

SPECIATION OF TRACE METALS IN TOP SOILS IN JOS INDUSTRIAL AREAS

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ABSTRACT

Total metal concentrations of copper (Cu), Nickel (Ni) Manganese (Mn), Iron (Fe), Lead (Pb) and Zinc (Zn) were determined in soil samples from 3 industrial areas in Jos metropolis. Five successive selective chemical fractions were used in the analysis to determine the heavy metals associated with exchangeable fraction, carbonate fraction, easily reducible/iron-manganese oxides, and residual fraction. Nickel was not detected in the exchangeable, organic and carbonate fractions, while iron predominated the five chemical fractions. Manganese and iron gave higher concentrations for the easily reducible/Fe-Mn oxides fraction. pH values of the soil samples ranged between 5.62 to 6.32, which indicate that the soils were acidic. Most of the metal studied were present in the reducible fraction. The concentration of manganese, iron and lead exceeded the threshold limit of the environmental Quality Standards (EQS) for soil pollution. The levels of these metals have been lined to industrial, mining and metallurgical activities in the city.

INTRODUCTION

Speciation is defined as the oxidation state, concentration and composition of each of the species present in a chemical sample, or the determination of the concentration of the different physio-chemical forms of the element which together make up its total concentration in the sample (Hersfall et al. 1999; Ebdon et al. 1985. and Lynch et al. 1984). The individual physico-chemical forms may include particulate matter and dissolved forms such as simple inorganic species, organic complexes and the element adsorbed on a variety of colloidal particles. All these species can co-exist and may not be in thermodynamic equilibrium with one another (Jø and Young. 1987).

The maximum permissible level of a polluting element in an environmental sample such as river water, biota, sediments or soil, refers to total concentration rather than the chemical form of the element (Florence. 1986). However this total concentration provides no information concerning the fate of the element in terms of its interaction with the soil, its ability to cross biological membrane (bioavailability) or its resultant toxicity. Speciation knowledge finds wider applications in areas of food and nutrition, drugs, industrial and environmental scenarios (Duffield and Williams. 1989).

Heavy metals continue to receive increasing attention due to the better understanding of their toxicological importance in ecosystem, agriculture and human health. They get into the soil, aquatic sediment and water by weathering, mining and industrial activities which eventually contaminate the environment, and

hence the effect on life in the aquatic environment and soil (Purves 1985; Abdel et al, 1985; Corcimaru et al, 2001).

The study of the heavy metal content in the soil has a great importance due to the fact that the soil effectively act as reservoir which after temporary storage of metals can act as a source under certain conditions. Therefore the soil is both a source and a sink for metal pollutants. The factors controlling the total and bioavailable concentrations of heavy metals in soil are of great importance for human toxicology and agricultural productivity (Martins et al, 2001)

The major mechanism of accumulation of heavy metals in soils leads to the existence of five categories: adsorptive and exchangeable phase, bound to iron-manganese phase, bound to organic mater and residual fraction (Solomon and Forstner, 1980; Tessier et al. 1979). These categories have different behaviors with respect to mobilization under changing environmental conditions such as pH, redox potential or presence of organic chelators (Forstner, 1985).

The aim of this research work is to study the heavy metal distribution and concentration in agricultural topsoils around industrial areas in Jos city and to ascertain the contamination risk by speciation study.

MATERIALS AND METHOD

Reagents: All chemicals used were of analytical reagent grade unless otherwise specified: and de-ionized water was used throughout

Preparation of stock solution: Stock solutions of Cu, Ni, Mn, Fe, Pb, Zn and Cd were prepared from their chloride and nitrate salts by dissolving in de-ionized water and making up the volume with 5ml of concentrated HCl or HNO₃ to give 1000mg/l solution.

Apparatus: A Pye Unicam SP9 Model Atomic Absorption Spectrophotometer with various hollow cathode lamps was used with an air-acetylene flame, following the specifications in the operational manual.

Sampling and sample treatment. Soil samples were collected from January to March, 2006 from three industrialized areas in Jos namely: Grand Cereals and Oil Mills Limited Bukuru (sample A), Europharm Laboratory, Zaramaganda (sample B) and Makeri-Smelting Company, Anglo-Jos (Sample C). The soil samples were taken from the surface of the terrain and at depth of 30 cm using plastic spoon. The samples were oven dried at 100^oC and sieved to 50µm particle size. The sieved samples were analyzed for total metal and species, according to the scheme reported by Tessier et al (1979).

Determination of pH of soil: 3.0g of the unprocessed soil sample was mixed with 5 ml of de-ionized water in a 50ml beaker, and stirred with a glass rod. The pH was measured by introducing a glass probe of the pH meter into the soil solution.

Total metal analysis: 1.0g of each dried sieved soil sample was digested with a mixture of 15ml concentrated hydrochloric acid and 25 ml concentrated nitric acid for 2 hours at 100^oC. After cooling, the mixture was filtered and made up to 50ml in a volumetric flask. Metal levels were then determined using Pye Unicam SP9 atomic absorption spectrophotometer at the respective wavelengths of the metals.

Exchangeable fraction: 1.0g of dried sieved soil sample was shaken with 20ml of 1M MgCl₂ (pH.7) in a stopper polyethylene bottle for 1 hour on a mechanical shaker at room temperature. The mixture was filtered and make up to 50ml volume and analyzed as above.

Carbonate fraction: 1.0g of dried sieved soil sample was shaken with 20ml 1M CH₃COONa pH 5 (adjusted with glacial acetic acid) in a stoppered polyethylene bottle at room temperature for 5 hours using mechanical shaker and made up to 5ml. The mixture was filtered and analysed for metal.

Fe-Mn oxides/reducible fraction: 1.0g of dried, sieved soil sample was digested with a mixture of 10ml 0.04M NH₂OH.OH and 10ml of 25% (v/v) CH₃COOH at 96^oC for 6 hours. The mixture was cooled, filtered and made up to 50ml volume. The filtrate was analysed as previously described (Tessier et al, 1979).

Residual fraction: 1.0g of dried, sieved soil sample was digested at 200^oC in a Teflon beaker with a mixture of 10ml 40% HF, 20ml 27% HClO₄ and 10ml HNO₃ for 4 hours. The digest was boiled with 20ml-de-ionized water, cooled, and filtered. The filtrate was made up to 50ml and analysed. Triplicate determinations were made for each fraction.

RESULTS AND DISCUSSION

Results of pH of soil samples from the industrial areas are shown in Table 1 and Table 2 shows total metal concentrations. The results of the speciation studies are shown in Tables 3-7

It has been established that soil pH of 5.50 to 7.0 is best for the growth of plants while values below 5.50 could make the soil more acidic and are not favorable for plants growth (Hartman, 1984). The pH values of soils studied in this research work (5.62-6.32) is within the value established for good soils.

In Table 2, the concentration of iron was high for the samples with values of 0.63µg/g for samples A,B and C respectively. This could be due to the abundance of iron in the earth crust, which could be released to the environment at low pH. The concentration of manganese and copper were high for sample C with values of 0.25µg/g and 0.212µg/g respectively, while Zinc has its highest concentration of 0.216µg/g in sample A. The high concentration of these metals in the soil is attributed to industrial and metallurgical activities, irrigation with wastewater, as well as wastewater disposal on land. The values of nickel were low in all the samples while cadmium was not detected in the soil samples.

Table 1. pH of soil samples

Sample	pH
A	6.20
B	6.32
C	5.62

Table 2. Total Metal Concentration in Soils

Sample	Metal Concentration ($\mu\text{g/g}$)*						
	Cu	Ni	Mn	Fe	Pb	Zn	Cd
A	0.150 \pm 0.006	0.008 \pm 0.002	0.147 \pm 0.020	0.630 \pm 0.002	0.015 \pm 0.002	0.216 \pm 0.216	ND
B	0.148 \pm 0.010	0.011 \pm 0.004	0.122 \pm 0.008	0.185 \pm 0.010	0.112 \pm 0.04	0.233 \pm 0.009	ND
C	0.250 \pm 0.009	0.006 \pm 0.002	0.212 \pm 0.001	0.418 \pm 0.003	0.013 \pm 0.001	0.133 \pm 0.013	ND

Table 3. Trace Concentration in the Exchangeable Fraction

Sample	Metal Concentration ($\mu\text{g/g}$)*					
	Cu	Ni	Mn	Fe	Pb	Zn
A	0.020 \pm 0.012	ND	0.020 \pm 0.012	0.120 \pm 0.04	0.002 \pm 0.001	0.021 \pm 0.010
B	0.030 \pm 0.004	ND	0.021 \pm 0.010	0.002 \pm 0.010	0.010 \pm 0.002	0.023 \pm 0.016
C	0.03 \pm 0.004	ND	0.030 \pm 0.010	0.026 \pm 0.016	0.002 \pm 0.001	0.020 \pm 0.012

Table 4. Trace Metal Concentration in the Organic Fraction

Sample	Metal Concentration ($\mu\text{g/g}$)*					
	Cu	Ni	Mn	Fe	Pb	Zn
A	0.030 \pm 0.004	ND	0.040 \pm 0.003	0.130 \pm 0.011	0.002 \pm 0.001	0.002 \pm 0.020
B	0.030 \pm 0.002	ND	0.020 \pm 0.012	0.040 \pm 0.003	0.030 \pm 0.004	0.050 \pm 0.016
C	0.060 \pm 0.020	ND	0.045 \pm 0.010	0.030 \pm 0.016	0.002 \pm 0.000	0.030 \pm 0.012

Table 5. Trace Metal Concentration in the Carbonate Fraction

Sample	Metal Concentration ($\mu\text{g/g}$)*					
	Cu	Ni	Mn	Fe	Zn	Pb
A	0.025 \pm 0.019	ND	0.035 \pm 0.010	0.180 \pm 0.012	0.025 \pm 0.011	0.003 \pm 0.001
B	0.030 \pm 0.024	ND	0.020 \pm 0.012	0.021 \pm 0.006	0.052 \pm 0.022	0.020 \pm 0.000
C	0.045 \pm 0.017	ND	0.049 \pm 0.010	0.020 \pm 0.012	0.050 \pm 0.012	0.003 \pm 0.002

Table 6. Trace Metal Concentration in the Fe – Mn Oxide/Reducible Fraction

Sample	Metal Concentration ($\mu\text{g/g}$)*					
	Cu	Ni	Mn	Fe	Zn	Pb
A	0.042 \pm 0.002	0.003 \pm 0.001	0.030 \pm 0.004	0.132 \pm 0.001	0.004 \pm 0.002	0.003 \pm 0.001
B	0.029 \pm 0.012	0.002 \pm 0.001	0.040 \pm 0.005	0.060 \pm 0.020	0.060 \pm 0.020	0.055 \pm 0.003
C	0.065 \pm 0.005	0.004 \pm 0.002	0.058 \pm 0.021	0.042 \pm 0.004	0.011 \pm 0.005	0.004 \pm 0.0042

Table 7. Trace Metal Concentration in the Residual Fraction

Sample	Metal Concentration ($\mu\text{g/g}$)*					
	Cu	Ni	Mn	Fe	Zn	Pb
A	0.032 \pm 0.015	0.005 \pm 0.002	0.022 \pm 0.011	0.130 \pm 0.001	0.030 \pm 0.002	0.003 \pm 0.002
B	0.029 \pm 0.012	0.007 \pm 0.001	0.021 \pm 0.005	0.042 \pm 0.004	0.053 \pm 0.002	0.021 \pm 0.005
C	0.051 \pm 0.011	0.002 \pm 0.000	0.040 \pm 0.015	0.030 \pm 0.004	0.002 \pm 0.001	0.002 \pm 0.001

*Average of triplicate determinations

The high concentration of lead in the soil samples could be as a result of regular influx of automobile and refuse dumping within the industrial areas. Copper and zinc are essential elements for plants and animals, but are toxic at high concentration. Industrial use of tools and cable manufacturing, wastewater sludge and antifungal or anti-algal fumigation over crops could contribute to copper pollution of the environment (Kiekens, 1995). The total concentration of manganese, iron and lead exceeded the limit of the Environmental Quality Standards (EQS) for soil pollution (1991). Sequential extraction procedures were used to study the bioavailable concentrations of heavy metals in soil around industrial areas in Jos (Tables 3-7.), which the concentration of iron was high for sample A (0.120 µg/g). Lead had low concentration in samples A and C (0.022 µg/g each). This fraction is more soluble, and metals present in this fraction can easily be released into the soil and made available to plants due to changes in environmental conditions such as pH, redox reaction or the presence of organic chelator (Forstner, 1985). The toxicity of heavy metals in the soil is generally linked to the ease of their remobilization.

The concentration of the metals bound to organic phase is shown in Table 4. Iron and zinc had higher concentration in sample A in this phase. The values were 0.130 µg/g and 0.100 µg/g; respectively. This high concentration in this area could be due to the discharge of waste water from the industry, which was used as source of manure on the farm. Nickel was not detected in this phase. Soil organic matter (SOM) retains this metal by iron-exchange proton displacement, and inner and out-sphere complex formation (Purves, 1985). Consequently considerable amount of trace metals are retained in this fraction, which is less mobile, since it is thought to be associated with higher molecular weight stable and humic substance which release small amounts of metal gradually (Zhang, 1989).

From Table 5, iron had the higher concentration in the carbonate fraction in samples A and B, while; manganese had the highest concentration in sample C. Values obtained for the metals were 0.180 µg/g and 0.49 µg/g respectively. Lead had the lowest concentration in this fraction with the values 0.003 µg/g, 0.020 µg/g and 0.003 µg/g for samples A, B and C respectively. Nickel was not detected in this fraction. The carbonate fraction makes up relatively stable, slowly labile forms of the metals Abdel et al (1994).

Iron predominates the reducible Fe-Mn oxide fraction in the samples (Table 6). The concentration ranges from 0.042 µg/g to 0.130 µg/g. The Fe-Mn oxide fraction could be considered as slowly mobile and poorly available, but could change with variations in redox conditions becoming more soluble under reducing conditions. An increase in the reducing property of the soil could increase its toxicity. Most of the metals were present in the reducible fraction.

The residual fraction had the highest concentration of Fe (0.130 µg/g), Zn (0.53 µg/g), and Cu (0.051 µg/g) for samples A, B and C respectively (Table 7). Metals present in this form are in non-available, non-reactive, non-mobile and non-toxic form. The higher the percentage of metal in this form, the smaller the pollution of the soil in the environment.

CONCLUSION

The concentration of Cu, Ni, Mn, Fe, Pb and Zn were determined in soil samples from three industrial areas in Jos metropolis. Cadmium was not detected in the soil samples, while the concentration of manganese, iron and lead exceeded the Environmental Quality Standard for soil pollution, EQS (1991). This could cause serious environmental hazard. In the speciation of the soils, five successive chemical fractions were used in the analysis to determine metals that were exchangeable, associated with easily reducible Fe-Mn oxides, associated with organic matter, carbonate form and residual fraction. The environmental impact of the five speciation categories depends upon the ease of remobilization, the exchangeable being the most dangerous form.

REFERENCES

- Abdel-Saheb, I., Schwab, A.P., Banks, M.K. and Hetrick, B.A. (1994). *Journal, Water, Air and Soil Pollution*, 78, 73-82.
- Centre for Heavy Metals Research. The University of Sydney (2002). *Environmental Research Programme*.
- Corcimaru, S., Emmanuel, S., Erel, Y., Novak, M., Polynsin, A., Veron, A. and Wickham S. (2001). *Integrated Environmental Impact of Heavy Metals on Soil-Water Systems as exemplified by the Biogeochemical behaviour of lead. Integrated Approaches to Water Quality issues. International Conference Center, Tinto*.
- Duffield, J.R. and William, D.R. (1989). *Chemical Speciation. Chemical in Britain* 373-378.

- Ebdon, L., Hill, S.J. and Jones, P. (1985). Speciation of tin in Natural Water using Coupled High-performance Liquid Chromatography Flame atomic absorption Spectrometry. *Analyst*, 110, 551-517.
- Florence, T.M. (1986). Electrochemical Approaches to Trace Elements Speciation in Waters. "Review Analyst", 3, 489-502.
- Forstner, U. (1985). Chemical Forms and Reactivities of Metals in Sediments in Chemical metal for Assessing Bioavailable Metal Suldges and Soils. *Analyst* 2, 356-400.
- Hersfall, M., Mitlie, N.H. and Spiff, A.I. (1999). Speciation of Heavy Metals in Inter-Trdal Sediments in Okrika River System. *Bull. Chem. Soc. Ethiopia* 3 (1), 1-9.
- Jan, T. and Young, D.R. (1978). Chromium Speciation in Municipal Wastewater and Seawater. *Journal of Water Pollution Control Federation*, 50, 2322-2336.
- Lynch, Y.P., Kernoghan, N.J. and Wilson, J.N. (1984). Speciation of Metals in Solution by Flow Injection Analyses. Part 1. SSequential Spectrophotometric and atomic-absorption Detectors. *Analyst*, 109, 839-842.
- Martins, M.J., Moreno, S., Martins, J.J., Moreno, J., Bayo J., Guilien, J.J. and Moreno Clavel, J. (2001). Distribution of the Metals, lead, cadmuin, copper and zinc in the top soil of Castagena, Spain. *Journal, Water, Air and Soil Pollution*, 131, 324-347.
- Purves, D. (1985). Trace Element Contamination of the Environs. *Analyst*, 5, 205-208.
- Solomon, N. and Forsner, U. (1980). *Environ Technol lett* 1, 517.
- Tessier, I., Compel, P.G.C. and Bisson, M. (1979). Sequential Extraction Procedure of the Speciation Particular Trace Metals. *Analytical Chemistry* 51 (7), 844-851.
- Hartman, D.T. (1984). *Fundamentals of Soil Science*, 7th edition. John Wiley and Sons, New York pp 30-35, 310-315.
- Kickens, L. (1995). Zinc in B. J. Alloway (ed). *Heavy Metals in Soil*, Blankie Academic and Professional London, U.K. 284-303.
- Zhang, S. (1989). 'Geochemical Characteristics of Heavy Metals in the Xiangjiang River China'. In PG. Sly and B.T. Hard (ed). *Interaction between Sediments and Freshwater* Kluwer Academic Publisher, London, 253-262.