Sumerianz Journal of Scientific Research, 2018, Vol. 1, No. 1, pp. 8-15
ISSN(e): 2617-6955, ISSN(p): 2617-765X
Website: https://www.sumerianz.com

Original Article Open Access

Heavy Metals Profile of Challawa River Basin around Challawa Industrial layout, Kano and It's Implications for Cultivated Vegetables

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Abstract

Challawa industrial layout is one of the three major industrial areas of Kano. This study was undertaken to assess the heavy metal profile of Challawa River basin around Challawa industrial area and its implication for cultivated vegetables. Lead, cadmium, chromium and zinc concentrations were analyzed using Shimadzu atomic absorption spectrophotometer (model AA-6800, Japan) after wet digestion. The range of concentrations (mg/kg) of these metals was: Pb (94.46-104.76), Cd (11.43 - 26.46), Cr (163.98 - 201.46) and Zn (154.98-254.46). The significant differences observed in soil metal levels between the control and the study area suggests that Challawa industrial area has a significant influence on the heavy metal profile of the basin. The results indicates that the study area does not pose significant health/environmental risk with respect to lead, chromium and zinc intoxication even though the mean soil lead level was found to be above Dutch Target value (85 mg/kg) which is the bench mark for soil quality. However, cadmium was seriously implicated in the study as the mean soil cadmium concentration was found to be above the United States Environmental Protection Agency (USEPA) Maximum Permissible Limits (MPL) and the European Regulatory Standard of 3.00 mg/kg. There is therefore a serious cause for concern as uptake by cultivated vegetables cannot be completely ruled out. Determination of the chemical form (speciation) of these metals in the basin is hereby recommended to evaluate their mobility and bioavailability.
Keywords: Challawa river basin; Metal profile; Speciation; Vegetable uptake health/environmental risk.

1. Introduction

With the ever increasing population, expanding industry and urbanization, large volume of wastewater is being generated on daily basis. Industrial wastewaters differ remarkably with respect to their chemical composition depending on the source from which they originates. The marked differences in chemical composition could easily be traced to the fact that different industries use different chemicals based on the purpose of their operations. Even within the same industry, effluents discharged from two different units vary largely in their chemical composition [1]. The release of industrial wastewater containing heavy metals and other toxic chemicals by industries is an increasingly common practice [2]. Effluents from different industries when discharged through drains and canals across industrial areas have their chemical activities either enhanced or exhibits due to synergistic or antagonistic effects on the chemical constituents [1]. In drought prone areas, wastewaters are often used directly for irrigation by farmers, though most often, surface water that receives these wastewaters serves as the major sources irrigation water. The application of both industrial and municipal wastewater on land dates back over 400 years and is currently a common practice in many parts of the world. It's estimated that over 20 million hectares of arable land globally are irrigated by wastewater [3]. Irrigation with waste water may have significant implications in two ways: alter the physicochemical properties and microbiological content of the soil and /or introduce and contribute to the accumulation of chemicals and biological contaminants in soil. The first may affect soil productivity and fertility; the second may pose serious risks to the human and environmental health [4]. Farmers generally are particularly interested in maximizing their yields and not bothered about the environmental /health consequences of the practice. Wastewater application can result in a number of problems such as pathogenic infection and heavy metal accumulation in soil, underground water and crops to toxic levels. Soil is a crucial component of rural and urban environments, and in both places land management is the key to soil quality. Soil quality parameters are significantly affected by long term wastewater irrigation. Amin, *et al.* [5] reported that long term use of sewage effluent for irrigation contaminates soils to such an extent that it does not only becomes toxic to plants but also causes deterioration of soil quality. Elevated levels of heavy metals in soil are regarded as 'chemical time bomb' because of their propensity for accumulation in the soil. Heavy metals are generally not removed even after the treatment of effluents at primary effluent treatment plants, and thus cause risk of heavy metal contamination of the soil.

Soils are major sinks for heavy metals released into the environment by anthropogenic sources. Most of the metals do not undergo microbial or chemical degradation to any reasonable degree and as such persist for a long

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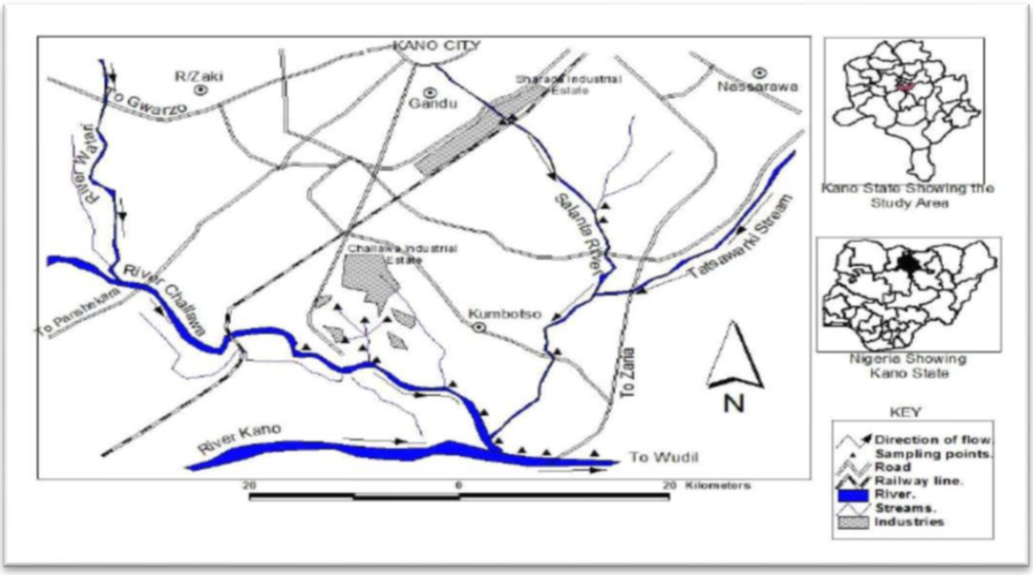
time after introduction. Mobility of a given metal into other component of the ecosystem and the food chain is dependent on its chemical form and the soil characteristics. Crops grown in soils with elevated levels of metals have greater accumulation of the metals than those grown in uncontaminated soil [6]. The uptake of metals from the soil depends on different factors such as their soluble content in it, soil pH, plant growth stages, types of species, fertilizers, and soil. Vegetables are an important part of human's diet. In addition to being a potential source of important nutrients, vegetables constitute important functional food components by contributing vitamins, iron, calcium and other minerals which have marked health effects. Potential health risks to humans from consumption of vegetables can be due to heavy metal uptake from contaminated soils via plant roots as well as direct deposition of contaminants from the atmosphere onto plant surface [7]. Dietary intake of heavy metals through contaminated vegetables may lead to various chronic diseases. There is therefore an increasing concern regarding the exceedance of statutory and advisory food standards for trace metals [8]. It is for this reason that this study was undertaken to assess the heavy metal contents of soil and its implications for vegetables cultivated in Challawa River basin around Challawa industrial layout Kano. Based on the 2006 census, Kano is on record the most populated city in Nigeria. The region faces long period of drought annually usually from September to May with low and unreliable rainfall between May and September. There is therefore acute water shortage in the ancient city for up to seven month every year. With the ever increasing population, increased industrial activities and urbanization the quality and quantity of both surface and ground water in the area is seriously threatened [7]. Currently, the government of the federal republic of Nigeria is diversifying its economy from oil into agriculture. Kano state government has made special budget to invest in agriculture to get the youths back to farm. There is also the presidential initiative on increased agricultural produce to grow the economy. It's therefore important to determine how safe it is to consume crops grown around Challawa industrial area to safeguard public health. Challawa industrial layout is one of the three major industrial areas of Kano. It harbours several industries such as textiles, tanneries, plastics and many other wet industries. Effluents from these industries are discharged through drain and canals which meets at a confluence point, flows down through farm land where it is used for irrigation and eventually empties into Challawa River. River Challawa itself is an important resource which supplies water for drinking, irrigation and other agricultural activities including fishing. Even when the metal concentrations in effluents are low long-term application on land or continuous use of receiving surface water bodies for irrigation can eventually result in heavy metal accumulation in the soil [7]. Intake of the contaminated crops is an important route of metal toxicity to humans.

2. Materials and Methods

2.1. Study Location

Kano (Lat. 11° 59 m 18.3s N, Long 08° 32 m 05.8s E) 418 m above sea level is located in Kano State, occupies central position of Northern Nigeria [9]. Industrially, it is one of the most developed cities in Northern Nigeria with three main industrial estates namely Bompai, Challawa and Sharada. Each harbours large number of wet industries tannery and textile are some of its dominating industries. The indiscriminate discharges of untreated effluent need to be addressed urgently. Presently the state is experiencing myrids of problems that are challenging its sustainable development [10, 11]. Effluent from Challawa industrial estate are discharged untreated through drains and canals that eventually flow into Chalawa River. Challawa River (Lat 11° 52 m 41s N, Long 08° 28 m 09s E) 515 m above sea level originate from the Challawa Gorge dam in Challawa village and stretches down to River Kano where it empties into Lake Chad [9]. The river receives waste from tanneries and textile industries, urban water storm and agricultural runoff from farming communities along the river course. The River is a major source of water supply to a large number of communities along its course. It is also used for irrigation, bathing, fishing, etc. The domestic water supply for Challawa, Sharada and Bompai industrial areas and the surrounding environment in general comes from River Challawa.

Figure-1. Kano showing the study area [12]



2.2. Sample Collection and Preservation

Procedure for sample collection preservation and preparation was adopted from Abida, *et al.* [13]. Four sampling points were established along Callawa River basin, around Challawa industrial layout. The first sampling point was around the point source (the identified effluent discharge point), sampling point number two was 500 meters downstream of sampling point 1 and the third sampling point was 500 meters downstream of sampling point 2. The fourth sampling point which was 1000 meters upstream of the point source (sampling point 1) served as control. Soil samples were collected at a depth of 0-10 cm from the soil surface at each sampling point into black polyethene bags. Collected samples were transported to the Environmental Laboratory, National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria for analysis.

2.3. Sample Preparation and Analysis

Soil samples from each sampling point were thoroughly mixed to obtain a representative sample, air dried for five days, crushed and sieved with 2 mm mesh before wet digestion. I g of a well mixed sample from each sampling point was taken into a 250 ml glass beaker and digested with 10 ml of concentrated nitric acid, perchloric acid and hydrofluoric acid in the ratio 3:1:1 on a hot plate. After evaporating to near dryness, 10 ml of 2 % nitric acid was added, filtered into 50 ml volumetric flask and the made up to the mark with distilled deionized water [14].

2.4. Metal Analysis

Lead (Pb), Cadmium (Cd), Chromium (Cr) and Zinc (Zn) concentrations in the digests were determined by Atomic Absorption Spectrophotometry, using Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) at National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. The calibration curve was prepared by running different concentrations of the standard solutions. The instrument was then set to zero by running the respective reagent blanks and metal concentrations determined. Average values of three replicates were taken for each determination. Data obtained were subjected" to statistical analysis.

2.5. Analytical Quality Assurance

Appropriate quality assurance procedures and precautions were taken to ensure the authenticity of the results. Samples were carefully handled to avoid cross-contamination. Glasswares were properly cleaned and deionized water was used throughout the study. All the reagents used- HNO_3 (Riedel-deHaen, Germany), hydrofluoric acid and $HClO_4$ (British Drug House Chemicals Limited, England) were of analytical grade. In order to check the reliability of the analytical method employed for metal determination, one blank and combine standards was run with every batch of samples to detect background contamination and monitor consistency between batches. The result of the analysis was validated by digesting and analyzing Standard Reference Material, Lichens coded IAEA-336 following the same procedure. The analyzed values and the certified reference values of the metals determined were compared to ascertain the reliability of the analytical method employed.

3. Statistical Analysis

Data collected was subjected to statistical test of significance using the Analysis of Variance (ANOVA) test to assess significant variation in metal levels across the sampling locations. Probabilities less than 0.05 ($p < 0.05$) was considered to be statistically significant. Duncan multiple test or Donnette T was adopted for multiple comparison of parameters between sampling stations depending on whether the homogeneity of variance test was greater than or less than 0.05. Pearson product moment correlation coefficient was used to determine the association between metal levels in soil samples at $\alpha = 0.05$. SPSS software 17.00 for windows was used for all statistical analysis.

4. Results

4.1. Analytical Quality Assurance

The analyzed values of the standard reference materials (lichen coded IAEA – 336) were found to be within the range of the certified reference values for the metals determined suggesting the reliability of the method employed (Table 1).

Table-1. Results of analysis of reference material (Lichen IAEA -336) compared to the certified reference value (mg/kg).

Metal (mg/kg)	Pb	Cr	Cd	Zn
A Value	5.18	0.167	3.86	65.86
R value	4,2-5.5	0.1-2.34	3.1-4.1	56-70

A. Value=Analyzed value *R. value =Reference value.*

4.2. Soil Metal Concentration

Result obtained from the determination of soil metal content across the different sampling points along Challawa River Basin, around Challawa industrial area, Kano, Nigeria are presented in Table 2, while the spatial distribution of the Average soil metal concentration across the different sampling points in the study area and the control are shown in Figure 2.

Table 2 indicates that lead ranged from a minimum value of 94.46mg/l to a maximum value of 104.76 mg/kg, Cadmium ranged from 11.43 mg/kg to 26.46 mg/kg, Chromium from 163.98 mg//kg to 201.46 mg/kg and Zinc from

154.98 mg/l to 254.46 mg/kg. The lowest value for each of the metals under study were recorded at sampling station 3 in the month of February and the highest value at sampling station 1 in April. The difference in the concentration of each metal across the established sampling stations from the point source downstream was found to be statistically significant (ANOVA, $p < 0.05$), the concentration of each metal at sampling station 1 being significantly higher than sampling station 3. Differences between station 1 and station 2 and between station 2 and station 3 were however not statistically significant at 95% confidence level for all the metals under study. Statistically significant difference was observed between the

Table-2. Metal levels of soils along River Challawa Basin around Challawa Industrial Area, Kano, Nigeria (mg/kg)

Element	Sampling Month	Sampling Station 1	Sampling Station 2	Sampling Station 3	Control
Lead	February	102.34	100.87	94.46	68.85
	March.	98.02	97.31	89.54	68.98
	April	104.76	100.67	98.56	67.68
	Mean ± SD	101.71±3.41	99.62±2.00	94.19±4.51	68.50±0.71
	Range	94.46-104.76			67.68 – 68.98
Cadmium	February	18.46	12.74	11.43	6.49
	March.	25.85	18.56	13.74	8.48
	April	26.46	22.49	13.54	9.98
	Mean ± SD	23.59±4.45	17.93±4.91	12.90±3.89	8.32±0.65
	Range	11.43 - 26.46			6.48 – 9.98
Chromium	February	173.53	170.34	163.98	35.87
	March.	183.98	178.45	166.37	34.52
	April	201.46	187.96	169.99	36.41
	Mean ± SD	186.32±14.11	178.91±8.89	166.78±3.03	35.6±0.97
	Range	163.98 - 201.46			34.52 - 36.41
Zinc	February	187.87	164.09	154.98	54.8
	March.	208.54	187.18	164.47	59.54
	April	254.46	205.68	174.43	58.43
	Mean ± SD	216.96±34.08	185.65±20.83	164.63±9.73	57.59±2.47
	Range	154.98-254.46			54.8 – 59.54

metals concentration at the control station and the sampling stations (Fig.2) under study for each of the metal (ANOVA, $p < 0.05$), concentration of each metal at the control station being significantly lower than the sampling stations under study (sampling stations 1, 2 and 3).

Fig-2. Spatial Distribution of the Average concentration Soil Lead, Cadmium, Chromium and Zinc of Challawa River basin

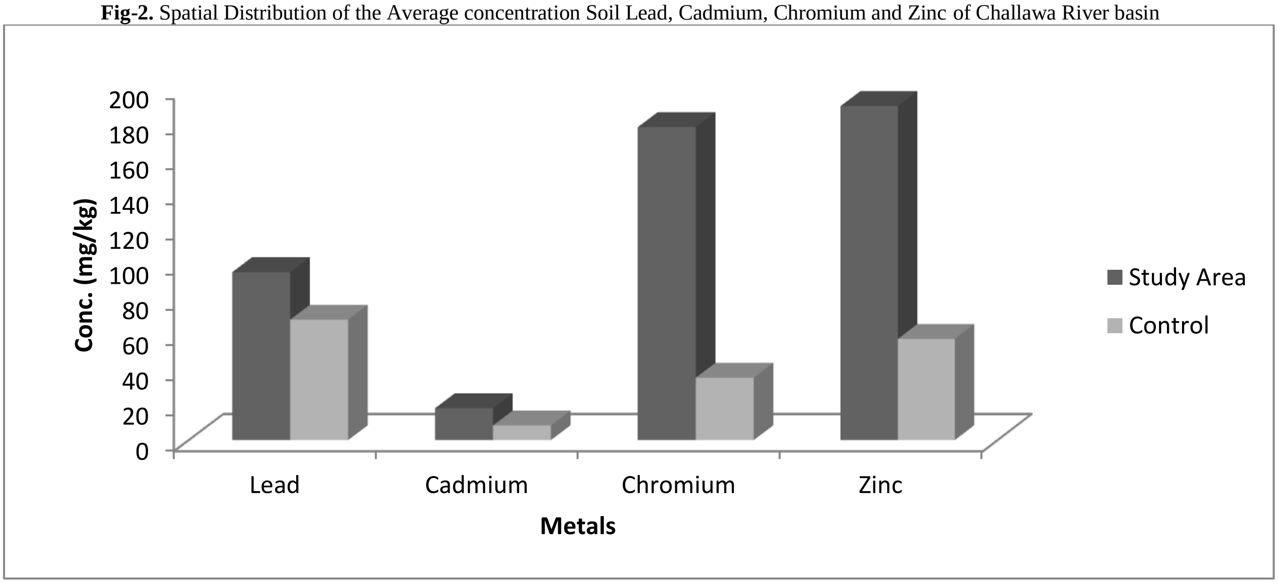


Table-3. Correlation between soil metal concentrations

		Lead soil	Cadmium soil	Chromium Soil	Zinc soil
Lead soil	Pearson Correlation	1			
	Sig. (2-tailed)				.
	N				
Cadmium soil	Pearson Correlation	.750**	1		
	Sig. (2-tailed)	.005			
	N				
Chromium Soil	Pearson Correlation	.979**	.767**	1	
	Sig. (2-tailed)	.000	.004		
	N				
Zinc soil	Pearson Correlation	.953**	.888**	.966**	1
	Sig. (2-tailed)	.000	.000	.000	
	N				

**. Correlation is significant at the 0.01 level (2-tailed)

Table 3 reveled that a strong positive correlation was observed between soil lead levels and soil cadmium levels (r = 0.750), soil lead levels and soil chromium level (r = 0.979), and between soil lead levels and soil Zinc levels (r = 0.953). All the correlations were found to be statistically significant at 99% confidence level. A strong positive correlation was observed between soil cadmium levels and soil chromium levels (r = 0.979), soil cadmium levels and soil Zinc levels (r = 0.953) and also between soil chromium levels and soil Zinc levels (r = 0.966). The correlations were significant at 99% confidence level.

5. Discussion

Soil Lead (Pb), Cadmium (Cd), Chromium (Cr) and Zinc (Zn) concentrations in the study were observed to decreases significantly downstream from the (point source) effluent discharge point. A similar pattern was displayed by the concentration of these metals in surface water of the River Challawa from the point source [15], suggesting that the use of water whose metal concentration decreases with increasing distance downstream for irrigation may be responsible for the observed decrease in soil metal concentration downstream. Sampling station 1 was characterized by influx of industrial effluent through seepages from the drains/canals, surface runoff from the industrial area and most importantly direct use of effluent for irrigation hence the observed high soil metal contents. The statistically lower metal concentration observed at the control station when compared to sampling stations 1, 2, and 3 suggests that Challawa industrial area has a significant adverse influence on the metal profile of the Challawa River basin. Research findings have shown that in excess concentration, some metals are phytotoxic to crops [16].

The overall mean soil lead level (Table 2) was found to be lower than USEPA guidelines for soil lead level (400 mg/kg). Nigeria has no soil lead standard but the department of petroleum resources adopts Dutch soil remediation standards for the assessment soil quality in the country. The observed mean soil lead level in the study was found to be lower than Dutch intervention value (530 mg/kg), a level above which the functional properties of the soil for plant, animals and human's life are considered to be seriously impaired. The findings of this study Indicates that River Challawa basin is fit for agricultural purposes and does not pose any threat with respect to lead contamination. However, the mean soil lead level around River Challawa basin was found to be above Dutch Target value (85 mg/kg) which is the bench mark for soil quality. A soil leads level below which all the functional soil properties plant, animals, and human's are considered to have been fully recovered. Lead accumulation in the soil could be attributed to long term continuous application of waste water from industrial and agricultural waste [17]. Soil lead level ranging from 52.77 – 120.40 mg/kg was previously reported for River Galma, zaria Nigeria [14]. A higher range of 35.9 mg/kg to 306.7 mg/kg for dry season, and 24.00 mg/kg to 316.14mg/kg for wet season were reported in Yauri, Nigeria [18]. A significantly higher range of 81.65 to 684.27 mg/kg dry weight was reported in Dareta village immediately after the remediation exercise [19]. Lead has been reported to exert significant adverse effect on the morphology, growth and photosynthetic process of plant. Bioaccumulation of the metal in edible crop tissues could result in lead poisoning [16].

The overall mean soil chromium level (Table 2) was found to be lower than (WHO, FAO) guideline for soil chromium level of 300 and 100 mg/kg respectively [19], It was also lower than the Maximum Permissible Limits (64 mg/kg) for chromium in agricultural soils [20], hence chromium was not implicated in the study. River Challawa basin could be said to be fit for agricultural purposes with particular reference to chromium contamination. The mean concentration of chromium occurring naturally in the earth's normal mineral soil is about 200mg/kg worldwide [21, 22]. Lower values ranging from 0.56 kg/kg to 8.08 mg/kg was reported for River Galma basin around Dakace industrial area, Zaria [14]. [16] reported that chromium stress in plant induces three possible types of metabolic modifications: (i) alteration in the production of pigments such as chlorophyll and anthocyanin which are involved in life sustenance of plant, (ii) increase in the production of metabolites such glutathione and ascorbic acid which may cause damage to plants and (iii) alterations in the metabolic pool to channelise the production of new biochemically related metabolites, which may confer resistance or tolerance to Cr stress (e.g., phytochelatins, histidine).

Environment agency gives the soil guideline values (SVGs) for Cadmium to be 10mg/kg for residential areas and 230mg/kg for commercial areas [23]. The United States Environmental Protection Agency (USEPA) Maximum Permissible Limits (MPL) for Cadmium in soil is 3ppm and the European Regulatory Standard is 3.00 mg/kg [24]. The mean soil cadmium concentration in the study area (Table 2) was found to be higher than the above standards except at the control station where it was less than the environment agency soil guideline values (SVGs) of 10mg/kg. Lower soil cadmium concentration ranging from 0.76ppm to 2.55ppm was reported for soils along Kubani River basin, Zaria, Nigeria [25]. A range of 2.01mg/kg-13.03 mg/kg was reported for top soil (0-10 cm) in Umuohia [26]. Cadmium was therefore not implicated in this study. In their study on the heavy metal content of soil and cabbage cultivated in the Bezi Bar farm area of Katima Mulilo, Namibia, [16] reported that plants grown on soils with elevated levels of cadmium show visible symptom of injury reflected in terms of chlorosis, growth inhibition, browning of root tips and death.

The United States Environmental Protection Agency (USEPA) Maximum Permissible Limits (MPL) for zinc in soil is 200 ppm and the European Union Regulatory Standards (EURS) for zinc in soil is 300 mg/kg [27, 28]. The mean values recorded in this study were below both USEPA- MPL and EURS except at sampling station 1 which corresponds to the point source. Lower mean concentrations of 2.05 ppm and 10.82mg/kg were reported for Azara derelict barite and Udege abandoned tin/columbite mining areas of Nasarawa State, Nigeria [29, 30]. A range of 12.6 – 183.4µg/g was recorded for US soil, 28.5 – 161 µg/g for china, 10.5 – 1547 µg/g for Poland and 140.9 – 302.8 µg/g for Ethiopia [18].

Zinc is needed for the formation of auxin (Plant growth hormone), chlorophyll and cytochrome pigment. It is also needed for proper root development and formation of enzymes and carbohydrates [31]. Incidence of zinc toxicity is not common. Cases have been reported for crops cultivated on acidic soils ($pH \leq 5$) rich in zinc. Zinc toxicity may cause severe reduction growth. Symptoms have been shown to include the development of red or dark pigmented spots or blotches on leaves. Severe damage to the roots at high zinc concentration may cause general yellowing and wilting. High concentration of zinc in soil may inhibit the uptake of iron thus inducing serious iron deficiency characterized by chlorosis and necrosis of leaves and growing points [32]. High zinc levels can interrupt the metabolic activity in soils, as zinc negatively harms microorganisms and earthworms, slowing down breakdown of organic matter that provides basic nutrition to plant roots [31]. Liming the soil to raise the pH may alleviate the problem of zinc toxicity by reducing the concentration of plant available zinc.

The significant ($p < 0.001$) positive correlations observed between soil lead levels and soil cadmium levels ($r = 0.750$), soil lead levels and soil chromium level ($r = 0.979$), and between soil lead levels and soil Zinc levels ($r = 0.953$) indicates that increase in soil lead levels is associated with increase in cadmium, chromium and zinc levels. Similarly the significant ($p < 0.001$) positive correlation observed between soil cadmium levels and soil chromium levels ($r = 0.979$), soil cadmium levels and soil Zinc levels ($r = 0.953$) and also between soil chromium levels and soil Zinc levels ($r = 0.966$) indicates that increase in soil cadmium concentration is associated with increase in chromium and zinc concentrations suggesting that same source is responsible for the presence of these metals at the concentrations determined in the study area.

6. Conclusion

The findings of this study revealed that Challawa River basin around Challawa industrial area does not pose significant threat to cultivated vegetable with respect to lead, chromium and zinc intoxication even though the mean soil lead level was found to be above Dutch Target value (85 mg/kg) which is the bench mark for soil quality. A soil leads level below which all the functional soil properties for plant, animals, and human's are considered to have been fully recovered. However, cadmium was seriously implicated in the study as the mean soil cadmium concentration was found to be above the United States Environmental Protection Agency (USEPA) Maximum Permissible Limits (MPL) anad the European Regulatory Standard of 3.00 mg/kg. There is therefore a serious cause for concern as uptake by cultivated vegetables cannot be completely ruled out. The significant differences observed in soil metal levels between the control and the study area indicates that Challawa industrial area has a significant influence on the heavy metal profile of the basin. The total concentration of a given metal in soil provides a useful and easier way of stating clearly pollution due to the metal but the chemical form of the metal is of great importance in evaluating its potential bioavailability and remobilization from the soil when physic-chemical conditions are favourable. The determination of the chemical form (speciation) of these metals in the basin is hereby recommended.

Acknowledgement

The research team wishes to express her profound gratitude to the National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria, for making their environment laboratory available for this research work.

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