Original Research Article

CORRELATION ANALYSIS OF TOXIC METALS DISTRIBUTION AND POLLUTION INDICES IN SOIL, BEANS AND MAIZE SAMPLES OF KANO STATE, NIGERIA

ABSTRACT

Correlational study and evaluation of pollution indices of toxic metals distribution in soil and crops of a population is imperative for accessing risk of chronic diseases associated with these metals. Correlational analysis for the distribution of; lead (Pb), cadmium (Cd), chromium (Cr) and mercury (Hg) in soil (S), bean (B) and maize (M) was conducted around Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) as sampling zones around Kano State, Nigeria. The samples were collected from farm harvests in each of the sampling zones under the study and designed as; BKRS, BKRB, BKRM, DBTS, DBTB DBTM, GRZS, GRZB GRZM, UGGS, UGGB, UGGM, WDLS, WDLB, WDLM. The metal Concentration was determined using atomic absorption spectrometery (AAS). Results in mg/kg across the local governments indicates respective ranges for Hg, Pb, Cd, and Cr of; 0.33 - 3.13, 0.14 - 0.84, 0.02 - 0.05 and 0.01- 0.49 in soil, 0.04-4.23, 0.06-0.23, 0.02-0.04 and 0.00-0.10 in maize and 0.20-4.23, 0.16-0.19, 0.03-0.04 and 0.00-0.03 in beans. Although with exception of mercury, the ranges of the toxic metals are within the tolerable ranges set by International Standard Tolerable Limits and European Regulatory Standard. Potential hazard may be speculated because the detected levels are on higher tolerable ranges. A higher level of mercury in almost all the samples indicates potential hazards associated with human activities in those areas. Strong positive correlation between soils samples with respect to level of some of the toxic metal may suggest a common nature of the soil, while the negative correlation may be due variation in agrochemicals in-use. For the pollution load index, Wudil had the highest soil pollution load index for Hg (3.13 ± 0.16), Cd ($1.6\times10^{-2} \pm 0.01$) and Cr ($4.9\times10^{-3} \pm 0.01$), while Ungogo had the highest pollution load for Pb. Also, all grains within the study zones exhibited a positive transfer factor, except Cr in Bunkure, Danbatta and Gwarzo. It may be concluded that crops grown in those areas may bioaccumulates some of these toxic metals, thereby incorporating them into food chain, hence potential health risk.

Keywords: toxic metals, Soil, Farm produce, Correlation, Distribution, pollution index Kano-LGAs

1.0 INTRODUCTION

Toxic metals are confined to those metals having higher atomic number (Norman, 1981), associated with little or no biochemical functions. However; they have many industrial and agricultural applications (Alloway, 1995) and are relatively high density metallic elements with potential toxicity at low concentration (Holding, 2004). According to WHO (2014) toxic metals occur in trace amount and are at least five times denser than water, They are stable and persistent in environmental samples, hence bioaccumulates to pass up via food chain to humans. According to Alhassan *et al* (2012) sources of heavy metals are varied and include natural sources and all human activities, with possibility of polluting the environment. In another perspective, environmental toxic metals are due to direct deposition from mining activities, industrial processes as well as waste water from domestic processes, in addition to agricultural practices (Madyiwa, 2006). Heavy metals contamination to agricultural soils could be through a variety of sources among which is land application of biosolids, fertilizers, livestock manure, agrochemicals (Pesticides), irrigation activities and atmospheric droplet. Worthy consideration is accumulation of these metals in agricultural soils and possible negative impacts on soil fertility and large potential accumulation in crops for possible incorporation to human food chains (Gray *et al*., 2003). Unlike the inorganic, the organic (alkylated) forms are readily taken up by body tissues and can be retained for a considerable length of time (Garrett *et al.*, 1992) this is due to their lipid solubility. The tissue penetrating power of organometals crown them more toxic to humans than the inorganic form (Carpenter, 2001).

Human exposure to soil accumulated toxic metal may be chronic via food chain transfer or acute by direct ingestion or dermal contact. The former may be associated with; mental lapses, kidney, liver, lung and gastrointestinal tract abnormalities, central nervous insufficiency, lower energy levels, damage to blood compositions, kidneys, and other vital organs (Gray *et al*., 2003). Long term exposure to low dose may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer`s disease, Parkinson`s disease, muscular dystrophy, and multiple Sclerosis (Srivastava and Goyal, 2010). Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer. The letter, depends on the degree to which a system, tissue, organ or cell is affected by a heavy metal type and the individuals degree of exposure (Vallero and Letcher, 2013).

Mercury combines with other elements to form organic and inorganic mercury compounds. Metallic mercury used to produce chlorine gas, caustic soda, in thermometers and dental fillings, switches, light bulbs, and batteries, including coal-burning power plants are the largest human-caused source of mercury emissions to the air in the United States. Mercury in soil and water is converted by microorganisms to methyl mercury, a bio accumulating toxin (Sabine and Wendy, 2009). The EPA reported that mercuric chloride and methyl mercury are possible human carcinogens and nervous system is very sensitive to all forms of mercury. Exposure to high levels can permanently damage the brain, kidneys, and developing fetuses. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems. Short-term exposure to high levels of metallic mercury may cause lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes, and eye irritation (Davidson et *al.,* 2004).

Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High level exposure in men can damage the organs responsible for sperm production (Emsley, 2011).

Chromium, chromium (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of chromium (VI) have been known since late 19th century, while Cadmium exposure is a phenomenon of the early 20th century, and onwards. In Japan in 1910, the Mitsui Mining and Smelting Company discharging cadmium into the Jinzugawa River, as a byproduct of mining operations. Residents in the surrounding area subsequently consumed rice grown in cadmium-contaminated irrigation water, experienced softening of the bones and kidney failure (Gray *et al*., 2003).

2.0 STUDY AREA

Kano State was formally established on April 1, 1968. It is situated in a semi-arid region, located between latitudes 10.30^{o}N to 13^{o}N and longitude 7.40^{o}E and 10.39^{o}E. Kano city is at 472.45 meters above sea level. The state is bordered by Jigawa State in the north-east, Katsina State in the north-west and Kaduna State is on the southern boundary. According to 2006 census, the state has a population of 9.5 million with projection of over 13 million in 2018. It has a total land area of 20,760 square kilometres with 1, 754, 200 hectares for agricultural and 75,000 hectares forest vegetation and grazing land. The state is noted for its fairly stable climate with relatively minor changes in temperature and humidity (Stilwell, 2000). Agriculture is the mainstay of the economy involving at least 75% of the rural population. Important crops produced in the State include maize, beans, rice, corn and varieties of vegetables.

3.0 MATERIALS AND METHODS

3.1 Sample Collection and Preparation

The samples were dehusked into grains washed with de-ionized water and dried to constant weight in hot air oven at 105°C for 6hrs, ground to powder and stored in clean air tied containers.

3.2 ANALYSIS

Five 5.0g of the prepared samples of subsection 3.1 were air dried, ground in an agate mortar and was placed in quartz crucibles for dry ashing and mineralized thermally in a muffle furnance at 450ºC for 12hrs. The mineralized samples was then acid digested according to Miller (1998), by dissolving in 20ml of 1:1 (v/v) concentrated HNO_3 and HCl acids in 100ml volumetric flask. The flask was then heated in an electro thermal heater with gentle swirling till digestion completed by evolution of white fumes. The cooled digests was filtered through what man No 1 filter paper into 50ml volumetric flask and was diluted to the mark with de-ionized water. The heavy metals content of the samples were determined using the atomic absorption spectrophotometer (AAS) and the concentration was calculated using the relation $y = mx + c$ from calibration of each metal standard (AOAC, 2005).

Comment [P1]: In bracket

3.3 Determination of Pollution Load Index (PLI), Transfer Factor (TR), Daily Intake of Metals (DIM) and Health Risk Index (HRI)

3.3.1 Pollution Load Index (PLI)

The following modified equation was used to determine the pollution load index (PLI) level in soils (Liu *et al.*, 2005).

$$\text{PLI} = \frac{Cs}{Cr}$$

Where C_{soil}= Concentration of metal in soil.

$C_{reference}$= Reference standard value of metal in soil.

3.3.2 Transfer Factor (TF)

Transfer factor (TF) from soil to grains was calculated as described by Liu *et al.* (2005).

$$\text{TF} = \frac{Cg}{Cs}$$

Where C_{g} = *Concentration of metal in grains*

C_{s} = *Concentration of metal in soil.*

3.3.3 Daily Intake of Metals (DIM)

The Daily intake of metals (DIM) was determined as described by Wang *et al*. (2005).

$$\text{DIM} = \frac{Cg \times Cf \times Dfi}{Babw}$$

Where: C_g = *concentration of heavy metals in grains (mg/kg)*

C_f = *0.085*

$_{Dfi}$ *(daily food intake)* = *0.345 kg per day for adult*

$_{Babw}$ *(average body weight)* = *55.90 kg for adult (Wang et al., 2005).*

3.3.4 Health Risk Index (HRI)

Health risk index was calculated as described by US-EPA (2002).

$$\text{HRI} = \frac{DIM}{RFD}$$

Where RFD= reference oral dose (USEPA, 2002).

DIM= Daily intake of metals

Statistical analysis:

The data were expressed as mean ± standard deviation, two-way ANOVA was conducted to examine the interaction between the source (soil, beans and maize) and location (Local

Government Areas) on the level of heavy metals (Hg, Pb, Cd and Cr). SPSS version 20.0 was used for statistical analyses and $P<0.05$ was set as level significant.

4.0 RESULT AND DISCUSSION

4.1 RESULTS

Figure 1 shows the imperfect linear distribution of mean Hg concentration in samples of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government areas. The near zero linear coefficient (r) correlation is suggesting the distribution of Hg across the local governments is not perfectly correlated. This is further supported by the square of coefficient of multiple variations (R^2), which gave a measure of the total variation in the dependent variable (soil), explained by variations in the explanatory variable (farm produce).

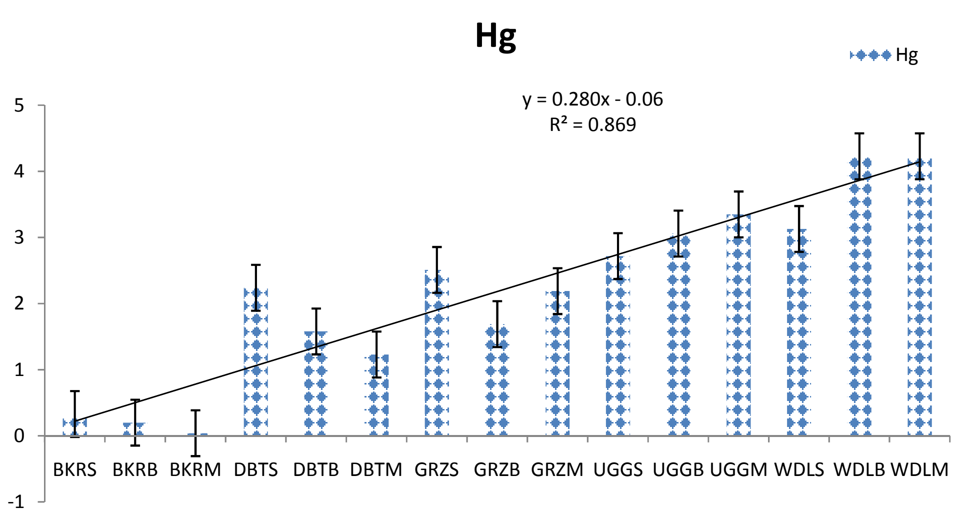

Figure 1: Non-linear distribution of mean Hg levels in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria.

Figure 2 displays weak linear correlations for the distribution of mean Pb levels in samples around Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria, as indicated by the value of linear coefficient (r). The measure of the total variation in the dependent variable (R^2) further justifies that.

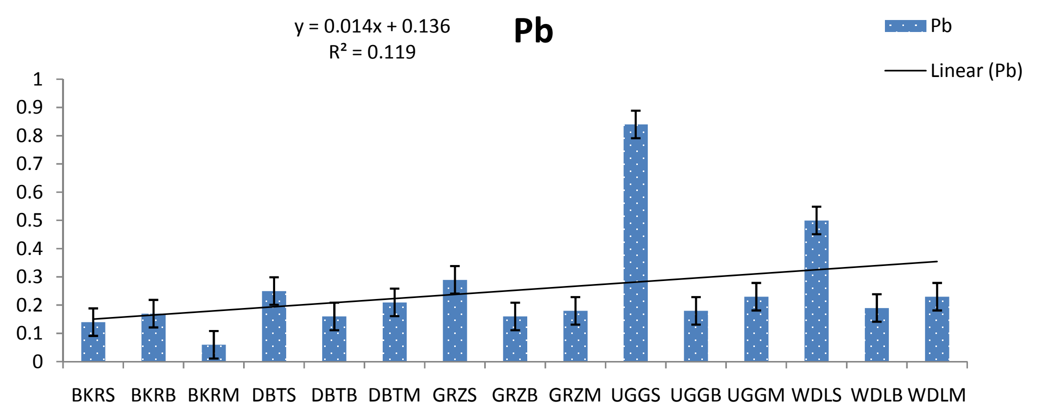

Figure 2: Non-linear distribution of mean Pb concentration in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria.

Strong non – linear correlation (r = 0.0015) for the distribution of mean Cd levels in samples around Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria is shown on Figure 3 with a reasonable measure of the total variation in the dependent variable (R^2).

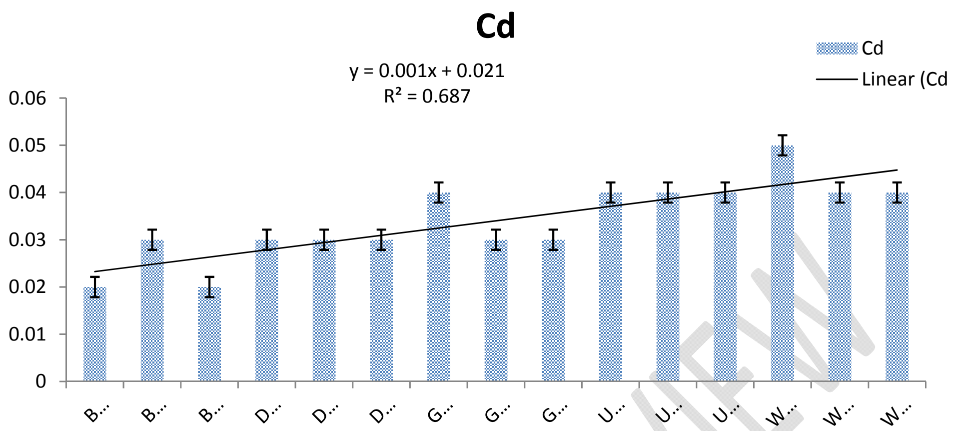

Figure 3: imperfect linear distribution of mean Cd value in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria.

Figure 4 shows an imperfect linear distribution of Cr in samples of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria. The near zero linear coefficient (r) correlation is suggesting the distribution of the Cr across the local governments is not perfectly correlated. This is further substantiated by the value of the square of coefficient of multiple variations (R^2), which gave a measure of the total variation in the dependent variable.

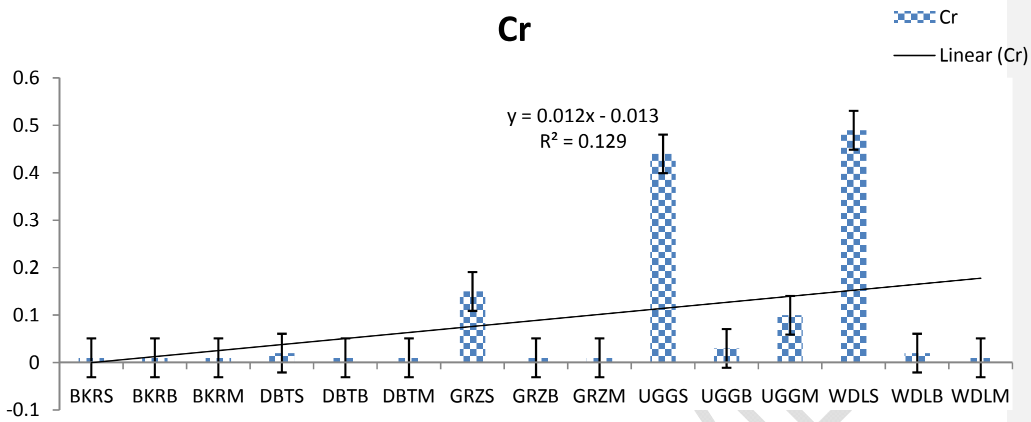

Figure 4: imperfect linear distribution of mean Cr value in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state Nigeria.

Table 1 shows the coefficient correlation matrix for Mercury (Hg) distribution in soil, beans and maize of the five local government areas of the study. It show a significant perfect correlation ($P<0.01$) between; WDLS vs WDLM, DBTS vs GRZB, UGGS vs BKRB, WDLS vs BKRM, UGGM vs GRZM, UGGM vs WDLB and imperfects positive correlation between GRZS vs GRZB.

Table 1: coefficient correlation of Mercury (Hg) distribution in soil, beans and maize of five local government areas of Kano state Nigeria

	Hg DBTS	Hg DBTB	Hg DBTM	Hg BKRS	Hg BKRB	Hg BKRM	Hg GRZS	Hg GRZB	Hg GRZM	Hg UGGS	Hg UGGB	Hg UGGM	Hg WDLS	Hg WDLB	Hg WDLM
HgDBTS	1.000														
HgDBTB	.000	1.000													
HgDBTM	.000	-1.000**	1.000												
HgBKRS	.816	.500	-.500	1.000											
HgBKRB	-1.000**	.000	.000	-.816	1.000										
HgBKRM	.333	-.816	.816	.000	-.333	1.000									
HgGRZS	.816	-.500	.500	.500	-.816	.816	1.000								
HgGRZB	1.000**	.000	.000	.816	-1.000**	.333	.816	1.000							
HgGRZM	.333	.816	-.816	.816	-.333	-.333	.000	.333	1.000						
HgUGGS	-1.000**	.000	.000	-.816	1.000**	-.333	-.816	-1.000**	-.333	1.000					
HgUGGB	.000	1.000**	-1.000**	.500	.000	-.816	-.500	.000	.816	.000	1.000				
HgUGGM	.333	.816	-.816	.816	-.333	-.333	.000	.333	1.000**	-.333	.816	1.000			
HgWDLS	.333	-.816	.816	.000	-.333	1.000**	.816	.333	-.333	-.333	-.816	-.333	1.000		
HgWDLB	.333	.816	-.816	.816	-.333	-.333	.000	.333	1.000**	-.333	.816	1.000**	-.333	1.000	
HgWDLM	.333	-.816	.816	.000	-.333	1.000**	.816	.333	-.333	-.333	-.816	-.333	1.000**	-.333	1.000

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

Table 2 shows coefficient correlation of Lead (Pb) distribution in soil, and farm produce (beans and maize) in five local government areas of the study. The lead distributions show significant negative correlation ($P<0.01$) between soil in DBT and the farm produce, maize in BKR and beans in WDL. In some instances it shows significant positive correlation ($P<0.01$) between; DBTS vs UGGS and UGGB, BKRB vs WDLM, GRZB vs GRZM and WDLM and UGGM vs WDLS. Imperfect positive correlation was shown between soil sample of each local government and respective farm produce.

Table 2: coefficient correlation of Lead (Pb) distribution in soil, beans and maize of five local government areas of Kano state Nigeria

	Pb DBTS	Pb DBTB	Pb DBTM	Pb BKRS	Pb BKRB	Pb BKRM	Pb GRZS	Pb GRZB	Pb GRZM	Pb UGGS	Pb UGGB	Pb UGGM	Pb WDLS	Pb WDLB	Pb WDLM
PbDBTS	1.000														
PbDBTB	-1.000**	1.000													
PbDBTM	-1.000**	1.000**	1.000												
PbBKRS	-1.000**	1.000**	1.000**	1.000											
PbBKRB	-.333	.333	.333	.333	1.000										
PbBKRM	1.000**	-1.000**	-1.000**	-1.000**	-.333	1.000									
PbGRZS	.333	-.333	-.333	-.333	.333	.333	1.000								
PbGRZB	-.333	.333	.333	.333	1.000**	-.333	.333	1.000							
PbGRZM	-.333	.333	.333	.333	1.000**	-.333	.333	1.000**	1.000						
PbUGGS	1.000**	-1.000**	-1.000**	-1.000**	-.333	1.000**	.333	-.333	-.333	1.000					
PbUGGB	1.000**	-1.000**	-1.000**	-1.000**	-.333	1.000**	.333	-.333	-.333	1.000**	1.000				
PbUGGM	.333	-.333	-.333	-.333	.333	.333	1.000**	.333	.333	.333	.333	1.000			
PbWDLS	.333	-.333	-.333	-.333	.333	.333	1.000**	.333	.333	.333	.333	1.000**	1.000		
PbWDLB	-.333	.333	.333	.333	-.333	-.333	-1.000**	-.333	-.333	-.333	-.333	-1.000**	-1.000**	1.000	
PbWDLM	-.333	.333	.333	.333	1.000**	-.333	.333	1.000**	1.000**	-.333	-.333	.333	.333	-.333	1.000

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

Table 3 show the coefficient correlation for the distribution of Cd in the local government area under study. It show significant positive correlation (P<0.01) between; DBTB vs DBTS, BKRS vs DBTM, GRZS vs DBTS and DBTB, GRZM vs BKRB, UGGB vs BKRM, UGGM vs BKRB, WDLS vs DBTS, DBTB and GRZS, and WDLM, DBTM and BKRS. The distribution projects significant negative correlation between BKRM vs DBTM and BKRS, UGGB vs DBTM and BKRS, WDLM vs BKRM and UGGB. Cd distribution in soil of each local government under the study show negative correlation with that of maize except for UGG that shows significant positive correlation (P<0.01). The distribution show positive correlation with that of beans except in UGG and WDL.

Table 3: coefficient correlation of Cadmium (Cd) distribution in soil, beans and maize of five local government areas of Kano state Nigeria

	Cd DBTS	Cd DBTB	Cd DBTM	Cd BKRS	Cd BKRB	Cd BKRM	Cd GRZS	Cd GRZB	Cd GRZM	Cd UGGS	Cd UGGB	Cd UGGM	Cd WDLS	Cd WDLB	Cd WDLM
CdDBTS	1.000														
CdDBTB	1.000**	1.000													
CdDBTM	-.333	-.333	1.000												
CdBKRS	-.333	-.333	1.000**	1.000											
CdBKRB	.333	.333	.333	.333	1.000										
CdBKRM	.333	.333	-1.000**	-1.000**	-.333	1.000									
CdGRZS	1.000**	1.000**	-.333	-.333	.333	.333	1.000								
CdGRZB	.816	.816	.000	.000	.816	.000	.816	1.000							
CdGRZM	.333	.333	.333	.333	1.000**	-.333	.333	.816	1.000						
CdUGGS	.333	.333	.333	.333	1.000**	-.333	.333	.816	1.000**	1.000					
CdUGGB	.333	.333	-1.000**	-1.000**	-.333	1.000**	.333	.000	-.333	-.333	1.000				
CdUGGM	.333	.333	.333	.333	1.000**	-.333	.333	.816	1.000**	1.000**	-.333	1.000			
CdWDLS	1.000**	1.000**	-.333	-.333	.333	.333	1.000**	.816	.333	.333	.333	.333	1.000		
CdWDLB	.000	.000	-.816	-.816	-.816	.816	.000	-.500	-.816	-.816	.816	-.816	.000	1.000	
CdWDLM	-.333	-.333	1.000**	1.000**	.333	-1.000**	-.333	.000	.333	.333	-1.000**	.333	-.333	-.816	1.000

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

The coefficient correlation of Chromium (Cr) distribution in the local government areas under study is shown on Table 4. It shows significant correlation (P<0.01) between; DBTS vs DBTB, DBTM, BKRB and GRZM, DBTB vs BKRB and GRZM, DBTM vs BKRB, GRZM, BKRS vs GRZB, GRZS vs WDLB, UGGS vs UGGB, UGGM vs WDLM. The lead distributions show significant negative correlation (P<0.01) in some instances Table 4. Positive correlation exists in each local government between soil and farm produce except in BKR and beans in GRZ and WDL that shows negative correlation.

Table 4: coefficient correlation of Chromium (Cr) distribution in soil, beans and maize of five local government areas of Kano state Nigeria

	Cr DBTS	Cr DBTB	Cr DBTM	Cr BKRS	Cr BKRB	Cr BKRM	Cr GRZS	Cr GRZB	Cr GRZM	Cr UGGS	Cr UGGB	Cr UGGM	Cr WDLS	Cr WDLB	Cr WDLM
CrDBTS	1.000														
CrDBTB	1.000**	1.000													
CrDBTM	1.000**	1.000**	1.000												
CrBKRS	-.500	-.500	-.500	1.000											
CrBKRB	1.000**	1.000**	1.000**	-.500	1.000										
CrBKRM	-.500	-.500	-.500	-.500	-.500	1.000									
CrGRZS	-.816	-.816	-.816	.000	-.816	.816	1.000								
CrGRZB	-.500	-.500	-.500	1.000**	-.500	-.500	.000	1.000							
CrGRZM	1.000**	1.000**	1.000**	-.500	1.000**	-.500	-.816	-.500	1.000						
CrUGGS	.816	.816	.816	-.816	.816	.000	-.333	-.816	.816	1.000					
CrUGGB	.816	.816	.816	-.816	.816	.000	-.333	-.816	.816	1.000**	1.000				
CrUGGM	.816	.816	.816	.000	.816	-.816	-1.000**	.000	.816	.333	.333	1.000			
CrWDLS	-.816	-.816	-.816	.816	-.816	.000	.333	.816	-.816	-1.000**	-1.000**	-.333	1.000		
CrWDLB	-.816	-.816	-.816	.000	-.816	.816	1.000**	.000	-.816	-.333	-.333	-1.000**	.333	1.000	
CrWDLM	.816	.816	.816	.000	.816	-.816	-1.000**	.000	.816	.333	.333	1.000**	-.333	-1.000**	1.000

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

The pollution load index of toxic metals in five Local Government Areas, Kano State, Nigeria is shown on Table 5. The result show that the highest soil pollution load (PL) of Mercury was in Wudil (3.13±0.16) followed by Ungogo soil with Hg PLI of 2.72±0.48, Gwarzo (2.51±0.46) Danbatta (2.24±1.30) and Bunkure with the lowest mercury PLI of 0.33±0.44. Ungogo shows the highest soil PL of Lead (5.6×10^{-3} ±0.04) while the lowest soil Lead PL was in Bunkure (0.93×10^{-3} ±0.08). Also, Wudil show the highest PL of Cadmium (1.6×10^{-2}± 0.01) and PL of Chromium (4.9×10^{-3}±0.01).

Table 5: Toxic metals pollution load index in soil of five Local Government Areas, Kano State, Nigeria

Study area	Hg	Pb	Cd	Cr
Bunkure	0.33 ± 0.44	0.93×10^{-3} ± 0.08	0.67×10^{-2}± 0.00	0.1×10^{-3}± 0.02
Danbatta	2.24 ± 1.30	1.66×10^{-3} ± 0.13	1.0×10^{-2}± 0.00	0.2×10^{-3}± 0.02
Gwarzo	2.51 ± 0.46	1.9×10^{-3} ± 0.05	1.3×10^{-2}± 0.00	1.5×10^{-3}± 0.03
Ungogo	2.72 ± 0.48	5.6×10^{-3} ± 0.04	1.3×10^{-2}± 0.00	4.4×10^{-3}± 0.04
Wudil	3.13 ± 0.16	3.3×10^{-3} ± 0.01	1.6×10^{-2}± 0.01	4.9×10^{-3}± 0.01

Table 6 shows the transfer factor of toxic metals from soil to grains in the five Local Government Areas under study. From the result, all the grains within the study zones exhibited a positive transfer factor, with the exception of Chromium in Bunkure, Danbatta and Gwarzo, where the transfer factor was zero.

Table 6: The transfer factor of toxic metals from soil to grains from five Local Government Areas, Kano State, Nigeria.

Study area	Hg		Pb		Cd		Cr	
	Beans	Maize	Beans	Maize	Beans	Maize	Beans	Maize
Bunkure	0.60	0.12	1.21	0.42	1.5	1	0	0
Danbatta	0.70	0.54	0.64	0.84	1	1	0	0
Gwarzo	0.67	0.87	0.55	0.62	0.75	0.75	0	0
Ungogo	1.12	1.23	0.21	0.27	1	1	0.06	0.22
Wudil	1.35	1.35	0.38	0.46	0.80	0.80	0.06	0.12

Table 7 show the daily intake of toxic metals in the five Local Government Areas under study. From the results, beans and maize from Wudil and Ungogo and maize from Gwarzo provided the highest daily intake of Mercury. This was followed by Gwarzo beans, beans and maize from Danbatta and Bunkure beans. The daily intake of Chromium from Bunkure beans and maize, Danbatta beans and maize and Gwarzo beans and maize was zero.

Table 7: Daily intake of toxic metals in beans and maize across five Local Government Areas under study

Study area	Hg		Pb		Cd		Cr	
	Beans	Maize	Beans	Maize	Beans	Maize	Beans	Maize
Bunkure	1.0×10^{-4}	2.0×10^{-5}	8.9×10^{-5}	3.1×10^{-5}	1.5×10^{-5}	1.0×10^{-5}	0	0
Danbatta	8.2×10^{-4}	6.4×10^{-4}	8.3×10^{-5}	1.0×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	0	0
Gwarzo	8.8×10^{-4}	1.1×10^{-3}	8.3×10^{-5}	9.4×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	0	0
Ungogo	1.6×10^{-3}	1.7×10^{-3}	9.4×10^{-5}	1.2×10^{-4}	2.0×10^{-5}	2.0×10^{-5}	1.5×10^{-5}	5.2×10^{-5}
Wudil	2.2×10^{-3}	2.2×10^{-3}	9.9×10^{-5}	1.2×10^{-4}	2.0×10^{-5}	2.0×10^{-5}	1.0×10^{-5}	3.1×10^{-5}

The health risk index of toxic metals across the five Local Government Areas, Kano State, Nigeria is presented on Table 8. From the results beans and maize from Wudil had highest health risk index due high Mercury content, followed by Ungogo, Gwarzo, Danbatta and Bunkure with the lowest health risk index of Mercury. All the remaining toxic metals showed a health risk index of less than one.

Comment [P2]: Possible omission

Table 8: Health risk index in beans and maize across five zones in Kano State, Nigeria

Study area	Hg		Pb		Cd		Cr	
	Beans	Maize	Beans	Maize	Beans	Maize	Beans	Maize
Bunkure	0.33	0.10	0.025	0.008	0.015	0.01	0	0
Danbatta	2.7	2.1	0.023	0.003	0.015	0.015	0	0
Gwarzo	2.9	3.6	0.023	0.026	0.015	0.015	0	0
Ungogo	5.3	5.6	0.026	0.035	0.02	0.02	0	0
Wudil	7.3	7.3	0.028	0.035	0.02	0.02	0	0

4.2 DISCUSSION

Current study evaluated the levels of toxic metals (mercury, lead, cadmium and chromium) in soil and farm produce (maize and beans) of five local governments of Kano state. Mean Pb, Cd and Cr concentration of the soil samples are within the respective limits of 150mg/Kg, 3mg/kg and 100 mg/Kg set by International Standard tolerable limits (2001). However, with exception of BKRS, all soil samples have mean mercury (Hg) concentration above 1mg/Kg, the limits set by international standard tolerable limits (2001). Mean Pb, Cd and Cr levels in beans and maize of the study area were all within the respective limits of 0.3mg/kg, 0.2 mg/kg and 0.2mg/kg set by International Standard tolerable limits (2001). While mean Hg concentrations in beans and maize are above 0.05mg/kg tolerable limit set by international standard tolerable limits (2001). Although, the mean levels of Pb, Cr, Cd are within tolerable limit, however, attention should be focused on low level chronic exposure to these toxic metals, mercury inclusive.

The study shows that the spatial soil distribution of the toxic metals in each of the study areas is significantly ($P < 0.01$) correlated with levels in the farm produce. The significant ($P < 0.01$) negative correlation may indicates uptake/removal of the toxic metals from soil into the crops, while the instances of positive significant ($P < 0.01$) correlation may indicates additional point sources of these metals, possible from the application of agrochemicals (fertilizers, pesticides and herbicides) and/or from non-point sources such as run off from environmental waste deposits of organic manure of animal origin, this is in line with the findings of Alhassan *et al* (2012) who established higher than reference value of some of these toxic metals in road site dust.

The established levels of these toxic metals in the farm produce relative to soil concentration could be alarming and may indicate their buildup to food chain. It may therefore serve as means of exposing human population to these toxic metals. This may be convinced by considering the outstanding characteristics of elements “non-destroyable and bioaccumulating”. The finding of the study established alarming concentration of Hg in most of the sample analyzed, despite the non or less toxic effect due to exposure of low levels of metallic mercury speculated by some researchers (Davidson *et al.,* 2004), biotransformation of the inorganic Hg to organic Hg such as methyl mercury may occur, that potentiate the toxic effects of the mercury which includes lung damage, nausea, vomiting, diarrhea, increase in blood pressure or heart rate, skin rashes, eye irritation, permanently damage to brain, kidneys, and developing fetuses (Sabine and wendy, 2009 and Davidson *et al.,* 2004). Alhassan *et al* (2012) pointed out that human exposure to lead may result in many biological effects depending on the level and duration of exposure. Lead resembles calcium as divalent ion, it is therefore handled by the body as if it were Ca^{2+}, hence replacing the calcium in many biological systems and protein matrix with concomitant loss in biological activity. In addition other biochemical toxicity of lead could be associated to it affinity to cell membrane and mitochondria, where it interfere with oxidative phosphorylation, it also interferes with Na, K and Ca ATP-ase pumps (Schumacher *et al.,* 1991). Chronic lead exposure to blood level > 1.4 µg/l in children is believed to cause mental retardation, selective deficits in language, cognitive function, balance, behavioural and school performance. Across all age chronic exposure to lead is associated kidney damage and interstitial nephritis, affect sperm and ova, anaemia, CNS defects, peripheral neuropathies, and reduced birth weight. Susceptibility to lead toxicity is governed by genetic factors, as established in Caucasians population with 15% variant of gene code for aminolevulinic acid dehydrogenase, hence become more susceptible to lead exposure (Pirzada *et al.,* 2009).

Cadmium is a very toxic metal, found in all soils, including coal and mineral fertilizers. Cadmium has many uses, including batteries, pigments, metal coatings, and plastics. It is used extensively in electroplating (Peter, 2005). Cadmium and cadmium compounds are known human carcinogens. Smokers get exposed to significantly higher cadmium levels than non-smokers. Severe damage to the lungs may occur through breathing high levels of cadmium common to cigarette smokers. High levels ingestion induces severe stomach irritation that induces vomiting and diarrhea, while Long-term exposure to lower levels leads to a buildup in the kidneys and possible kidney disease, lung damage, and fragile bones (Somers, 1983).

Chromium is found in rocks, animals, plants, and soil, its compounds bind to soil and are not likely to migrate to ground water but, they are very persistent in sediments in water. Chromium is used in metal alloys such as stainless steel; protective coatings on metal (electroplating); magnetic tapes; and pigments for paints, cement, paper, rubber, composition floor covering and other materials. Its soluble forms are used in wood preservatives (Lynch, 2005). Chromium (VI) compounds are toxins and known human carcinogens, whereas Chromium (III) is an essential nutrient. Breathing high levels can cause irritation to the lining of the nose; nose ulcers; runny nose; and breathing problems, such as asthma, cough, shortness of breath, or wheezing (Alabdulaaly *et al.,* 2009).

The level of Cadmium and Chromium in the soil, beans and maize samples from all the local government are not considered a health hazard. However, chronic exposure to such a low levels may lead to the toxicity and carcinogenic properties of chromium, softening of bones and kidney failure (Akintola, 2008). It is worth noting that most of the above mentioned sign and symptoms of heavy metals toxicity could be very common clinical cases in most hospitals nowadays and may not be unconnected to buildup of these toxic metals in foods and ultimately in human tissues.

Based on the findings of this study, mercury was found to possess a health risk index in four of the five Local Government Areas studied. The calculated health risk index of mercury in the studied areas was greater than one, and which shows obvious risk of exposure by the population in the zones (Zhan *et al*., 2012). According to the world health organization (2007), the majority of mercury in the environment results from coal-fired power station, residential heating systems and waste incinerators. Mercury is also released into the environment in the process of mining gold and other metals. WHO (2007), also established that consumption of contaminated fish, shellfish and marine mammals is the main source of methyl mercury exposure, especially for people who rely on predatory fish as their main source of protein. A recently conducted study by Zhang *et al*. (2010) found an elevated concentration of methyl mercury in rice (9.3ug/kg) throughout the Guizhou province of China. According to the Al-saleh and Shinwari, (2001), Mercury continues to be found in rice even in regions where mercury based pesticides are no longer in use. A study conducted in Saudi Arabia found that the concentration in rice was (3.18 ug/kg). In addition to past or ongoing fungicide use, mining and other industrial activities introduce another route of mercury exposure into the food chain through grain consumption in some regions of the world.

CONCLUSION

Heavy metals contamination constitutes a major factor of environmental pollution. However, from this study, it appears that all the toxic metals of the samples (soils, beans and maize) were below the maximum tolerable levels and might appear harmless. However, it is imperative to note that chronic exposure to these even at low concentrations should be avoided.

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