HEAVY METALS CONTENT IN SOIL AROUND THE VICINITY OF BLACKSMITH WORKSHOPS IN ZARIA, NIGERIA

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Abstract: This research workwas carried out to determine the heavy metals content in soil around the vicinity of blacksmith workshops in Zaria, Nigeria. Soil samples were collected from five different locations Chikaji, Danmagaji, Gwargwaje, Jushi waje, and Kasuwan mata where local blacksmith activities are being carried out. Soil sample was also collected about 10 km away from these locations to serve as the control. Dried and sieved soil samples were digested using aqua regia and Cd, Cr, Cu and Pb were determined using atomic absorption spectrophotometer.The physicochemical parameters such as moisture content, particle size/soil texture, organic matter, cation exchange capacity, pH, chloride, sulphate and phosphate contents in the soil were also determined. The results obtained indicated that the soil was sandy loam. The Cd(0.10±0.00 -2.35±0.05 mg/kg), Cr(0.49±0.07-2.64±0.06mg/Kg, Cu(36.1±0.75 -105.56±8.97 mg/kg)and Pb(46.19 - 140.70 mg/kg) levels at the study sites were higher than the corresponding control values. The degree of pollution of various metals using the graded standard of Nemero pollution index varied. The concentrations of the metals were found to be above the recommended limits given by USEPA/WHO. This could pose risks and hazards to human and the ecosystem through direct ingestion of contaminated soil.

Keywords: Blacksmith, contamination, health hazards, heavy metals, pollution index, soil

Introduction

Heavy metals occur in the environment naturally and are released during anthropogenic activities. Soil contamination with heavy metals results from human-related activities such as mining, smelting and agriculture (Najib *et al*., 2012; Ruqia *et al*., 2015), as well as earth related activities. Contamination of the environment by heavy metals due to certain industrial activities has been on the rise in recent times. They accumulate over time in soils which act as a sink from which these toxicants are released to the groundwater and plants, and end up through the food chain in man thereby causing various toxicological manifestations (Momodu & Anyakora, 2010). Chemical and metallurgical activities are the most important sources of heavy metals in the environment, sewage-treated sludge, known as bio solids and used as fertilizers on the soil can contribute to heavy metal levels in soil (Yang *et al*., 2011).

These pollutants are putting the health of people at risk especially in developing countries where environmental pollution prevention and regulation measures have not been taken serious (Idris & Kamaluddeen, 2015). Most problems of soil pollution are associated with large amount of heavy metals deposited on it through disposed waste. These metals which are not biodegradable are accumulated in living organisms when released in the environment. Although trace quantities of certain heavy metals are essential to animal and plant growth, they are of considerable environmental concern due to their toxicity and cumulative behavior (Ruqia *et al.*, 2015). Heavy metals may pose risks and hazards to human and the ecosystem through: direct ingestion of contaminated soil, the food chain (soil-plant-human or soil-animal-human), reduction in land usability for agricultural production causing food insecurity, and land tenure problems (Raymond & Felix, 2011; Mclaughlin *et al.*, 2000). In most countries (developed and developing alike) despite overwhelming literature on the toxicity of these metals, avoidable contaminations are on the increased. Nigeria soil has been bio accumulated by most heavy metals in the environment resulting to serious disease infection to crops, animals and human beings. The auditing and monitoring of metals in environment (soil, water and food) are becoming essential aspects of pollution studies (Mandre *et al*., 1998).

A blacksmith is a metal smith who creates objects from wrought iron or steel by forging the metal, using tools to hammer, bend, and cut. Blacksmiths produce objects such as gates, grilles, railings, light fixtures, furniture, sculpture, tools, agricultural implements, decorative and religious items, cooking utensils and weapons.High concentration of heavy metals is toxic and hazardous to health and can cause some disorder thereby disruption of function in vital organs and glands such as the heart, brain kidney, and liver.Therefore, determination of the amount of these heavy metals and the trend of change in their concentration will enhance proper awareness and development.

It has been recently observed that the soil within vicinity of Zaria has been extensively polluted by heavy metals due to anthropogenic activities. This research work was carried out to determine the amount of heavy metals such as lead cadmium, chromium, nickel and copper in soil around metal smelting areas (blacksmith) in Sabon Gari-Zaria in Kaduna statewith a view to establish the pollution or contamination status of the soils as a result of anthropogenic input.

Materials and Methods

Sample collection

Soil samples were collected randomly into polythene bags from different blacksmith workshops in different locations: Chikaji, Danmagaji, Gwargwaje, Jushi waje, and Kasuwan mata in Zaria metropolis, Kaduna state Nigeria in the month of May, 2015. The soil samples (150 g) werecollected from the surface to a depth of 20 cm around each blacksmith workshop using hand trowel, mixed and a composite sample was used for analysis. Another sample was collected about 15 km away from the sites to serve as control.

Sample treatment

The soil samples collected were air dried at room temperature for a period of three days. Stones and macro organic matter were hand picked out from dried samples, after which the soil samples were grounded in a mortar and sieve through a 2 mm sieve. The 2 mm air dried samples were kept in polythene bags and stored under dry conditions for further analysis.

The physicochemical parameters of the soil such as moisture content, pH (in 0.01 moldm^{-3} $CaCl_2$ solution), particle size/soil texture (Bousous hydrometer method), organic matter (Walkley-Black, dichromate oxidation method), cation exchange capacity (ammonium acetate method), chloride, sulphate (Turbidimetric method) and total phosphorus (stannous chloride method) were determined as described by Agbenin *et al*. (1995).

One gram (1.0 g) of each of the sieved soil samples were weighed into separate digestion flasks, 10cm^3 of HNO_3 – $HClO_4$ acid mixture (3:1 by volume) was added and the content mixed. The flask was placed on the hot plates inside fume cupboard. The sampleswere digested until a clear solution was obtained (white fuming stage). Distilled water was added periodically to avoid drying up of the digest. The flask was then removed from the hot plate and 30 cm^3 of distilled water was added within a few minutes. The content was filtered through a Whatman No. 41 filter paper into a 50 cm^3 volumetric flask and then made up to the mark with distilled water (Zakka *et al.,* 2014). Cadmium, chromium, copper,leadand nickel were analysed in the soil samples using atomic absorption spectrometer (Model D100XB4J), with the analyses being done in triplicate.

Physicochemical Parameters of the Soil

Table 1 shows the results of the physicochemical parameters of the soil samples. The results indicated that the soil is sandy loam. These soils contain various levels of sand, silt and clay particles which exhibit light and heavy properties in various proportions. The soil of Kaduna-Zaria is reported to be sandy clay loam to sandy clay with sandy loam mainly on the top soil (Zakka *et al.,* 2015). The pH of the soil ranges between 6.95 ± 0.05 to 7.75 ±0.05. The soil at the study sites is slightly acidic and slightly alkaline at the control site. Soils generally have pH values range of 4.0-8.5 owing to the buffering by Al at the lower end and $CaCO_3$ at the upper end of the range (Wild, 1988). The percentage moisture content of the soil ranges from 0.20 ± 0.00 to 1.11 ± 0.10% which is below the given standard of 1.25 to 1.40% (Jeff, 2001). This reveals that the sample sites and control site is a kind of soil with less moisture content because sand is predominant which causes higher infiltration rate of water. Soil texture is important in determining the amount of water soils can hold. Increase in sand particles causes small amount of water to be held tightly close to the surface by adhesion.

Results and Discussion

Table 1: Results of the analysis for Physicochemical Parameters of soil

Sample	%Clay	%Silt	%Sand	Soil Texture	pH	Organic matter	Moisture Content	CEC (Meq/100g)
Chikaji	16	18	66	Sandy loam	7.65±0.06	3.61 ±0.66	0.55 ± 0.05	10.50 ±0.50
Danmagaji	14	18	68	Sandy loam	7.73±0.07	2.88 ±0.02	1.11 ± 0.10	10.05 ±0.15
Gwargwaje	16	18	66	Sandy loam	7.75±0.05	1.99 ±0.07	0.65 ± 0.05	9.60 ± 0.10
Jushi waje	14	18	68	Sandy loam	7.55±0.05	3.58 ±0.08	0.86 ± 0.05	9.70 ± 0.10
Kasuwan mata	16	20	64	Sandy loam	7.75±0.05	3.34 ±0.05	0.40 ± 0.00	7.30 ± 0.10
Control	14	10	76	Sandy loam	6.95±0.05	3.80 ±0.19	0.20 ± 0.00	9.45 ± 0.15

This study showed that the soil is sandy loam which has high percentage of sand, hence low water-holding capacity (Jeff, 2001). The cation exchange capacity (CEC) for the soil samples ranges from 7.30 ± 0.10 to 10.50 ± 0.50. The CEC of mineral soil have higher values than those of sandy clay. Cation exchange capacity tends to increase with increase clay content (Mordi *et al.*, 2002). The values for the organic matter of the soil ranges from 1.99 ± 0.01 to 3.80 ± 0.10 % compared to that of Nigerian savannah (0.8 to 2.9 %) (Wild, 1988). This type of soils falls into classes of soils known as mineral or inorganic soils. This type of soil has been described as the upper and biological weathered portion of the regolith (Olle, 2013; Swartjes, 2011). The soil organic matter (SOM) controls several soil properties. These substances increase CEC of soils; from 20% to70% of CEC value due to organic matter (e.g., Chernozems/Mollisols). Great sorption capacity for trace cations is beneficial in reducing activity of an excess of trace metals. On the contrary, organic by-products (municipal biosolids) may reduce bioavailability of some micronutrients. Theadsorption of some metals (Cd, Ni, and Cu) is significantly enhanced at the presence of humicsubstances (McCauley *et al*., 2009).

Heavy metal concentrations in the soil

Figure 1 shows the mean concentrations of the metals analysed in the soil from various sampling locations: Chikaji, Danmagaji, Gwargwaje, Jushi waje, and Kasuwan mata and compared with the control and standard limits given by USEPA/WHO.The results indicated that the Cd (0.10±0.00 - 2.35±0.05 mg/kg), Cr (0.49±0.07 - 2.64±0.06 mg/Kg, Cu (36.1±0.75 -105.56±8.97 mg/kg) and Pb (46.19 - 140.70 mg/kg) levels at the study sites were higher than the corresponding control values. Using one way ANOVA followed by Turkey's HSD Test (Table 2), the means sharing the same superscript are not significantly different from each other (P > 0.05) or means that have no superscript in common are significantly different from each other (P < 0.05).

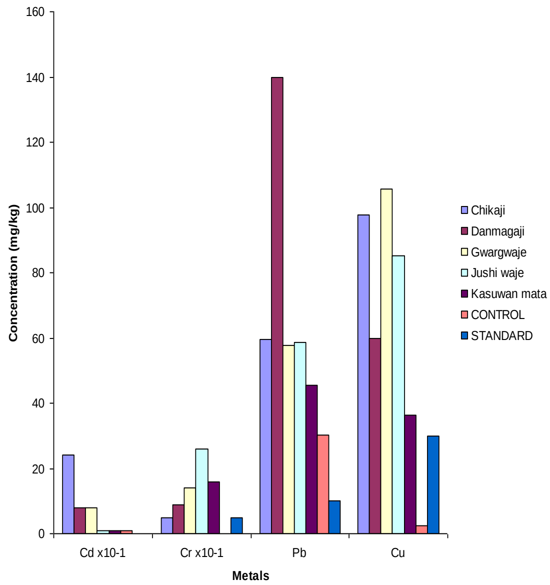

Fig. 1: Concentration of heavy metals in soil around the vicinity of different blacksmith workshops

Single contamination index (CI) was employed to evaluate the degree of heavy metal pollution in soil. The graded Nemero Pollution Index (Table 3) reflects the degree of soil pollution caused by various heavy metals pollutants (Hong-gui *et al*., 2012). The degree of soil polluted with Cd, Pb and Cu was very high (P > 3) at Chikaji and Gwargwaji, while soil from

Jushi waje and Kasuwan mata was very high with Cr and Pb, but Cd and Pb were very high at Danmagaji. The pollution status for Cr and Cu was high ($2 < P \leq 3$) at Gwargwaji and Jushi waje, respectively. The soils at Danmagaji and Kasuwan mata were slightly polluted ($1 < P \leq 2$) with Cr, Cu and Cd, Cu, respectively. Only Cr and Cd were at warning stage ($0.7 < P \leq 1$) at Chikaji and Jushi waje respectively. Non of the soil samples collected from the five blacksmith workshops was found to be clean ($P \leq 0.7$) from the heavy metals analysed, due to the impact of the blacksmith activities in these studied areas.

Table 2: Mean Concentration (mg/kg) Levels of Heavy Metals Using One Way ANOVA Multiple Comparison

Sampling site	Cd	Cr	Pb	Cu
Chikaji	2.35 ± 0.05^{c}	0.49 ± 0.07^{b}	59.50 ± 1.06^{c}	97.73 ± 0.28^{de}
Danmagaji	0.82 ± 0.12^{b}	0.85 ± 0.05^{c}	139.71 ± 0.10^{d}	60.01 ± 0.56^{c}
Gwargwaje	0.80 ± 0.10^{b}	1.39 ± 0.01^{d}	57.84 ± 0.160^{c}	105.56 ± 8.97^{e}
Jushi waje	0.10 ± 0.00^{a}	2.64 ± 0.06^{f}	58.59 ± 2.01^{c}	85.08 ± 0.56^{d}
Kasuwan mata	0.11 ± 0.01^{a}	2.64 ± 0.06^{e}	45.60 ± 0.60^{b}	36.15 ± 0.75^{b}
Control	0.10 ± 0.00^{a}	0.00 ± 0.00^{a}	30.20 ± 1.20^{a}	2.41 ± 0.045^{a}

n = 2; Mean ± S.E.M

Table 3: The Graded Standard of the Nemero Pollution Index Method for Soil From Different Blacksmith Workshops

	I $P \leq 0.7$ Clean	II $0.7 < P \leq 1$ warning	III $1 < P \leq 2$ slight	IV $2 < P \leq 3$ high	V $P > 3$ very high
Chikaji	-	Cr	-	-	Cd, Pb, Cu
Danmagaji	-	-	Cr, Cu	-	Cd, Pb
Gwargwaje	-	-	-	Cr	Cd, Pb, Cu
Jushi waje	-	Cd	-	Cu	Cr, Pb
Kasuwan mata	-	-	Cd,Cu	-	Cr, Pb
Control	Cr, Cu	Cd	-	-	Pb

– = not detected

The cadmium concentration ranged from 0.10±0.00 to 2.35±0.05 mg/Kg for the study sites and 0.10±0.00 mg/Kg for control site. The average value was found to be below the permissible limit.Cadmium is a non-essential metal and is toxic to human and animals or plants even at lower concentration. Once accumulated in the kidney then it staysthere, resulting in high blood pressure and kidney disease and difficultto remove by excretion. Cadmium directly damages nerve cells. It inhibits the release of acetylcholine and activates cholinesteraseenzyme, resulting in a tendency forhyperactivity of the nervous system (Alloway, 1990). Critical level of cadmium in soilis 3 – 5 mg/kg (Kabata-Pendias & Pendias, 1992). At this level it could pose risks and hazards to human and the ecosystem through: direct ingestion of contaminated soil.

The mean concentration of chromium in all samples ranges from 0.49±0.07 to 2.64 ± 0.06 mg/Kg and found to be below the detection limit for the control sites. This shows that the mean concentrations are above acceptable limit of 0.5 mg/Kg in the soil given by New York State Department of Conservation (NYSDEC) standards due to the activities of the blacksmith.Chromium is one of the known environmental toxicpollutants in the world (McGrath & Smith, 1990). Besides thesechromium plating and alloys in motor vehicles is considered to be amore probable source of chromium (Shaheen, 1975). An elevatedconcentration between 5-30 mg kg^{-1} is considered critical for plantsand could cause yield reduction (Vern and Don, 2011; Kabata-Pendias & Pendias, 1992).The presence of an excess amount of chromium beyond the tolerable limits makes the land unsuitable for crop growth. Although the majority of the researchers consider that Cr(VI) is removed by anionic adsorption onto the biomaterials, basically the removal mechanism of Cr(VI) by natural biomaterials is adsorption-coupled reduction (Dhal *et al*., 2013; Badel *et al*., 2011). The toxic effects of chromium intake is skin rash, nose irritations,bleeds, upset stomach, ulcers, weakened immune system, kidney andliver damage, nasal itch and lungs cancer (US Health Services, 2000).

The lead concentrations ranged from 46.19 mg/kg to 140.70 mg/kg which is higher than the control value (29.00 mg/kg).This indicates the presence of lead in the soils polluted withwastes from different operations. This concentration of lead can lead to health risk. High concentration of lead in thebody causes anemia, pale skin, decreased hand grip strength, abdominal pain severe constipation, nausea, paralysis of the wristjoint, increases chances of miscarriage or birth defects. Lead is a poisonous metal that can damage nervous connections (especially in young children's) and cause blood and braindisorders. One of the most important and serious biochemical effects of lead is its interference with haemosynthesis, which leads to haematological damage (Chaitali & Jayashree, 2013). The centralnervous system becomes severely damaged at blood leadconcentration starting at 40 mg/dL and above 70 mg/dL causesanemia, reduction in hemoglobin levels and erythropoisis (Costa, 2015; ATSDR, 2012).

The mean concentration for copper in the soil was found to be 36.1±0.75 to 105.56±8.97 mg/Kg for the sample site and 2.41± 0.045 mg/Kg for the control sites. This indicates that copper present is above acceptable limit (30 mg/Kg) in the soil.Theconcentrationof copper in the polluted area is more than the unpolluted area due to the activities of the blacksmith (Kabata-Pendias & Pendias, 1992). Copper toxicity is ascribed to the induction ofreactive free oxygen species in the Fenton type reaction causing breakdown of DNA strands as well as damage to membranes andmitochondria (Maderova *et al*., 2011). Copper is an essential element for plants and animals. Critical concentration for copper in plants is in between 20 – 100 mg kg^{-1}. Phytotoxicity can occur if copper concentration in plants is higher than 20 mg kg^{-1} dry weight

(Nikki, 2015; Gupta, 1975). Copper (Cu) is a trace element essential for the healthy functioning of soil biological systems. However, at elevated concentrations Cu can be a potential toxicant. Consequently, an understanding of Cu availability and toxicity to soil biota is essential for effective ecological assessment of metal impacts in soil. High levels of copper may cause metal fumes fever with fluelike symptoms, hair and skin discoloration, dermatitis, irritation of the upper respiratory tract, metallic taste in the mouth and nausea (Lenntech, 2016). Copper accumulates in liver and brain. Copper toxicity is a fundamental cause of Wilson's disease (Gebrekidan & Samuel, 2011). WHO has recommended the lower limit of the acceptable range of oral intake of copper as 20 µg kg^{-1} body weight day^{-1}.

Conclusion

The Cd, Cr, Cu, Ni and Pb levels at the study sites were higher than the corresponding control values. This was as a result of the activities of the blacksmith at the study areas which caused the soil to be contaminated. The metal levels in the soil were found to be above the recommended limits (except Ni). This could pose risks and hazards to human and the ecosystem through: direct ingestion of contaminated soil. Therefore, it is recommended that all the activities of the blacksmith be relocated from the market and residential areas to the out-sketch of the cities to avoid humans and animals ingestion of the contaminated soil and dust.

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