Examination of the Speciation of Trace Metals in Some Selected Areas of Jos, Nigeria

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Abstract   Analysis of total metal concentrations and speciation of Lead (Pb), Zinc (Zn), Chromium (Cr), Manganese (Mn), Copper (Cu), and Iron (Fe) were carried out on soil samples from West of Mines, Tudun Wada and Dadin Kowa in Jos, Plateau state. Results show that zinc has the highest concentration of total metals while lead was not detected at all. Speciation results show an average of 4.47% of total metals in the exchangeable fraction, 9.95% in the carbonate fraction with chromium and copper not detected, 28.47% in the Fe-Mn oxides fraction with manganese being predominant, 8.44% in the organic fraction and 46.86% in the residual. The general pattern was that the bulk of the trace's metals studied were present in the non-mobile, slightly or non-reactive, poorly or non-available forms.

Keywords: concentration, speciation, metals, organic, lead, chromium, manganese

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1. Introduction

It is of note that urban soils receive significant amounts of several pollutants from traffic, industry and wastes and are often mixed with anthropogenic materials that modify soil properties and may increase pollutant contents, especially some potentially toxic trace elements [1]. Heavy metals can accumulate in the topsoil from atmospheric deposition by sedimentation, impaction and interception. Unlike soils in rural areas, urban soils are seldom related with mass food production. However, they still can have a direct influence on human health, as they can be transferred into the human body by different pathways, e.g. inhalation of dust or contaminated suspended particles, soil ingestion, with special attention for children in playground areas via hand-to-mouth, dermal absorption by direct contact, or contamination of groundwater or edible plants grown in urban gardens [2]. Bioavailability and mobility of metals in soils are related with these different pathways.

Soil serves many vital functions, but its effect on food production is universal to all societies. It is thus of extreme importance to protect this resource and to ensure its sustainability. In this context special attention should be paid to the concentrations of trace elements in agricultural soils as these can be ingested by humans and animals through the food-chain structure as a result of their initial uptake by edible plants. A deficit or excess of these elements can cause serious problems in plant growth and animal and/or human health [3]. The total content of trace elements in soils depends mainly upon the bedrock type from which the soil parent material was derived but also on which pedogenic processes were carried out [4]. Among the anthropogenic activities that can be considered to be important sources of trace element contamination of the surface environment is base-metal mining together with milling and grinding operations, the concentration of ore and the disposal of tailings along with the acid mine and water.

Elevated concentrations of heavy metals are generally found in and around abandoned and active mines due to the discharge and dispersion of the mines' waste materials, including tailings, into nearby agricultural soils, food crops and stream sediments. As a result, large areas of agricultural soil can also be contaminated. In addition, agricultural soils are also prone to pollution with toxic trace element and other contaminants from fertilization processes, industrial and municipal waste discharges, transport activities and atmospheric deposition. Trace elements can also enter agricultural soils through irrigation [5].

In view of the importance now attached to knowing the forms in which trace metals occur in samples, commonly known as speciation, this work is aimed at determining the

various forms in which trace metals exist in some agricultural top soils in Plateau state and to access the level of pollution of soil by these metals.

1.1. Pollution

Environmental pollution is the unfavorable alteration of our surroundings, wholly or largely as a by-product of man's actions, through direct or indirect effects of changes in energy patterns, radiation levels, chemical and physical constitution and abundance of organisms. These changes may affect man directly or through his supply of water and of agricultural and other biological products, his physical objects or possessions or his opportunities for recreation and appreciation of nature [6]. Pollution is the fouling of the environment by natural phenomenon or by human activities. Pollution need not involve constituents hazardous to health. They may be offensive to sight, taste, smell etc. This connotes a certain concentration on the other hand is intended use of land, water and air. Contamination on the other hand is the pollution involving constituents that are hazardous to health because of their nature and quality. Pollution may also be referred to as any increase in the concentration of the respective constituents above its natural variation [7].

1.2. Speciation of Metals and Toxicity

There is a growing realization that analyzing the total concentrations of polluting elements is insufficient. Indeed, the form in which an element exists popularly known as speciation is of vital importance in a number of fields e.g. toxicology and environmental monitoring [8]. It may be said that speciation begins where analytical chemistry gives way to real life chemistry. Speciation may therefore be said to mean 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 physico-chemical forms of the element which together make up its local concentration in the sample. The individual physico-chemical forms may include particulate matter and dissolved forms such as simple inorganic species, organic complexes and the element absorbed on a variety of colloidal particles. All species can co-exist and may or may not be in thermodynamic equilibrium with one another.

As important as speciation in environment analysis is, it is still beset with the problems of liability. Changing the ambient conditions from those prevailing in industrial, biological or environmental systems often disturbs the existing equilibria and so the species detected and monitored are not full representative of those which really occur [6].

Metals in soil are associated with different components and are divided generally into five fractions: water-available and exchangeable, bound to carbonates (week acid-available), Fe-Mn oxides (reducible), organic matter (oxidizable) and residual forms. Several factors influence the mobility, bioavailability, and toxicity of metals, such as soil characteristics (texture, pH value, redox potential) and anthropogenic factor [9] (McLean & Bl In order to achieve a comprehensive risk assessment regarding pollution, it is necessary to fractionate heavy metals using either a five-step extraction according to the Tessier scheme by [10], or a three-step extraction proposed by the European Community Bureau of Reference (BCR). These procedures were used both in laboratory conditions (batch or column approach), where different environmental situations were simulated [11], and in on-site studies to evaluate the influence of different pollution factors [12]. Drawbacks of the extraction methods dwell in the complete isolation of compounds due to the non-selectivity of several extractants and possibility of metals redistribution in phases [13]. That is why sequential leaching experiments should be evaluated using structural control by non-destructive analysis. Extraction procedures are also time-consuming, e.g. the BCR procedure requires ca. 33h. The time can be reduced down to 65 min using a microwave assisted continuous flow sequential extraction system without losing accuracy and precision of the fractionation analysis. The accuracy of the sequential extraction can be evaluated either using suitable certified reference materials, such as BCR 701, or by comparing the total content calculated as a sum of the extracted fractions with the content determined by a reference analysis method. There is, however, no suitable CRM for the Tessier scheme available [14]. Another approach to sequential extraction relies on the use of one extractant at varying pH and multivariate data treatment in order to identify the physic-chemical phases present in the sample [14].

Selection extraction methods have been used to target element species in soil, or elements bound to, or associated with, particular soil phases or compounds. Examples include the use of extractants to release metals in exchange sites, or metals bound or associated with soil organic matter. Thus, undoubtedly selective extraction methods can assess the amounts of mobile or potentially mobile species which in turn may correlate with plant available contents under certain environmental or agricultural conditions [15]. In soils and sediments, elements of interest exist in several forms and are associated with a range of components [16]. It is generally recognized that information about the physicochemical forms of the elements is required for understanding their environmental behavior (mobility, pathways, bioavailability) [17].

1.3. Speciaition Techniques

Speciation measurements are not readily accessible, but have improved with the conceptual advances in analytical methodology over the past 30 years and also with the use of modern computers and software, so that new techniques for direct experimental measurement can be extrapolated to levels of detectability previously unreachable [18]. Some methods for studying speciation include:

i. Atomic absorption spectroscopy
ii. Bioassay
iii. Computer simulation modeling
iv. Extraction into lipids or solvent,
v. UV-visible spectroscopy
vi. Election spectroscopy
vii. Chemiluminiscence analysis
viii. Electrochemical techniques (polarography, anodic stripping voltammetry, cathodic stripping voltammetry, potentiometric stripping analysis, etc),

ix. Ion-exchange chromatography.

2. Materials and Method

Soil samples were collected from Police Barracks, West of Mines; Tundun wada and Dadin Kowa, all in Jos Plateau state. The soil samples were collected in plastic bottles before subjecting them to total metal analysis where 400mg of each soil sample was digested with 2ml hydrofluoric acid and 8ml aqua regia which was later diluted to 500ml with nano-pure water. Metal levels were then analyzed using AAS. The metals analyzed were Lead (Pb), Zinc (Zn), Chromium (Cr), Manganese (Mn), Copper (Cu) and Iron (Fe).

2.1. Speciation of Metals

2.2.1. Exchangeable Fraction

1g of each of the soil samples was weighed into 50ml centrifuge tubes and 8ml of 1M magnesium chloride solution was added. These were agitated at room temperature for 1 hour, and then centrifuged at 12000 rpm for 30 minutes. The supernatant was aspirated into a sample tube using a pipette. This was then analyzed with PinAAcle 900T Atomic Absorption Spectrometer (AAS).

2.2.2. Carbonate Bound Fraction

8ml of 1M sodium acetate, adjusted to pH 5.0 with acetic acid were added to the centrifuge tube with the residue from the exchangeable fraction. The sample was agitated at room temperature for 5 hours, and then centrifuged at 12000 rpm for 30 minutes. The supernatant was aspirated into a sample tube and then analyzed with PinAAcle 900T AAS.

2.2.3. Fe-Mn Oxide Fraction

20ml of 0,04M hydroxylamine hydrochloride in 25% v/v acetic acid were added to the centrifuge tube with the residue from the carbonate fraction. The sample was agitated occasionally at approximately 96^0C in hot water bath for 6 hours. The supernatant was aspirated into a sample tube by using a pipette and then analyzed with PinAAcle 900T AAS.

2.2.4. Organic Fraction

3ml of 0.02M trioxonitrate (v) acid and 5ml of 30% hydrogen peroxide adjusted to pH 2 with HNO_3 were added to the centrifuge tube with the residue from fraction 3. The sample was heated to approximately 85^0C for 2 hours with occasional agitation. After cooling, 5ml of 3.2M ammonium acetate in 20% (v/v) trioxonitrate (v) acid were added. The sample was diluted to 20ml and again agitated for 30minutes at room temperature. The sample was centrifuged at 12000 rpm for 30minutes and the supernatant was aspirated into a sample tube by using a pipette, and then analyzed with PinAAcle 900T AAS.

2.2.5. Residual

The residue from the organic fraction was digested with a 5:1 mixture of hydrofluoric and perchloric acids. The sediment was first digested in a platinum crucible with a solution of concentrated $HClO_4$ (2ml) and HF (10ml) to near dryness. Subsequently, a second addition of $HClO_4$ (1ml) and HF (10ml) was made, and again the mixture was evaporated to near dryness. Finally, $HClO_4$ (1ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12M HCl and diluted to 25ml, then analyzed.

2.3. pH Determination

The pH measurement of the soil samples was carried out with Jenway Portable pH meter on the unprocessed samples. 1 g of each soil sample was weighed into 10ml distilled water. The pH was then read using a pH meter.

2.4. Dry Matter

The dry matter content was determined first by weighing an empty petri dish and heating in the oven at 105°C for 1 hour. This was left in the desiccators for about ten minutes to cool. The dry matter was then determined by putting 0.5g of soil sample in the petri dish for 1 hour and then weighed

$$\% \; dry \; matter = (dry \; weight \, / \, wet \; weight) x100.$$

The percentage dry matter of the soil samples ranged from 98.8% in West of Mines to 99.0% in Dadin Kowa and 99.2% in Tundun Wada.

2.5. Organic Matter

The organic matter was determined by first placing an empty crucible in a furnace at 600°C for 1 hour and then weighed.

$$\% \; organic \; matter$$
$$= \frac{weight \; before \; firing - weight \; after \; firing}{weight \; before \; firing} x100.$$

The percentage organic matter of the soil samples ranged from 4.0% in Tundun Wada t_0 7.4% in Dadin Kowa and 9.2% in West of Mines.

2.6. Carbonate

The carbonate contents of the samples were determined by placing 1g of each of the soil sample in $50cm^3$ of water and then titrated against $0.01mol/dm^3$ HCl using methyl red indicator.

$$\% \; carbonate$$
$$= \frac{2 \; x \; mol \; of \; acid \; x \; vol \; of \; acid \; used \; x \; wt \; of \; CO_3^{2-}}{vol \; of \; water \; x \; wt \; of \; sample} x100$$

The percentage carbonate content of the soil samples ranges from 0.24% in Tundun Wada to 0.96% in West of Mines and 1.44% in Dadin Kowa.

2.7. Preparation of Standards

2.7.1. Lead (Pb)

A 1000ppm of lead was prepared by dissolving 1.5980g of lead (II) trioxonitrate (v) Pb(NO3)2 in 100ml of

distilled water in 1 litre volumetric flask and made up to the mark. Further dilutions were made to obtain 5ppm, 10ppm, 30ppm and 50ppm and the solutions were stored in polyethylene bottles.

2.7.2. Zinc (Zn)

A 1000ppm of zinc was prepared by dissolving 1.2450g of zinc oxide (ZnO) in 5ml of distilled water followed by 25ml of 5M of HCl and diluted with distilled water to $1000cm^3$ in a volumetric flask. Further dilutions were made to obtain 1ppm, 3ppm, 5ppm and 10ppm and the solutions were stored in polyethylene bottles.

2.7.3. Chromium (Cr)

A 1000ppm of chromium was prepared by dissolving 7.696g of chromium (II) trioxonitrate (V) $(Cr(NO_3)_3.9H_2O)$ in 250ml of distilled water and made up to $1000cm^3$ in a volumetric flask. Further dilutions were made to obtain 5ppm, 10ppm, 30ppm and 50ppm and the solutions were stored in polyethylene bottles.

2.7.4. Manganese (Mn)

A 1000ppm of manganese was prepared by dissolving 3.6077g of manganese chloride $(MnCl_2.4H_2O)$ in 50ml hydrochloric acid and diluted distilled water to $1000cm^3$ in a volumetric flask. Further dilutions were made to obtain 0.5ppm, 1ppm, 3ppm, 5ppm and 10ppm and the solutions were stored in polyethylene bottles.

2.7.5. Copper (Cu)

A 1000ppm of copper was prepared by dissolving 1g of copper metal with 50ml of 5M trioxonitrate (V) acid in a $1000cm^3$ in a volumetric flask and diluted to mark with distilled water. Further dilutions were made to obtain 1ppm, 3ppm, 5ppm and 10ppm and the solutions were stored in polyethylene bottles.

2.7.6. Iron (Fe)

A 1000ppm of iron was prepared by dissolving 1g of iron granules in 20ml of 5M hydrochloric acid and 5ml trioxonitrate (V) acid diluted with distilled water to $1000cm^3$ in a volumetric flask. Further dilutions were made to obtain 3ppm, 5ppm, 10ppm and 20ppm and 50ppm and the solutions were stored in polyethylene bottles.

2.8. Preparation of Calibration Curves

For each of the metals analyzed, a graph of absorbance against concentration was prepared and a straight-line curve passing through the origin was obtained according to Beer Lambert's law.

3. Results and Discussion

The results of the total metal concentrations of soils from West of Mines, Tudun Wada and Dadin Kowa in Jos, Plateau state are represented in Table 1 below.

Table 1. The pH, Percentage Dry Matter, Percentage Organic Matter and Percentage Carbonate Content of the Different Soil Samples

Sample	pH	Dry Matter %	Organic Matter %	Carbonate %
West of Mines	6.8	98.8	9.2	0.96
Tundu Wada	6.8	99.2	4.0	0.24
Dadin Kowa	6.8	99.0	7.4	1.44

Table 2. Total Metal Concentrations in Soil Samples

Soil	Metal Concentration (mg/kg)					
	Pb	Zn	Cr	Mn	Cu	Fe
West of Mines	ND	1328.36	89.93	637.81	79.02	12934.94
		±29.33	±2.16	±13.55	±2.61	±42.76
Tundu Wada	ND	289.93	17.34	568.61	ND	13228.94
		±2.50	±1.29	±2.00		±21.45
Dadin Kowa	ND	551.83	204.02	1002.10	ND	12873.68
		±17.41	±3.52	±1.66		±10.84

Table 3. Chemical Fractionation of Trace Metals in West of Mines Soil Sample

Chemical Fraction	Metal Concentration (mg/kg)					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	146.21	ND	13.58	ND	96.13
		±0.98		±0.32		±0.88
Carbonated	ND	621.56	ND	46.14	ND	1489.71
		±1.43		±0.16		±1.91
Fe-Mn (Oxides)	ND	334.15	36.28	42.66	33.44	3138.51
		±2.27	±1.08	±2.12	±0.55	±7.54
Organic	ND	55.13	ND	6.38	ND	1336.02
		±0.44		±0.39		±4.34
Residual	ND	168.47	45.67	222.83	44.83	6860.07
		±0.46	±0.35	±2.47	±1.44	±6.65

Table 4. Percentage Trace Metal Concentration in West of Mines Soil Sample

Chemical Fraction	% Composition					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	11.01	ND	2.15	ND	0.74
Carbonate	ND	46.79	ND	7.30	ND	11.52
Fe-Mn oxides	ND	25.15	40.34	54.23	42.31	24.26
Organic	ND	4.15	ND	1.00	ND	10.33
Residual	ND	12.68	50.78	35.27	56.73	53.04

Table 5. Chemical Fractionation of Trace Metals in Tudun Wada Soil Sample

Chemical Fraction	Metal Concentration (mg/kg)					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	21.15 ±0.21	0.14 ±0.00	70.52 ±1.14	ND	70.03 ±0.87
Carbonated	ND	44.94 ±0.1	ND	25.51 ±0.98	ND	62.72 ±1.82
Fe-Mn (Oxides)	ND	145.44 ±2.65	ND	178.58 ±4.10	0.52 ±0.17	4152.37 ±20.51
Organic	ND	76.67 ±0.54	ND	ND	ND	1489.81 ±1.29
Residual	ND	1.55 ±0.45	17.13 ±0.17	245.48 ±3.02	ND	7417.27 ±17.84

Table 6. Percentage Trace Metal Concentration in Tudun Wada Soil Sample

Chemical Fraction	% Composition					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	7.29	0.81	12.40	ND	0.53
Carbonate	ND	15.50	ND	4.49	ND	0.47
Fe-Mn oxides	ND	50.16	ND	31.41	ND	31.39
Organic sulphide	ND	26.44	ND	ND	ND	11.26
Residual	ND	0.53	98.79	43.17	ND	56.07

**Table 7. Chemical Fractionation of Trace Metals in Dadin Kowa Soil Sample**

Chemical Fraction	Metal Concentration (mg/kg)					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	25.68 ±0.64	ND	149.97 ±1.57	ND	243.47 ±2.84
Carbonated	ND	105.35 ±2.33	ND	265.19 ±3.98	ND	108.92 ±1.07
Fe-Mn (Oxides)	ND	170.60 ±1.10	ND	261.11 ±1.05	ND	2914.79 ±67.80
Organic sulphide	ND	60.79 ±0.66	54.13 ±1.35	20.75 ±0.69	ND	1491.07 ±4.15
Residual	ND	186.70 ±3.21	145.39 ±10.65	291.67 ±1.43	ND	8084.54 ±19.53

Table 8. Percentage Trace Metal Concentration in Dadin Kowa Soil Sample

Chemical Fraction	% Composition					
	Pb	Zn	Cr	Mn	Cu	Fe
Exchangeable	ND	4.65	ND	14.97	ND	1.89
Carbonate	ND	19.09	ND	26.46	ND	0.85
Fe-Mn oxides	ND	30.92	ND	26.06	ND	22.64
Organic sulphide	ND	11.02	26.53	2.07	ND	11.58
Residual	ND	33.83	71.26	29.11	ND	62.80

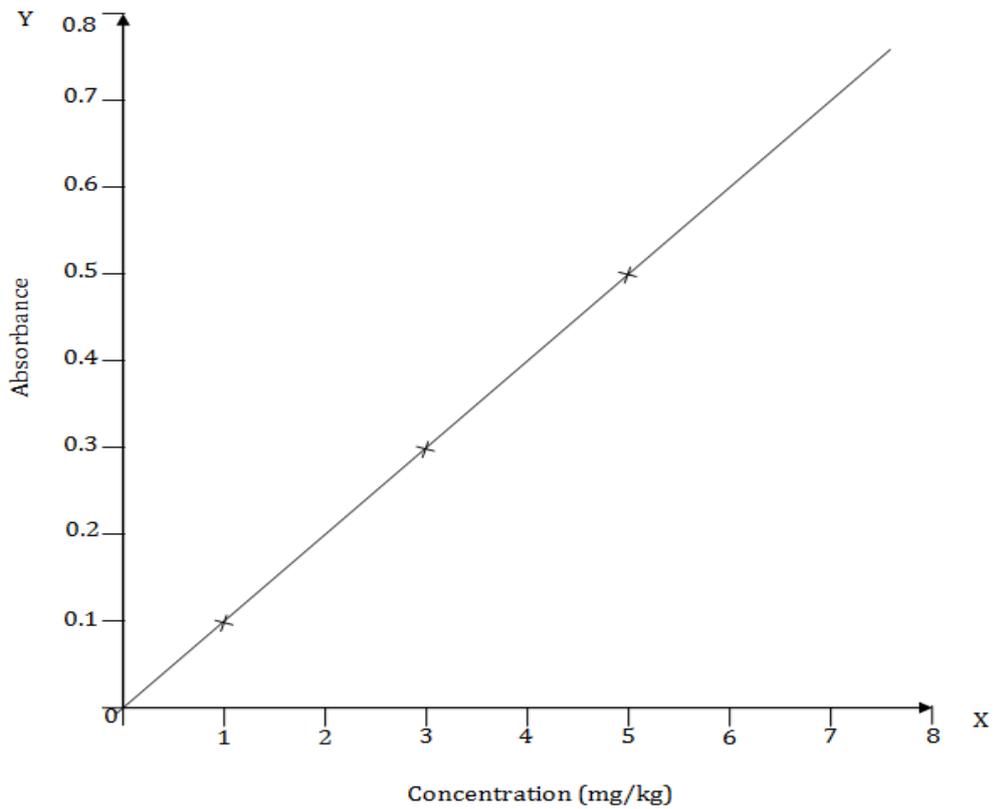**Calibration Curve for Lead (Pb) (Standard)**

SCALE -   X axis   -   2cm rep. 5 units

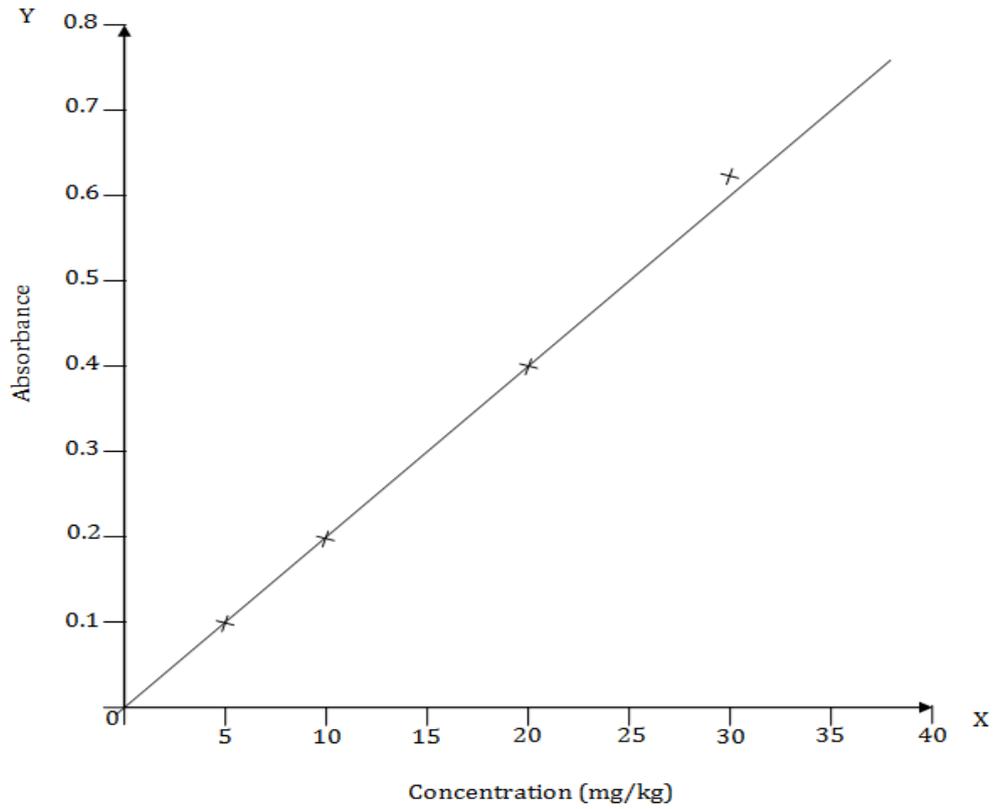   Y axis   -   2cm rep. 0.1 unit

Concentration (mg/kg)
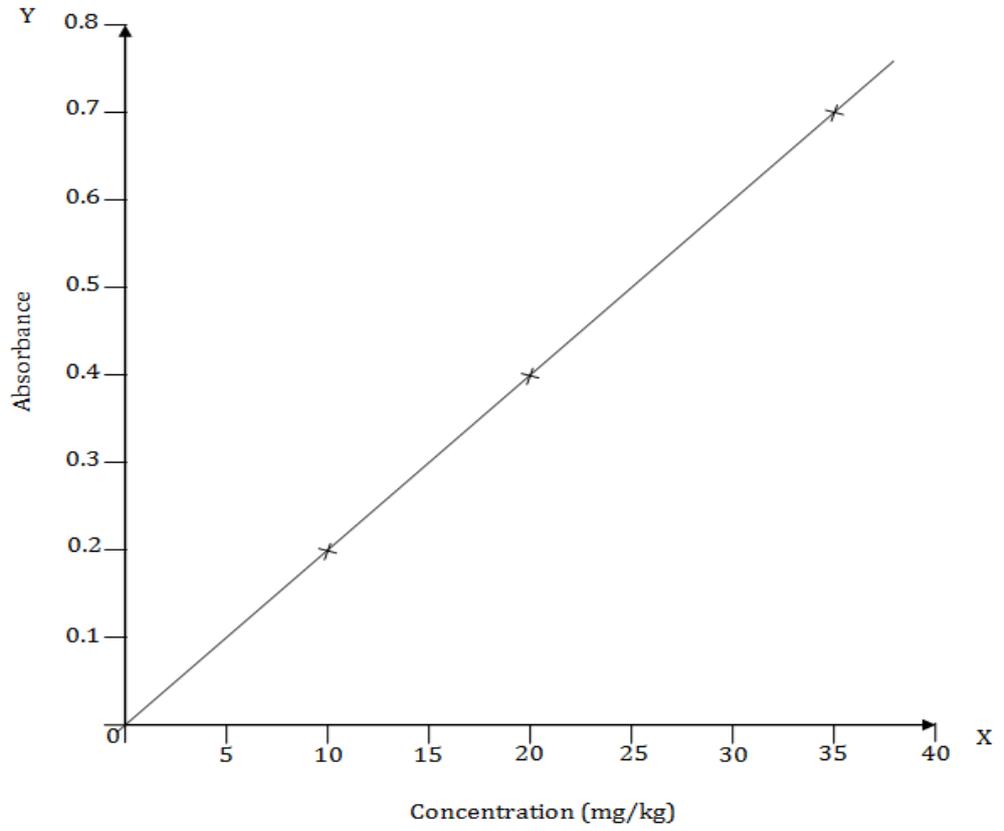
Caliberation Curve for Zinc (Zn) (Standard)

SCALE -   X axis   -   2cm rep. 1 unit

                Y axis   -   2cm rep. 0.1 unit

Concentration (mg/kg)
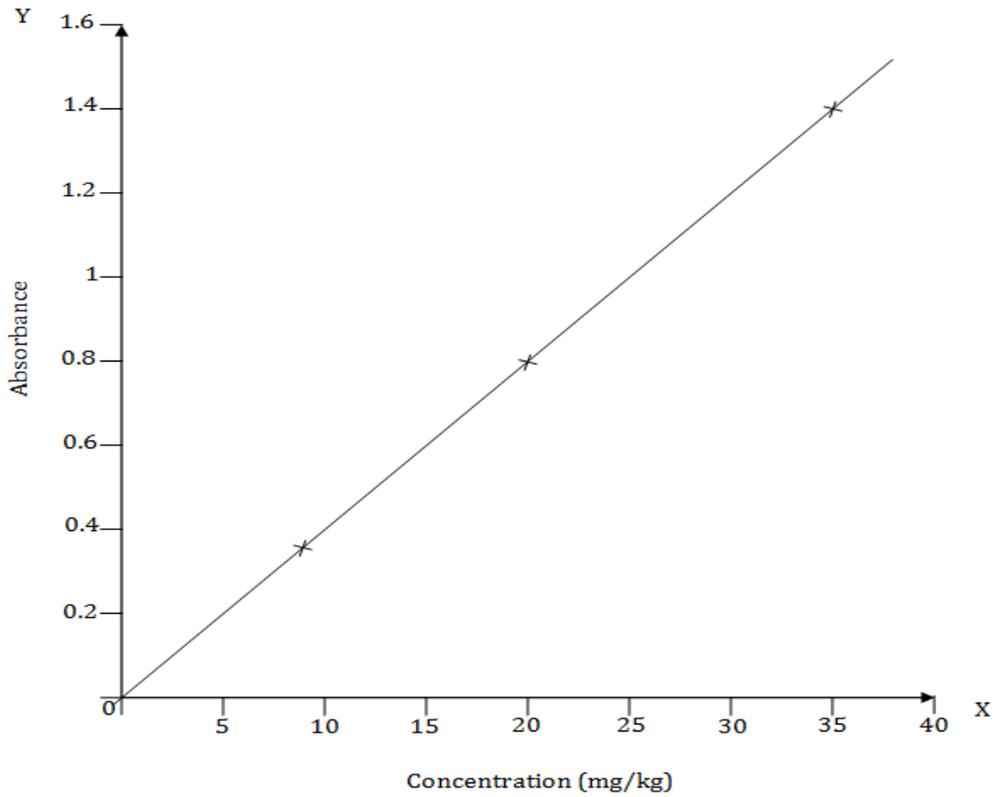
Caliberation Curve for Chromium (Cr) (Standard)

SCALE -   X axis   -   2cm rep. 5 units

                    Y axis   -   2cm rep. 0.1 unit
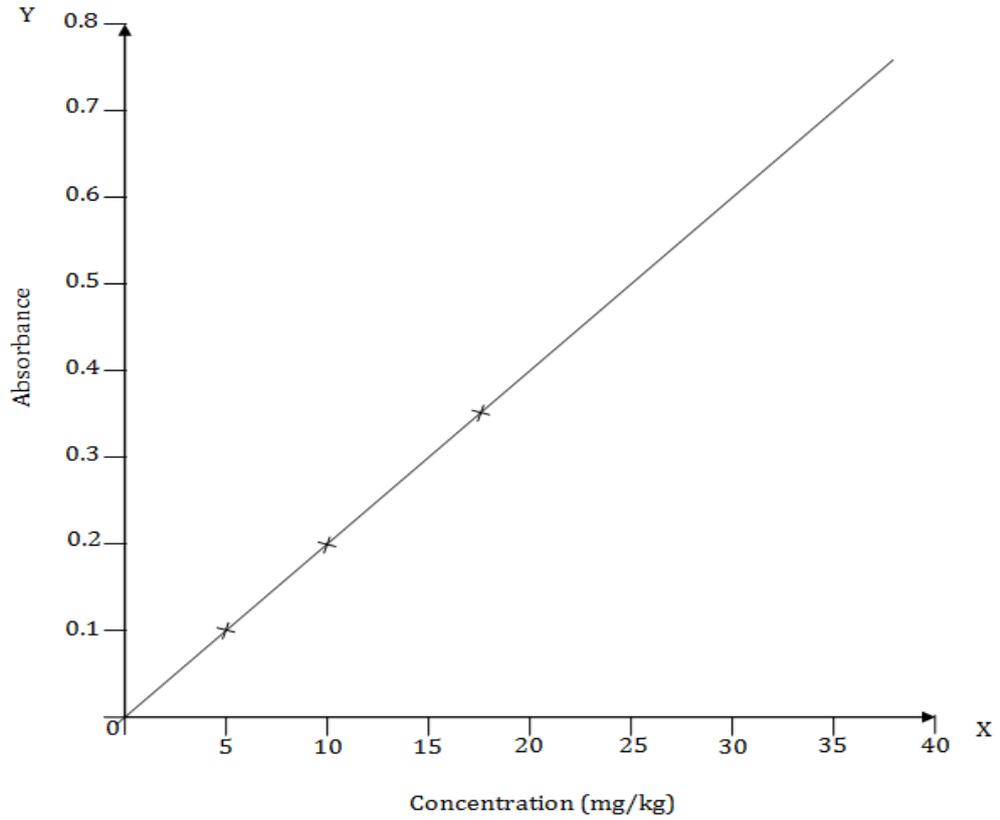

Caliberation Curve for Manganese (Mn) (Standard)

SCALE -   X axis   -   2cm rep. 5 units
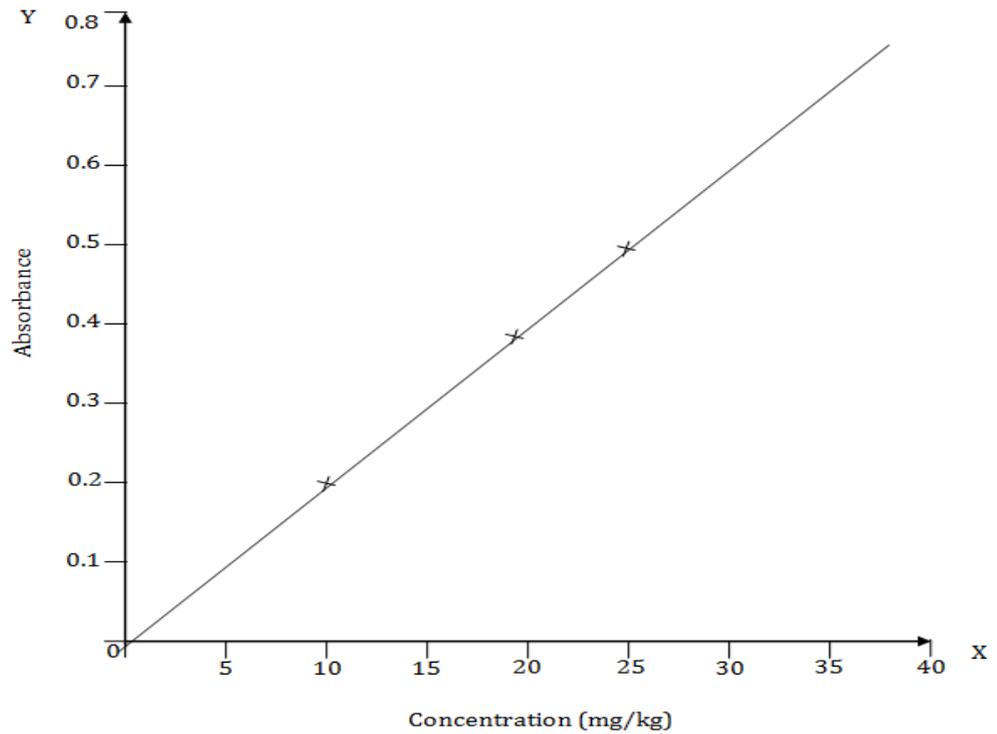
                    Y axis   -   2cm rep. 0.1 unit

Caliberation Curve for Copper (Cu) (Standard)

SCALE -   X axis   -   2 cm rep. 5 units
                 Y axis   -   2 cm rep. 0.1 unit

Concentration (mg/kg)

Caliberation Curve for Iron (Fe) (Standard)

SCALE -   X axis   -   2 cm rep. 5 units
                 Y axis   -   2 cm rep. 0.1 unit

Concentration (mg/kg)

3.1. Discussion

The concentrations of Lead (Pb), Zinc (Zn), Chromium (Cr), Manganese (Mn), Copper (Cu), and Iron (Fe) were determined from the three soil samples collected from the West of Mines, Tudun Wada and Dadin Kowa in Plateau state (Table 1). In all the three samples analyzed, Pb was absent. This could be due to its presence in concentrations below the detection limit of the instrument used. Copper and chromium were also absent in soil samples of Tudun Wada and Dadin Kowa. Zinc was found to be 1328.36 ±29.33mg/kg in West of Mines soil sample, 289.93 ±2.50mg/kg in Tudun Wada soil sample, and 551.83 ±17.41mg/kg in Dadin Kowa soil sample. Chromium was in the range of 89.93 ±2.16mg/kg in West of Mines soil sample, 17.34 ± 1.29mg/kg in Tudun Wada soil sample, and 204.02 ±3.55mg/kg, 568.61 ±2.00mg/kg and 1002.12 ±1.66mg/kg in West of Mines, Tudun Wada soil sample, and Dadin Kowa soil samples respectively. Iron ranged from 12934.94 ±42.76mg/kg in West of Mines soil sample, 13228.94 ±21.45mg/kg in Tudun Wada soil sample and 12873.68 ±10.84mg/kg in Dadin Kowa soil sample.

The range of these metals, except for zinc fall within the range specified for unpolluted soils and soil clean up [5]. Recoveries of these metals are between 85-106%. The concentration of these metals could be different depending on the month of collection of the samples [19]. The results can therefore be affected by the method of drying of the soil samples. From Table 2, there was no clear pattern of metal concentration between the soil samples.

3.2. Speciation

The five sequential extraction methods were used for the chemical speciation of the metals in soil samples from West of Mines, Tudun Wada and Dadin Kowa. Results of metal concentrations in each fraction are presented in Table 3, Table 5 and Table 7 respectively. Table 4, Table 6 and Table 8 represent the percentage total metal concentrations in soil samples of West of Mines, Tudun Wada and Dadin Kowa respectively.

3.2.1. Exchangeable Fraction

In all the soil samples studied, Lead (Pb) and Copper (Cu) were not detected in this fraction (Table 3 to Table 8). Chromium was also not detected except for Tudun Wada soil sample in which it is just 0.81%. Copper (Cu) also could not be detected and hence, confirms that the origin of copper was mainly anthropogenic since in uncontaminated soils this element is usually present at very low concentrations in the exchangeable and carbonate bound fractions or is even not detected (with flame AAS or ICP-AES) in the form [20]. Small fractions of Iron (0.53% - 1.89%), Zinc (4.65% - 15.50%) and manganese (2.15% - 14.99%) of total metal concentrations were found. This bulk of metals were in the non-exchangeable fraction.

3.2.2. Carbonate Fraction

In all the soil samples studied, Chromium and Copper were not detected in this fraction. This could mean that Chromium does not exist in this form due to the source of this metal in the soil samples. It could also be that the concentration was below the detection limit of the

instrument used. The distribution of metals in this fraction is generally low except for zinc. Zinc was found in all the fractions especially the carbonate, Fe-Mn and organic fractions for all the samples, owing to its high chemical mobility. The highest percentages were bound to carbonates and the reducible fractions scavenged by iron oxides whereas approximately 1-3% is the most important from an environmental point of view as the corresponding quantity is easily leached by water. High concentrations of this metal extracted into these fractions show the risk of release into the environment [21].

Iron is shared out among the Fe-Mn, organic and residue fractions, with the highest percentages in the Fe-Mn and residual fractions. The distribution of metals in this fraction is as follows: Zinc, 15.50% - 46.79%; Manganese, 4.49% - 26.46% and Iron, 0.47% - 11.52%. Copper and Chromium were not detected in this fraction. The carbonate fraction is relatively stable (slowly labile, poorly leachable) [21].

3.2.3. Fe-Mn Oxides Fraction

In all the soil samples manganese was present at low levels in the exchangeable, carbonate (except in Dadin Kowa soil sample) and organic bound fractions whereas it was extensively released into the Fe-Mn oxide bound fraction having concentrations of 54.23% in Table 3, 31.41% in Table 5 and 26.06% in Table 8. This reflects the dissolution of manganese. The percentages in the residue were usually lower than 50%. A similar behavior of manganese was observed in soils affected by different anthropogenic sources of pollution such as mining, industries and traffic. Risk of release into the environment exists for this metal [12]. In Table 4, iron has a concentration of 24.26%, 31.39% in Table 5 and 26.64% in Table 8. Zinc was found to have a concentration of 25.15%, 50.16% and 30.92% in Table 4, Table 6 and Table 8 respectively. The use of 0.04M hydroxylamine hydrochloride to extract metals associated with easily reducible manganese and iron was found to remove an average of 37.23% of manganese and an average of 26.09% of iron in the soil samples [14].

3.2.4. Organic Fraction

In this fraction, Zinc and Iron were found in concentrations of 4.15% and 10.33% respectively in Table 4, 26.44% and 11.26% respectively in Table 6 and 11.02% and 11.58% respectively in Table 8. Manganese was present only in Tudun Wada soil sample while Chromium was present only in Dadin Kowa soil sample. The organic fraction is not considered very mobile or available, since it is thought to be associated with high molecular weight stable humic substances, which could release small amounts of metal in a very slow fashion. Hence metals in this form are less harmful [22].

3.2.5. Residual Fraction

In all the soils analyzed, apart from Zinc in West of Mines and Tudun Wada soil samples, the residual fraction was predominant. Chromium and Iron were found in West of Mines, Tudun Wada and Dadin Kowa soil samples to have concentrations of 50.78% and 53.04%, 98.79% and 56.07%, and 71.26% and 62.80% respectively. Chromium

is mainly present in the residual fraction. This agrees with the results of many other studies, which reported a low availability for this element, both in clean and contaminated soils [23]. The residual fraction is considered the most stable, less reactive, less bioavailable of all extracted samples, since it is thought to be occluded within crystal lattice of layer silicates and well crystallized oxide minerals [24]. This means that the bulk of the heavy metals in the samples were a non-available, non-reactive, non-mobile and non-toxic form [1].

4. Conclusions

The aim of this study was to determine the chemical availability of trace of metals in soils of Police barracks in West of Mines, Tudun Wada and Dadin Kowa, in Jos, Plateau state. The total metal concentrations of Lead, Zinc, Chromium, Manganese, Copper and Iron were determined. There was no clear pattern of metal concentration between the soil samples. Five successive selective chemical fractions were used in the analysis to determine metals easily exchangeable, associated with easily reducible iron-manganese oxides, associated with organic matter, carbonate form and residual fraction.

In the exchangeable fraction, Lead and Copper were not detected in all the soil samples analyzed. Chromium was also not detected in two out of the three soil samples analyzed. The use of 0.04M hydroxylamine hydrochloride to extract metals associated with easily reducible manganese and iron oxides was found to remove an average of 37.23% of manganese and 26.09% of iron in the soil samples. Manganese was bound to organic matter in two out of the three soil samples while Chromium is bound to only one. Zinc and iron were found to be bound to organic matter. High level of zinc indicate that it may be derived from traffic sources especially vehicle tyres. Chromium and copper were not detected in all the soil samples analyzed for the carbonate fraction. The residual fraction is considered the most stable, less reactive, less bioavailable of all fractions extracted.

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