DETERMINATION OF HEAVY METAL CONCENTRATIONS IN TOP-SOIL OF SOME RESIDENTIAL AREAS OF KADUNA USING ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

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Abstract
This study assesses the concentration of some environmentally toxic heavy metals in selected residential areas of Kaduna city using Energy Dispersive X-Ray Fluorescence (EDXRF). The study is restricted to the southern areas of the city characterized by high population and industrial activities. Three composite samples of surface soil were collected from each of Barnawa, Narayi and Sabo areas using soil auger within a depth of 0 – 15 cm. Samples were homogenized and subjected to cone and quartering as well as pulverization and sieving, in order to obtain standard particle size for XRF determination of the metal concentrations. The range of mean concentrations (µg/g dry weight) of heavy metals were As (1.0 – 10.7), Pb (467 – 1833), Ni (583 – 753), Cr (267 – 300), Cu (407 – 467) and Zn (31- 320), respectively. The mean concentration of Cd was constant (1.0) for all locations. The mean concentrations of As and Cd were generally below the WHO/FAO maximum permissive limit while that of Pb, Ni, Cr and Cu were generally above. This calls for concern, especially in the case of Pb which is highly toxic and of no known biological use, as this could pose a potential risk to residents.

Keywords: heavy metals, soil, pollution, EDXRF, Kaduna

Introduction

Heavy metals are natural components of the earth crust which cannot be degraded or destroyed [1]. Rocks and soils are the principal natural sources of heavy metals in the environment. Pedogenesis is the major source of heavy metal contamination which may be overriding the effect of anthropogenic contamination wherever the parent material contains high level of heavy metals [2]. Atmospheric deposition as a result of acid rain and dew is another natural source of heavy metal pollution [3]. Dust storms, wild forest fires and volcanic eruption have also been identified as natural sources of heavy metal pollution of the environment [4].

Anthropogenic sources of heavy metal pollution include agricultural activities (such as the use of fertilizers, manures and pesticides), metallurgical activities (such as mining, smelting, metal finishing), energy production, transportation, microelectronic products and waste disposal [5].

Although, several metals are essential for biological systems, they must be present in a certain concentration range, such metals include copper, iron, manganese and zinc. At too high concentrations these metals become toxic. Non-essential metals are tolerated at very low concentrations and at high concentrations inhibit metabolic activities [6]. Heavy metals such as mercury, plutonium, lead and cadmium are highly toxic and have no known vital or beneficial effect on organisms [7].

The prolong presence of contaminants in the urban environment, particularly in soils, and their close proximity to the human population can significantly amplify the exposure of the urban population to metals via inhalation, ingestion and dermal contact [8]. The heavy metal pollution of urban soils investigated in many cities of Western Europe such as London [9], Berlin [10] or Hamburg [11], indicates large amounts of anthropogenic inputs and could have serious health implications.

In Northern Nigeria, Kaduna ranks second only to Kano, in terms of population (about 4,000,000 residents), industrial and commercial activities. The southern part of the city is more populated with the majority of the industries located there [12]. The aim of this study is to determine the concentrations of selected toxic heavy metals in surface soil in the residential areas of Barnawa, Narayi and Sabo districts in the southern part of the city, using Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry. These districts, though residential, are characterized by small scale agricultural activities, chemical industries, metal works, auto repair workshops, etc. The potential health implications of the metal concentrations were determined by comparison with WHO/FAO standards. DXRF had been shown to be a suitable technique for multi-element analysis in this type of sample. No chemical pretreatment is required, minimizing sample contamination, and small amounts of sample is required. It is a rapid and inexpensive method with a simple sample preparation. Quantitativeand qualitative analyses are performed without acid digestion processes and a great number of elements can be determined simultaneously within a short time [13].

Materials and Methods

Sample Collection: Each of the district; Barnawa, Narayi and Sabo, were divided into three zones from where composite samples of surface soil were collected at a depth of 0 – 15 cm, using a soil auger. Samples were collected into labeled polythene bags. Control soil samples were also taken from Paso village, an unpolluted rural area located far from the study sites. Samples were collected in July, 2012.

pH Determination: Soil pH were determined using a digital pH meter (Model: Kent EIL 7045/46). For each soil sample 2-mm sieved portion was added to distilled water (ratio 1:5) and allowed to stand for 30 min, stirring occasionally with glass rod. The electrodes of the pH meter were then inserted into the partly settled suspension and the pH taken [14].

Sample Preparation and Pre-Treatment for EDXRF Analysis: After removal of debris from samples, samples from each zone were arranged in a cone form and a sharp straight edge meter rule was used to divide the coned sample into four equal parts. Two opposite potions of the divided cone were collected back into the sample bag while the remaining two opposite portions were remixed, coned and quartered and the collection of the two opposite portions was repeated until a sizeable analyzable portion of the samples were obtained. 50 g of the sizeable portion of each sample was weighed on a petri dish and oven-dried at 40°C for about 3 hrs, to remove moisture and facilitate grinding and sieving. The dried samples were then disaggregated in a porcelain mortar to a pulverized size (loose powder), which were then pulverized in a pulverizing machine to a fine powder (150 micron) and sieved with a 2 mm mesh to remove coarse particles and homogenized. 5 g of the dried, ground, sieved and homogenized sample was then placed in an XRF sample cup for analysis [15].

Elemental Analysis: Metal concentrations in soil samples were determined using Energy Dispersed X-Ray Fluorescence (EDXRF) Spectrometer (Model: Minipal 4), following the manufacturers specified conditions. For quality assurance of methods, reference samples of soil (SRM 989, WEPAL), were analysed under similar conditions.

Results and Discussion

The pH of the soil samples ranges between 6.4 (weakly acidic) and 7.1 (neutral). In the analysis of certified reference sample, good agreements were achieved between the certified and obtained values, with % recovery ranging from 97 to 104 %. This is comparable with the results obtained by Robinson, *et al* [16], in the analysis of same reference sample. t-test results (at 95 % confidence interval) showed that statistically there exist no significant difference between the certified and obtained values.

Table 1 shows the mean concentrations of heavy metals in the study areas. The range of mean concentrations (µg/g dry weight) were As (1.00 – 10.67), Pb (467 – 1833), Cd (1.02 – 1.50), Ni (583 – 753), Cr (267 – 300), and Cu (407 – 467), respectively.

Table 1: Mean Concentrations (µg/g dry weight) of Heavy Metals in Soil Samples

	Mean Concentration of Heavy Metals						
District	As	Pb	Cd	Ni	Cr	Cu	Zn
Barnawa	1.00 ±0.00	1600.33 ±88.21	1.50 ±0.10	753.33 ±37.56	273.33 ± 40.55	466.67 ± 46.31	320.00 ± 72.43
Narayi	2.00 ±0.00	467.33 ±46.33	1.02 ±0.12	606.67 ±81.70	300.00 ± 26.46	456.67 ± 32.83	30.67 ± 9.42
Sabo	10.67 ±9.67	1833.67 ±131.59	1.45 ±0.10	583.33 ±17.64	266.67 ± 26.67	406.67 ± 14.53	256.67 ± 28.48
Control	1.00 ±0.00	41.70 ± 9.25	1.00 ± 0.10	33.31 ± 11.21	21.00 ± 4.45	15.61 ± 3.25	52.21 ± 4.73
WHO/FAO Limit [17]	25	100	3	75	400	100	300

Barnawa has the highest concentrations of Cd, Ni, Cu and Zn while Sabo has the highest concentrations of As and Pb. Narayi has the highest concentrations of only Cr. The high concentrations of As and Pb in Sabo soil could be traced to high volume of traffic and industrial activities, such as metal works, chemical industries and auto repairs, in the area. It has the major road leading to the Kaduna Refinery and Petrochemical Company (KRPC). The high level of Cu and Zn in Barnawa might be due to additional burden from soil and crop treatments, as this zone is associated with more agricultural activities. The concentration of Cu in soil could be elevated by soil and crop treatment such as fungicides, fertilizers and the use of chicken dung [1].

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The mean concentrations of As, Cd and Zn were generally below the WHO/FAO maximum permissible limits while that of Pb, Ni, Cr and Cu were generally above. This calls for concern, especially in the case of Pb which is highly toxic and of no known biological use, as this could pose a potential health risk to residents. Pb is associated with the damage of bones, brain, blood kidney and thyroid gland [18] while high accumulation of Ni causes lipid peroxidation resulting in cell damage as well as interference with the metabolism of essential metals [19]. Cr^{6+} is carcinogenic while Cu accumulation inhibits enzyme activities and oxidation of haem iron to form methaemoglobin which results in decrease oxygen-carrying capacity of blood [20].

Conclusion

It is evident that accumulation of the studied heavy metals occurred in the study areas, as the concentrations of the metals in soil samples are higher than that of the control site. This could be attributed to high level of industrial and domestic activities in these highly populated areas of the city. Continuous monitoring of the accumulation of these metals is recommended, especially Pb, Ni, Cr and Cu, as they pose a potential health risk to the residents. Leaching and run-off could cause these metals to pollute the underground and surface waters. Uptake and accumulation of the metals from the soil by garden crops could be detrimental to their consumers. Residents need to avoid drinking water from shallow wells. Remediation measures could also be applied to farms and gardens before use for crop production.

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