followed by SF (45.8 mgkg⁻¹) and least at SA (15.76 mgkg⁻¹). Cu concentration at SC

was highest in bound to organic form (55.53%) followed by residual form (39.3%). Similarly Cu was present in bound to organic form at SA (49.49%), SB (58.56%), SD (70.63%) and SE (68.63%). However at SF, Cu was predominant in Fe-Mn oxide form (47.16%).

Highest concentration of Zn was found at SF (558 mgkg⁻¹) prominent in residual form (83.15%), followed by SB (115.8 mgkg⁻¹) present predominantly in bound to organic matter (56.13%). Least concentration of Zn was at SC (20.3 mgkg⁻¹) again predominant in fraction 4 (58.13%). Zn concentration at other sites was found as SA (25.7 mgkg⁻¹) SD (88.9 mgkg⁻¹) and SE (88 mgkg⁻¹).

Highest concentration of Cd was found at SA (29.12 mgkg⁻¹) present predominantly in exchangeable form (20.05%) and bound to organic matter form (45.67%). At SC total Cd concentration was 15.64 mgkg⁻¹ (exchangeable 34.02% and bound to carbonates 36.83%) and least at SB (4.8 mgkg⁻¹). Cd at SB was nearly equally distributed in all the fractions. Concentration of Cd at other sites was SD (10.4 mgkg⁻¹), SE (6.2 mgkg⁻¹) and SF (7.92 mgkg⁻¹).

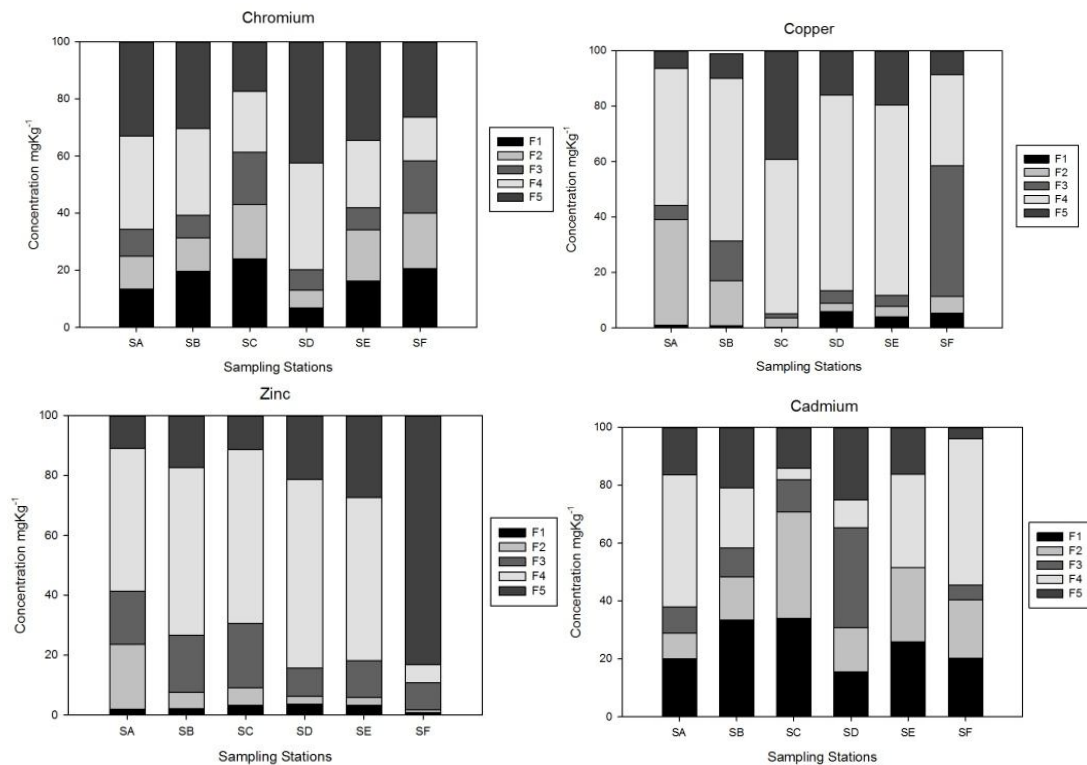


Figure 1: Fraction Distribution of Heavy Metals at Study Sites.

The above result reveals that metals present mostly in bound to organic matter and residual form. At the site of anthropogenic activities, metals are present significantly in available form (exchangeable and bound to carbonate) which may easily leached out to different spheres of the environment on the slight variation of physico-chemical parameters like temperature, pH, redox potential etc.

4. Conclusion

Metal speciation study on soil is first kind of study in the region. This study would certainly help to understand the metal movement in the soil and also fill the data gap for the relevant studies. Metal speciation in six soil samples shows variable results. Bound to organic matter and residual forms of studied metals predominate in the samples. However, Cd found predominantly in exchangeable and bound to carbonate form in some samples (SA, SB, SC and SE). Leaching and transfer of metal and their forms from soil may ultimately lead to surface and ground water pollution. Significant contamination factor and geo accumulation index range indicates practically uncontaminated to moderate metal contaminated conditions which may aggregate in the near future. Therefore, mitigation measures are necessary to check the metal concentration. High metal intake by flora and fauna through food and water may affect their normal physiological and biochemical process. Sources of the metal contamination in soil may not be none other than anthropogenic as construction and maintenance activities are common in the study area. Results from the present study also suggest that sequential extraction process is more efficient and reliable than total digestion method. A holistic and interdisciplinary approach is required to study the metal speciation in soil of the area to assess the long term impact of the metals, with special reference to biomagnifications, bioaccumulation and metal toxicity, on biodiversity of the given region.

5. Acknowledgement

Authors are thankful to University Grant Commission, New Delhi for providing financial support and Institute of Environment and Sustainable Development and Department of Botany, Banaras Hindu University, Varanasi, India for providing necessary infrastructure.

References

- [1] D'Amore J.J., Al-Abed S.R., Scheckel K.G., and Ryan J.A. (2005), Methods for Speciation of Metals in Soils, A Review. *J Environ. Qual.* 34, 1707-1745.
- [2] Fukue M, Yanai M, Sato Y, Fujikawa T, Furukawa Y and Tani S. (2006), Background values for evaluation of heavy metal contamination in sediment. *J Hazard Mater* 136:111–119
- [3] Passos, E. de A., Alves, J.C., Santos, I.S., dos, Jose, do, Patrocínio, H., Alves, A., Carlos, Alexandre, B., Garcia, Antonio, C., and Spinola Costa. (2010), Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal.* 96, 50–57.
- [4] Rauret G, Lopez-Sanchez JF, Luck D, Yli-Halla M, Muntau H and Quevauviller Ph (2001), The Certification of the extractable contents (mass fractions) of Cd, Cr, Cu, Ni, Pb and Zn in fresh water sediment following a Sequential Extraction Procedure BCR 701, EUR 17775 EN

- [5] Salomons W. and Förstner U. (1984), *Metals in the Hydrocycle*. Springer-Verlag
- [6] Sutherland, R.A. (2010), BCR-701, A review of 10-years of sequential extraction analyses. *Analytica Chimica Acta*. 680, 10–20.
- [7] Tessier, A., Campbell, P.G.C. and Bisson, M. (1979), Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*. 51(7), 844-851.
- [8] US Environmental Protection Agency; Acid Digestion of Sediment, Sludges and Soils, Method 3050B
- [9] Zhang, H. (2008), A comparison between heavy metals released from soil and its efficient speciation extracted by sequential extraction procedure. *Chin. J. Geochem.* 27, 36–40.