

Original Research Article

Heavy Metals Contents in soils and Some Crops Irrigated along the Bindare Stream Zaria- Kaduna State, Nigeria

Abstract

Heavy metal contents of some crops and farm soil irrigated along the Bindare stream in Chikaji Zaria were investigated. The results of the analysis indicate that the crops contained substantial amount of heavy metals (Pb, Cr, Zn and Fe) compared to similar crops irrigated far distance from the stream. The concentration of the heavy metals (Zn, Cr and Fe) in the crops and the farm soil were found to be below the FAO/WHO safe limit, while the concentration of Pb was higher than the FAO/WHO safe limit. This suggest that the crops and the farm soil along the stream were contaminated by these heavy metals as the stream receives industrial waste discharges. Contamination factors and Geo-accumulation index for Pb, Cr, Zn and Fe in the areas under investigation were carried out. The results revealed that the soils are currently polluted with Pb and Zn.

Key words :Crops, Soil, Heavy metals, Geo-accumulation index, Contamination factor

1.Introduction

The knowledge of heavy metals in soils and plants are important due to the potential environmental and health implications posed by the heavy metals. Heavy metals have been known to play a variety of role in the environment which ranges from known human health hazard to ecological hazards due to their toxicity and bioaccumulative behavior [1]. Vegetables constitute essential diet components by contributing carbohydrates, proteins, vitamins, iron, calcium and other nutrients that are in short supply.

Pollutants are the causes of alterations in water quality in streams and rivers, and soil degradation around the world. Major water and soil pollutants include microbes, nutrients, organic chemicals, oil, heavy metals and sediments [2]

Though some metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, other like Cd, Cr and Pb have no known physiological activity and have been proved detrimental beyond a certain limit [3, 4].

Most of the few rivers in the northern Nigeria are over utilized for various activities such as farming, dumping of refuse and wastes [5, 2]. One of such streams is Bindare, a major stream in Chkaji industrial layout of Zaria in Kaduna State- Nigeria. The stream receives urban runoffs, industrial effluent and seepages from agricultural farmlands. These has compromised the water quality and the surrounding soil by way of pollution with poisonings chemicals and heavy metals which kill some of the subsists. When crops are irrigated with this polluted water, the crops absorb the heavy metals and accumulate them in the edible and non-edible parts. The absorption capacity of the heavy metals depends upon the nature of plant [6]. The ability of plants to absorb and accumulate metals not only poses a potential human exposure pathway through food consumption, but also provides an opportunity to remove metals from contaminated soils through phytoremediation. The levels of heavy metals waters and sediments has attracted concerns from researchers, as a result of their health implications on living organisms especially man. The literature is exhaustive on the subject, and every study examined the level of these metals in water sources in their respective environments [2, 7, 8, 9] . However, despite the abundance of literature on heavy metals in these aforementioned medium, there is little information on heavy metal levels of crops irrigated along streams and surrounded

soils in Kaduna State. This study therefore attempts to examine the levels of heavy metals in soils and some crops irrigated along the Bindare stream, Zaria- Kaduna state.

2. MATERIALS AND METHODS

2.1 Study area description

Bindare Stream which is about 6km long took its source from Kwangila hills and empties into River Galma, which flows in a west-east direction along a gulley situated to the North-West of Sabon-Gari and Chikaji Industrial Area of Zaria. The Stream has a catchment area of about 30.122km². The gully also receives various industrial effluents. Municipal and industrial wastes are channelled into the same drain and subsequently into the stream without treatment. Chikaji Industrial Estate which is almost encompassed by the Bindare stream, has the following industries: - Electricity meter Company of Nigeria (EMCOM) which produces electricity meter and circuit breakage, U.A.C Pharmaceuticals and personal product company, Kaduna chalk manufacturing company, John Holt Agricultural Industry, Harco Textile Company, U.A.C seed company and Pioneer Seed Company both of which produce different seed hybrids, Comrade bicycle company and several ware houses [2]. Waste generated by these industries include heavy metals, pesticides, dye, used containers, caustic soda, spent solvent, drugs, brake fluid and electric wires.

2.3 Reagents and Equipment: Chemicals of analytical grade purity and distilled deionized water were used. All glass wares and plastic containers used were washed with detergent solution followed by (20% v/v) nitric acid and then rinsed with tap water and finally with distilled deionized water. Also, standard solutions of the metal salts and other reagents were prepared.

The digestion mixture used is made up of nitric acid (Sg.1.42; purity 70.5%, A.R), Perchloric acid (70-72% A.R) and concentrated sulphuric acid (sg.1.84; purity 98%, A.R) mixed in the ratio

acid(70-72%) acid(70-72%) 33:4:1 respectively. Atomic Absorption Spectrometer (AAS) was used for the determination of the heavy metals.

2.3 Sample collection and sample treatment

Crops

The crops used for this study include corn (maize) seeds, okra and beans. Three farms located along the Bindare stream were chosen. The farms were labeled 1 to 3. Farm no.1 was 150 metres way from the industrial waste discharge, while farms no. 2 and 3 were 435 and 624 meters away respectively. The fourth farm was chosen upstream at about 7.63 kilometres away from the discharge point as control. After collection, the samples were transferred to the laboratory and washed with distilled water to removed aerial deposition. The samples were then air-dried in the laboratory. The dried samples were separately grounded in a mortar and sieved through a 2 mm sieve prior to the analysis.

Soil

A mild steel soil auger was used for soil sampling. Soil samples were taken at a depth of 15cm from the top. One control sample was also collected (generally about 7.63 kilometres away from each sampling point) where neither industrial discharge nor commercial activities are carried out. The samples were placed in labeled polythene bags and transported to the laboratory. All soil Samples were subsequently air-dried to constant weight to avoid microbial degradation [10]. They were homogenized, made lump free by gently crushing repeatedly using an acid pre-washed mortar and pestle, and passed through a 2 mm plastic sieve ready for analysis.

2.4 Heavy metal analysis

Crops

The sieved products were ashed in a muffle furnace at 500⁰C for 5 hrs [11].Each of the ashed sample (0.5g) was digested with 30cm³ of the digestion mixture at 200⁰C for 3hrs on a hot plate .The digest was allowed to cool, filtered into a 50cm³ volumetric flask and the volume made up with water .Analysis of the heavy metals was done on the prepared samples using ASS.

Soil

For the soil sample, 0.2g of the sieved soil was treated with the digestion mixture on a hot plate at 150⁰C for 2hrs. The solution was filtered and then made up to 50cm³ with water and analysed for metals using AAS . Heavy metal concentrations both in soils and crops were determined using an Atomic Absorption Spectrophotometer (AAS) at the National Research Institute for Chemical Technology (NARICT), Zaria. The instrument settings and operational conditions were in accordance with the manufacturer's specifications. The instrument was calibrated with analytical grade standard metal solutions (1 mg/dm³) in triplicates

3. RESULTS AND DISCUSSION

Heavy metals have maximum permissible level in soils and vegetables specified by different bodies . In this study, the standard used by WHO/ FAO was adopted. Therefore a comparison and interpretation of the results of analysed soils and vegetables is based on the control values and standards set by WHO/FAO . The soils and vegetables plants materials digested in the similar way as contaminated samples for quality control contained low levels of most metals when compared to standards(Table 1)

Lead (Pb)

The lead content of the farm soil no1 was 0.77μgg⁻¹, were as the concentrations of Pb in the vegetables were 0.69μgg⁻¹(Maize), 0.48μgg⁻¹(beans)and 0.87μgg⁻¹(Okra) for farms number 1,

2 and 3 respectively. However, the Pb content of the vegetables from the control farm were found to be $(0.05\mu\text{gg}^{-1})$, $(0.03\mu\text{gg}^{-1})$ and $(0.360\mu\text{gg}^{-1})$ for okro, maize and beans respectively (table 1). Lead contents from farm soil 2 and 3 were however observed to be $0.405\mu\text{gg}^{-1}$ and $0.431\mu\text{gg}^{-1}$. Pb is a toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield. The Pb contents of the plants in this study are higher than the FAO/WHO [12] safe limit of 0.3 mg/kg. The higher Pb level in these vegetables could be attributed to loading of debris containing this element into the stream from the industries since water from this stream is used to irrigates the plants. Thus, the Pb level in these vegetables seems not to be alarming except in a case of excessive consumption.

Zinc (Zn)

In this study, the crop Zn content were observed to be $(0.085\mu\text{gg}^{-1})$ in the okro from farm no.1, followed by the beans $(0.058\mu\text{gg}^{-1})$ in farm no.3 and $(0.049\mu\text{gg}^{-1})$ in the maize from farm no.1. However, the Zn contents of the vegetables from control farm were found to be $(0.026\mu\text{gg}^{-1})$, $(0.035\mu\text{gg}^{-1})$ and $(0.022\mu\text{g}^{-1})$ for okro, maize and beans respectively. The Zn contents of the farm soils were found to be $0.807\mu\text{gg}^{-1}$ for farm 1, $0.712\mu\text{gg}^{-1}$ farm 2 and $0.432\mu\text{gg}^{-1}$ farm 3. The control farm had a mean Zn value of $0.508\mu\text{gg}^{-1}$. The contents of Zn in all the plants examined are generally lower than the permissible levels by the FAO/WHO in vegetables as shown in Table 2. The recommended dietary allowance for Zn is 15 mg/day for men , 12 mg/day for adult women, for formulated-fed infants 5.00mg/day, and preadolescent children 10.00mg/day [13]. Judging from the forgoing, it is believed that regular consumption of these vegetables may assist in preventing the adverse effect of zinc deficiency which results in retarded growth and

141 delayed sexual maturation because of its role in nucleic acid metabolism and protein synthesis [14].

146 **Iron(Fe)**

147 Fe is essential for the synthesis of chlorophyll and activates a number of respiratory enzymes in
148 plants. The deficiency of Fe results in severe chlorosis of leaves in plants. High levels of
149 exposure to iron dust may cause respiratory diseases such as chronic bronchitis and ventilation
150 difficulties. Fe, maintains a healthy central nervous system, prevents anaemia.

151 Mean vegetable contents of Fe was highest ($5.490\mu\text{gg}^{-1}$) in Okro from farm no.3, followed by
152 ($4.43\mu\text{gg}^{-1}$) and $3.38\mu\text{gg}^{-1}$ for farms nos.2 and 3 respectively.

153 Mean Fe content of the beans was highest ($3.125\mu\text{gg}^{-1}$) from farm1,($2.45\mu\text{gg}^{-1}$) farm no.3 and
154 ($2.077\mu\text{gg}^{-1}$) from farm no.2. Highest Fe content of the Maize ($2.50\mu\text{gg}^{-1}$) was obtained from
155 farm no.3, followed by ($2.120\mu\text{gg}^{-1}$) farm no.1 and ($2.062\mu\text{gg}^{-1}$) farm no.2. The Fe contents of
156 the vegetables from control farm were found to be okro ($1.526\mu\text{gg}^{-1}$), maize ($2.540\mu\text{gg}^{-1}$) and
157 beans ($5.496\mu\text{gg}^{-1}$).

158 **Chromium(Cr)**

159 Mean chromium content of the vegetables was found to be ($0.26\mu\text{gg}^{-1}$)maize , ($0.74\mu\text{gg}^{-1}$)
160 beans and ($0.58\mu\text{gg}^{-1}$)Okro. However, the chromium contents of the vegetables from the control
161 farm were observed to be Okro($0.053\mu\text{gg}^{-1}$), maize($0.093\mu\text{gg}^{-1}$) and beans($0.271\mu\text{gg}^{-1}$).

Table 1. Heavy metal concentrations ($\mu\text{g/g}$ dry weight) in crops and soils from Bindare Stream (mean standard deviation).

Farm	Crops/soil	Pb	Cr	Fe	Zn
1.	Okra	0.870 $\pm$ 0.01	0.743 $\pm$ 0.02	4.425 $\pm$ 1.03	0.041 $\pm$ 0.02
	Beans	0.481 $\pm$ 0.03	0.337 $\pm$ 0.06	3.125 $\pm$ 0.42	0.056 $\pm$ 0.00
	Maize	0.690 $\pm$ 0.10	0.261 $\pm$ 0.05	2.120 $\pm$ 0.31	0.049 $\pm$ 0.01
	Soil	0.770 $\pm$ 0.12	0.198 $\pm$ 0.06	10.821 $\pm$ 2.07	0.807 $\pm$ 0.02
2.	Okra	0.630 $\pm$ 0.02	0.582 $\pm$ 0.03	3.380 $\pm$ 1.20	0.041 $\pm$ 0.02
	Beans	0.077 $\pm$ 0.00	0.205 $\pm$ 0.03	2.077 $\pm$ 0.03	0.038 $\pm$ 0.01
	Maize	0.630 $\pm$ 0.23	0.127 $\pm$ 0.04	2.062 $\pm$ 0.04	0.048 $\pm$ 0.02
	Soil	0.445 $\pm$ 0.16	0.145 $\pm$ 0.02	10.283 $\pm$ 0.04	0.712 $\pm$ 0.03
3.	Okra	0.327 $\pm$ 0.12	0.930 $\pm$ 0.15	5.490 $\pm$ 1.23	0.026 $\pm$ 0.01
	Beans	0.32 $\pm$ 0.10	0.024 $\pm$ 0.00	2.45 $\pm$ 0.87	0.022 $\pm$ 0.00
	Maize	0.32 $\pm$ 0.1	0.093 $\pm$ 0.02	2.50 $\pm$ 0.62	0.035 $\pm$ 0.01
	Soil	0.413 $\pm$ 0.14	0.067 $\pm$ 0.03	7.914 $\pm$ 1.04	0.432 $\pm$ 0.06
Control Farm	Okra	0.05 $\pm$ 0.00	0.053 $\pm$ 0.02	1.526 $\pm$ 0.43	0.026 $\pm$ 0.03
	Beans	0.360 $\pm$ 0.14	0.271 $\pm$ 0.05	5.496 $\pm$ 1.72	0.022 $\pm$ 0.01
	Maize	0.030 $\pm$ 0.02	0.093 $\pm$ 0.08	2.540 $\pm$ 0.87	0.035 $\pm$ 0.02
	Soil	0.318 $\pm$ 0.03	0.147 $\pm$ 0.03	6.820 $\pm$ 0.12	0.508 $\pm$ 0.04

Table 2: Mean concentrations of heavy metals in Crops and soil

Crops/soil	Pb		Cr	Fe	Zn
Okra	0.582		0.577	4.93	0.044
Beans	0.310		0.209	4.38	0.046
Maize	0.418		0.144	3.075	0.056
Soil	0.487		0.139	11.945	0.564
FAO/WHO (2001) Limit	Pb	Fe	Zn	Cu	
	0.30	425.0	99.40	73.0	

3.1 Variation in metal concentration in the study area

In order to have a comparative idea about the levels of contamination, data from this work was compared with those from the control sampling point taken to be the unpolluted or background value. There are low levels of variation in the investigated soils with small standard deviations (figure 1). Large variations imply great heterogeneity of metals in soils while low variations show more or less homogenous distribution of metals in the soil [15] and this could be traced to different levels of pollution, caused by varying degree of industrial waste dumps in Chkaji industrial layout

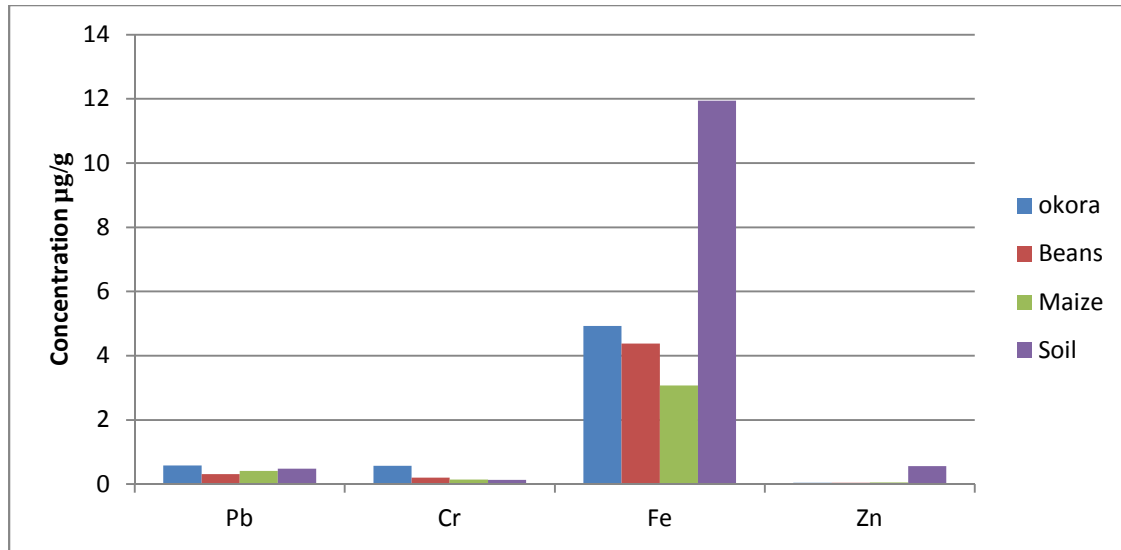


Figure 1: Variation in Heavy metal concentration in soil and vegetables

3.2 Assessment of the impact of heavy metals on the surrounding soil environment

Various quantitative indices have been employed to assess the impact of human activities on the concentration toxic trace metals in soil namely: (i) Index of geo-accumulation (I-geo) and (ii) Contamination factor (CF). The I-geo enables the assessment of contamination by comparing current and pristine concentrations of the contaminants; this index is computed using the following Equation (1) [16, 17, 18, 19]

$$I\text{-geo} = \log_2 (C_n/1.5B_n) \quad (1)$$

Where C_n is the concentration of the heavy metal in the enriched sample and B_n is the concentration of the metal in the unpolluted (control) samples. The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the soil [19]. The degree of metal pollution is assessed in terms of seven contamination classes in order of increasing numerical value of the index as shown in Table 3 [20 , 21] .

229
 230 The second approach is using the Contamination factor (Cf) and the degree of contamination. In
 231 calculating Cf the equation suggested by [22] and [17] was used.

232
$$C_f = C_{i0-1}/C_{in} \quad (2)$$

233 Where C_{i0-1} is the mean content of metals from sample sites and C_{in} is the pre-industrial
 234 concentration of individual metals.

235 In this study, the concentration of the control samples is taken to represent the pre-industrial
 236 concentration as suggested by [23]. C_f can be used to differentiate between the metals
 237 originating from anthropogenic activities and those from natural processes and to assess the
 238 degree of anthropogenic influence [20]. Five contamination categories of contamination factor
 239 are recognized in Table 4. High C_f values suggest strong anthropogenic influence.

240 **Table 3: Seven classes of geo-accumulation index (I-geo).**

Class	Value of Soil Quality
<0	unpolluted
0-1	unpolluted to moderately polluted
1-2	moderately polluted
2-3	moderately polluted to highly polluted
3-4	highly polluted
4-5	highly polluted to very highly polluted
>5	Very highly polluted

241

242 **Table 4:Categories of contamination factors [22, 17]**

Contamination factor	Category
$C_f < 1$	Low contamination factor indicating low
$1 < C_f < 3$	Moderate contamination factor
$3 < C_f < 6$	Considerable contamination factor
$6 < C_f$	Very high contamination

Contamination factor (C_f)

In this study, C_f was calculated from the mean concentrations of the heavy metals in the study areas with the control sampling sites taken to represent the background values (Table 5). According to Akoto et al. [24], C_f values between 0.5 and 1.5 indicate that the metal is entirely from crust materials or natural processes; whereas C_f values greater than 1.5 suggest that the sources are more likely to be anthropogenic. The C_f revealed that most of the soils show highest Contamination factors for Pb(1.74) and Zn(3.91) which ranged from moderate contamination to considerable contamination , while Fe and Cr had low contamination factors. High (>1.5) C_f values of a metal indicate significant contribution from anthropogenic origins. Therefore, the high values of C_f in Table 5, especially for Zn and Pb, is a clear indication that the contamination in the soils in farms are from human activities.

Geo-accumulation index

The geo-accumulation index (*I-geo*) for the soils are also presented in Table 5. The pollution status of the metals in the environment expressed in terms of this index showed that the soil is polluted by Pb and Zn but for Cr and Fe, the environment for now remain unpolluted by them. The negative values for Cr and Fe are indications that the soil is not polluted by them.

Table 5. Soil contamination factor and Geo-accumulation index

Farm	Contamination factor			
	Pb	Cr	Zn	Fe
1	2.42	1.34	0.76	1.59
2	1.40	0.90	6.78	1.51
3	1.39	0.45	4.19	1.16

Mean	1.74	0.9	3.91	0.92
Geo-accumulation index.				
	Pb	Cr	Zn	Fe
1	-0.69	-0.15	0.078	0.08
2	-0.1	-0.59	-0.095	0.007
3	0.89	-1.67	0.80	-0.35
Mean	0.1	-3.78	0.88	-0.263

4. CONCLUSION

The vegetable crops may be said to be contaminated with these toxic metals. The contribution of these metals towards the vegetable uptake may be associated to the close proximity of the farm lands to the source of industrial waste discharge. The concentration of Pb was higher than the FAO/WHO safe limit an indication that the crops and the farm lands along the stream were contaminated by these heavy metals as the stream receives industrial waste discharges. Although, the concentration of the heavy metals like Zn, Cr and Fe in the crops and the farm soil were found to be below the FAO/WHO (2001) safe limit. However, safe limits of metals based on acute evaluations alone may be misleading as concentrations judged to be low as not to kill an organism at that point in time may still depress its reproduction and growth capacities incidentally thereby leading chronic toxicity. Hence, regular monitoring and evaluation of Bindare stream and the surrounding soil in which these vegetables are cultivated is encouraged to check the elevated concentrations of the these metals. The data from such assessment could serve as index on which remediation variables in modeling could be anchored.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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