DETERMINATION OF Pb, Cd, Cu AND Zn CONCENTRATIONS IN SOIL OF AN ABANDONED CITY MARKET IN MINNA, NIGERIA

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Abstract

Concentrations lead, cadmium, copper and zinc were determined in soil samples from a large portion of land in the central area of Minna, North-central Nigeria. The land was formerly used as the city central market. The area was divided into 20 zones from which composite samples of surface soil were collected for analysis. Control samples were also collected at a distance of 500 m from the area. Samples were digested using a 3:1 mixture of concentrated HNO_3 and $HClO_4$ acids. Recovery test on the method of digestion gave % recoveries > 95 % while in the analysis of reference materials of soil, t-test results (at 95 % confidence interval) showed that statistically there exists no significant difference between certified and obtained values. Digests were analysed using a flame atomic absorption spectrophotometer. Mean concentration of the heavy metals (µg/g dry weight) in the soil samples were Pb; 115 ± 11, Cd; 2.8 ± 1.2, Cu; 132 ± 12 and Zn; 322 ± 43. Pollution load index (PLI) values revealed that the abandoned market soil is generally more polluted with these metals due to commercial activities. The mean concentrations of the metals in soil samples were generally higher than the WHO maximum permissive limits, except for Cd. This calls for concern because of possible contamination of sources of domestic water of adjourning residential areas due to run-off and leaching. Also the area might later be utilized for other purposes posing the risk of human exposure.

Keywords: heavy metals, soil, contamination, city market, Minna

Introduction

In recent years, pollution in large areas of land by heavy metals and chemicals has become a major concern. All toxic heavy metals can endanger human health on slight exposure; the critical organs they affect in the body differ from one metal to another [1]. As the metals journey through the environmental and biological reservoirs, they can undergo chemical transformations which determine their bioavailability and toxicity [2]. They may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture, industrial, or residential settings. Ingestion is the most common route of exposure in children. Children may develop toxic levels from the normal hand to mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food. Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous nutrition, or from a suicide or homicide attempt [3]. At high concentrations in the environment, these heavy metals may enter food chains and result in health hazards. They can directly or indirectly damage DNA, increasing risk of cancer. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues [3]. The presence of toxic metals in soil can severely inhabit the biodegradation of organic contaminants. It can also pose risks and hazards to humans and the ecosystems through direct ingestion or contact with contaminated soil, the food chain, drinking of contaminated ground water, reduction in food quality via phytotoxicity, reduction in land usability [2]. The toxicity of heavy metals has been, for many years, a global challenge. Historical cases of catastrophic and endemic exposures of heavy metals abound in literature, such include the Minamata disease [4], the Pink disease [5], the Bradford sweet poisoning [6], the *itai-itai* disease [7], Iraq mercury poisoning [8], Alexander Litvinenko poisoning [4], and of recent the Zamfara State lead poisoning [9], to mention but few.

Depending on the dose, lead exposure in children and adults can cause a wide spectrum of health problems, ranging from convulsions, coma, renal failure and death at high level to subtle effects on metabolism and intelligence at low level of exposure [10]. The health implications of cadmium exposure are exacerbated by the relative inability of human beings to effectively excrete cadmium [11]. High dose exposures can result in chronic lung disease, testicular degeneration, prostate cancer, kidney failure and bone fractures [12]. High level of copper accumulation in the body leads to nausea, vomiting, abdominal pain, breakdown of red blood cells and Wilson's disease in children while acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches [10]. Though studies on several sources of these heavy metals accumulation in the soils are well documented, little attention has been focused on vicinities of other human activities such as markets [13, 14, 15]. The aim of this study is to assess the levels of the heavy metals Pb, Cd, Cu and Zn in soil of an abandoned city market in Minna, a city in the North-Central region of Nigeria, vis- a- vis the possible health risks of these metals as compared to established international permissive limits.

Materials and Methods

The abandoned land (formerly the city central market) was divided into 20 zones of approximately equal sizes. Composite samples of surface soil (0 – 20 cm depth) were collected from each of the zones with a stainless hand-trowel, and also from two other zones (as control) at a distance of about 500 m to the study site. Samples were collected in August 2012. The area used as control was without any traffic, commercial or agricultural activities and free of refuse dumps. The soil samples were air-dried for 7 days before analysis. Prior to analysis, the samples were re-dried in the oven at 110 °C for about 3 hours, crushed in a porcelain mortar and sieved through a 2 mm plastic sieve to obtain fine soil particles [16]. 1 g of the fine soil particles from each zone was digested in triplicates, with 3: 1 HNO_3 – $HClO_4$ in 150 cm^3 conical flask on hot plate in a fume cupboard for 3 hours at 80 °C. The digest was allowed to cool and then filtered into 100 cm^3 standard flask and make up to the mark with de-ionized water ready for atomic absorption spectrometric determination [17]. The pH of the soil samples was determined in water using a digital pH meter (Model: Kent EIL 7045/46). For each soil samples 2-mm sieved portion was added to water in the ratio 1:1. The mixture was allowed to stand for 30 minutes stirring occasionally with glass rod. The electrodes of the pH meter were then inserted into the partly settled suspension and the pH taken [18]. For quality assurance of methods, a recovery study was carried out by spiking 1g of five different soil samples each with 1 cm^3 of standard solutions of the metals Pb, Cd, Cu and Zn. In addition, reference samples of soil (SRM 989 WEPAL), were analysed, under similar conditions [19]. Metal concentrations in the working standards and digests were determined using flame atomic absorption spectrophotometer (Perkin Elmer A-ANALYST 200), using air-acetylene flame. Blanks were also determined to ascertain the contribution of reagents to metal levels. Instrument calibration and blank determination were carried out at intervals of ten samples. The results obtained were subjected to statistical analysis [17].

Results and Discussion

The pH of the soil samples ranges between 6.5 (weakly acidic) and 7.1 (neutral). The results of the recovery study of heavy metals spiked soil samples are given in Table 1. The mean percentage recovery ranged between 95.3 % and 98.5 %, confirming the efficacy of methods.

Table 1: Results of Recovery Study of Spiked Soil Samples: Mean Percentage Recovery

Metal	Pb	Cd	Cu	Zn
Mean % Recovery	95.3	95.9	98.5	97.4

The t-test results (at 25 % confident interval) for the analysis of certified reference material are shown in Table 2. The % recovery in the analysis of the reference sample is > 95%. This is comparable to the results obtained by Robinson, et al [19], in the analysis of the same reference sample. t-test results (at 95 % confidence interval) showed that statistically there exists no significant difference between the certified and obtained values. This further confirms the efficacy of the methods.

Table 2: Results of the analysis of soil reference sample (SRM 989 WEPAL)

Metal	Pb	Cd	Ni	Cr	Cu	Zn
Certified Value (μg/g)	282 ±4	8.22 ±0.11	53.9 ±1.3	178 ±5	153 ±4	1020 ±30
Observed Value (μg/g)	285 ±2	7.9 ±1.2	52.7 ±2.2	175 ±7	146 ±3	1067 ±14
Recovery (%)	101	96	98	98	95	105
t_{tab}*	4.30	4.30	4.30	4.30	4.30	4.30
t_{cal}	2.60	0.46	0.94	0.74	4.04	5.8

* At 95% Confident Intervala, n = 3

The mean concentrations of the heavy metals (μg/g dry weight) are given in Table 3. The concentrations of the metals were generally higher in soil samples from the abandoned city market than in samples from the control area. These differences are statistically significant ($p < 0.005$) and show some levels of pollution by these metals in the study site. There existed positive correlations between concentrations of metals in soil, suggesting similar sources of metal enrichment which could be linked to the market activities. As the major sources of heavy metal pollution in urban areas are anthropogenic while contaminations from natural sources predominates in the rural areas [20]

Table 3: Mean Concentration (μg/g dry weight) of Heavy Metals in Soil of Study and Control Sites

	Pb	Cd	Cu	Zn
Study Site	115 ± 11	2.8 ±1.2	132 ± 12	322 ± 4 3
Control Site	14.2 ± 4.1	1.2 ± 0.1	19.3 ± 7.1	72.4 ± 9.3
PLI	8.10	2.33	6.84	4.45
WHO Permissive Limits [21]	100	3	100	300

Generally the order of accumulation of metals in soil was Zn > Cu > Pb > Cd. The Pollution Load Index (PLI) (Table 3), shows the degree of pollution of the study site compare with the control site. This was calculated using the following equation [22]:

$$PLI = \frac{\text{concentration of metal in study side}}{\text{concentration of metal control site}}$$

PLI values show that the abandoned market soil is more polluted with the metals. This could be attributed to the commercial activities and small scale industries associated with the market. The order of the PLI value is Pb > Cu > Zn > Cd. This shows that the study site is strongly polluted with Pb and Cu followed by Zn.

Conclusion

It is evident from this study that the abandoned city market soil is polluted with the metals Pb, Cu and Zn, as the concentrations of these metals in soil samples were higher than the WHO maximum permissive limits (Table 3). The high concentrations of these metals in the soil call for concern, especially in the case of Pb, which is highly toxic and of no known biological use. Leaching and run-off could cause these metals to pollute underground and surface waters, which is a potential health risk to residents in the vicinity of the abandoned market. Future utilization of the area for other purposes could also pose the risk of human exposure to these metals. The treatment of the surface soil is recommended, this could include phyto-remediation, before the area is converted to another use.

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