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 are imperative for assessing the 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. The metal concentration was determined using atomic absorption spectrometry (AAS). Results in mg/kg across the local governments indicate 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 the exception of mercury, the ranges of the toxic metals are within the tolerable range 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. A strong positive correlation between soils samples in respect to the level of some of the toxic metal may suggest a common nature of the soil, while the negative correlation may be due to 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 bioaccumulate some of these toxic metals, thereby incorporating them into the food chain, hence potential health risk.

Keywords: Toxic metals, Soil, Farm produce, Correlation, Distribution, pollution index, Kano-Local Government Areas

1.0 INTRODUCTION

Toxic metals are those metals having a 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 a trace amount and are at least five times denser than water, They are stable and persistent in

40 environmental samples, hence bioaccumulate to pass up via food chain to humans. According to

41 Alhassan *et al* (2012), sources of heavy metals are varied and include natural sources and all

42 human activities, with the possibility of polluting the environment. In another perspective,

43 environmental toxic metals are due to direct deposition from mining activities, industrial

44 processes as well as wastewater from domestic processes, in addition to agricultural practices

45 (Madyiwa, 2006). Heavy metals contamination to agricultural soils could be through a variety of

46 sources among which is the land application of biosolids, fertilizers, livestock manure,

47 agrochemicals (Pesticides), irrigation activities and an atmospheric droplet (Rajeswari & Sailaja,

48 2014). Worthy consideration is the accumulation of these metals in agricultural soils and possible

49 negative impacts on soil fertility and large potential accumulation in crops for possible

50 incorporation to human food chains (Gray *et al.*, 2003). Unlike the inorganic, the organic

51 (alkylated) forms are readily taken up by body tissues and can be retained for a considerable

52 length of time (Garrett *et al.*, 1992) this is due to their lipid solubility. The tissue penetrating

53 power of organometals crowns them more toxic to humans than the inorganic form (Carpenter,

54 2001).

55 Human exposure to soil accumulated toxic metal may be chronic via food chain transfer or acute

56 by direct ingestion or dermal contact. The former may be associated with; mental lapses, kidney,

57 liver, lung and gastrointestinal tract abnormalities, central nervous insufficiency, lower energy

58 levels, damage to blood compositions, kidneys, and other vital organs (Gray *et al.*, 2003). Long

59 term exposure to low dose may result in slowly progressing physical, muscular, and neurological

60 degenerative processes that mimic Alzheimer`s disease, Parkinson`s disease, muscular

61 dystrophy, and multiple Sclerosis (Srivastava and Goyal, 2010). Allergies are not uncommon and

62 repeated long-term contact with some metals or their compounds may even cause cancer. The

2

63 letter depends on the degree to which a system, tissue, organ or cell is affected by a heavy metal

64 type and the individual's degree of exposure (Vallero and Letcher, 2013).

65 Mercury combines with other elements to form organic and inorganic mercury compounds.

66 Metallic mercury used to produce chlorine gas, caustic soda, in thermometers and dental fillings,

67 switches, light bulbs, and batteries, including coal-burning power plants are the largest human-

68 caused source of mercury emissions to the air in the United States. Mercury in soil and water is

69 converted by microorganisms to methyl mercury, a bioaccumulating toxin (Sabine and Wendy,

70 2009). The EPA reported that mercuric chloride and methyl mercury are possible human

71 carcinogens and nervous system is very sensitive to all forms of mercury. Exposure to high

72 levels can permanently damage the brain, kidneys, and developing fetuses. Effects on brain

73 functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory

74 problems. Short-term exposure to high levels of metallic mercury may cause lung damage,

75 nausea, vomiting, diarrhoea, increases in blood pressure or heart rate, skin rashes, and eye

76 irritation (Davidson et *al.,* 2004).

77 Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause

78 death. In pregnant women, high levels of exposure to lead may cause miscarriage. High-level

79 exposure in men can damage the organs responsible for sperm production (Emsley, 2011).

80 Chromium, chromium (III) compounds and chromium metal are not considered a health hazard,

81 while the toxicity and carcinogenic properties of chromium (VI) have been known since the late

82 19th century, while Cadmium exposure is a phenomenon of the early 20th century, and onwards.

83 In Japan in 1910, the Mitsui Mining and Smelting Company discharging cadmium into the

84 Jinzugawa River, as a byproduct of mining operations. Residents in the surrounding area

85 subsequently consumed rice grown in cadmium-contaminated irrigation water, experienced

86 softening of the bones and kidney failure (Gray *et al*., 2003).

87

2.0 STUDY AREA

89 Kano State was formally established on April 1, 1968. It is situated in a semi-arid region, located

90 between latitudes 10.30^{o}N to 13°N and longitude 7.40^{o}E and 10.39^{o}E. Kano city is at 472.45

91 meters above sea level. The state is bordered by Jigawa State in the north-east, Katsina State in

92 the north-west and Kaduna State is on the southern boundary. According to the 2006 census, the

93 state has a population of 9.5 million with a projection of over 13 million in 2018. It has a total

94 land area of 20,760 square kilometres with 1, 754, 200 hectares for agricultural and 75,000

95 hectares forest vegetation and grazing land. The state is noted for its fairly stable climate with

96 relatively minor changes in temperature and humidity (Stilwell, 2000). Agriculture is the

97 mainstay of the economy involving at least 75% of the rural population. Important crops

98 produced in the State include maize, beans, rice, corn and varieties of vegetables.

99

3.0 MATERIALS AND METHODS

3.1 Sample Collection and Preparation

102 The samples were dehusked into grains washed with de-ionized water and dried to constant

103 weight in a hot air oven at 105°C for 6hrs, ground to powder and stored in clean air tied

104 containers.

3.1.1 Soil Preparation and Digestion

106 Unwanted materials were removed from the soil. The samples was air dried in a clean room to

107 avoid contamination and ground to pass through 600μm sieve and stored in polyethylene bags

108   for analysis. 0.4 g of soil samples from each of the farm lands was weighed separately into a

109   beaker. To each beaker, 3 ml of concentrated HCl and 1 ml of concentrated HNO_3 was added and

110   heated on a hot plate at 100^oC for 10 minutes to destroy any oxidizable materials and carbonates.

111   The solutions was topped with deionised water to the 50 ml mark and filtered using a Whatman

112   filter paper (No. 1). The filtrate was then analyzed for the presence of heavy metals.

113   **3.2 ANALYSIS**

114   Five (5.0) g of the prepared samples of subsection 3.1 were air dried, ground in an agate mortar

115   and was placed in quartz crucibles for dry ashing and mineralized thermally in a muffle furnace

116   at 450^oC for 12hrs. The mineralized samples were then acid digested according to Miller (1998),

117   by dissolving in 20ml of 1:1 (v/v) concentrated HNO_3 and HCl acids in 100ml volumetric flask.

118   The flask was then heated in an electro thermal heater with gentle swirling till digestion

119   completed by the evolution of white fumes. The cooled digests were filtered through Whatman

120   filter paper (No. 1) into a 50ml volumetric flask and were diluted to the mark with de-ionized

121   water. The heavy metals content of the samples were determined using the atomic absorption

122   spectrophotometer (AAS) and the concentration was calculated using the relation $y = mx + c$

123   from calibration of each metal standard (AOAC, 2005).

124

125   **3.3 Determination of Pollution Load Index (PLI), Transfer Factor (TR), Daily Intake of**
126   **Metals (DIM) and Health Risk Index (HRI)**
127

128   **3.3.1 Pollution Load Index (PLI)**

129   The following modified equation was used to determine the pollution load index (PLI) level in

130   soils (Liu *et al.*, 2005).

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

131 *Where C_{soil=} Concentration of metal in soil.*
132 *C_{reference=} Reference standard value of metal in soil.*
133

134

3.3.2 Transfer Factor (TF)

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

137

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

138 *Where C_{g=} Concentration of metal in grains*
139 *C_{s=} Concentration of metal in soil.*
140

3.3.3 Daily Intake of Metals (DIM)

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

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

143 *Where: C_g = concentration of heavy metals in grains (mg/kg)*
144 *C_f = 0.085*
145 *D_{fi} (daily food intake) = 0.345 kg per day for adult*
146 *B_{abw} (average body weight) = 55.90 kg for adult (Wang et al., 2005).*
147

3.3.4 Health Risk Index (HRI)

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

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

150 *Where RFD= reference oral dose (USEPA, 2002).*
151 *DIM= Daily intake of metals*
152

Statistical analysis:

154 The data were expressed as mean ± standard deviation, two-way ANOVA was conducted to

155 examine the interaction between soil, beans and maize and Local Government Areas on the level

156 of heavy metals (Hg, Pb, Cd and Cr). SPSS version 20.0 was used for statistical analyses and

157 $P<0.05$ was set as level significant.

158

159

160 **4. RESULTS**

161 Figure 1 shows the imperfect linear distribution of mean Hg concentration in samples of Bunkure

162 (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government

163 areas. The near zero linear coefficient (r) correlation is suggesting the distribution of Hg across

164 the local governments is not perfectly correlated. This is further supported by the square of the

165 coefficient of multiple variations (R^2), which gave a measure of the total variation in the

166 dependent variable (soil), explained by variations in the explanatory variable (farm produce).
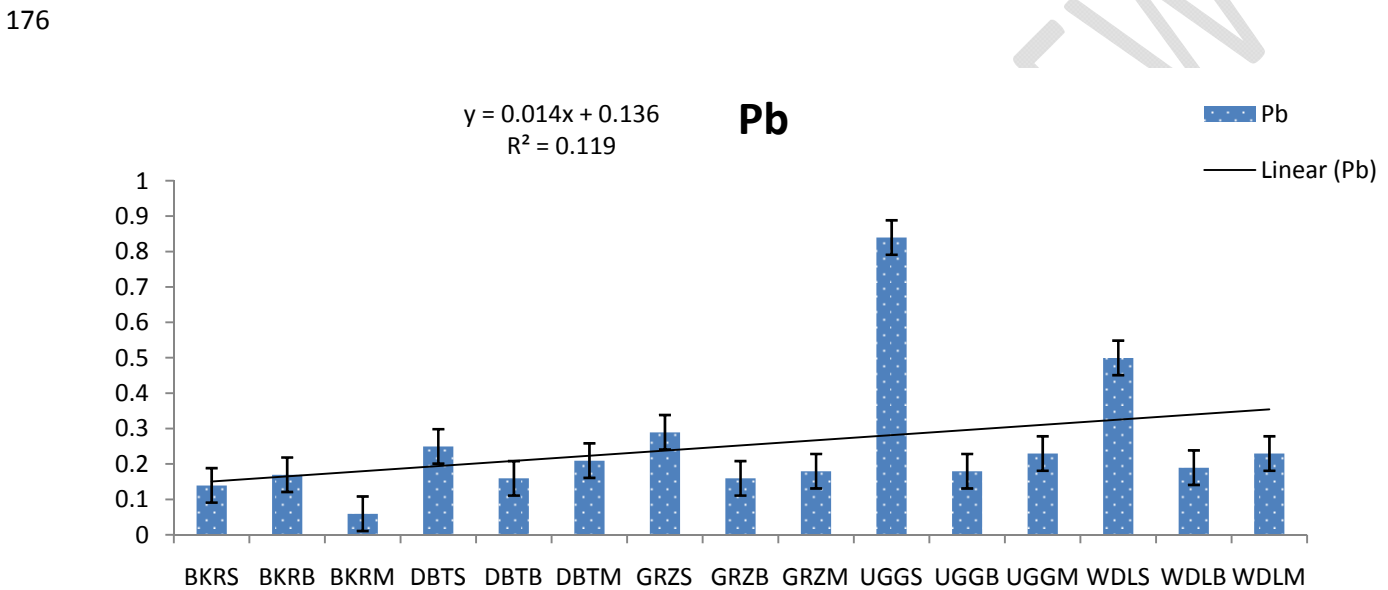
167

Hg

$y = 0.280x - 0.06$
$R^2 = 0.869$
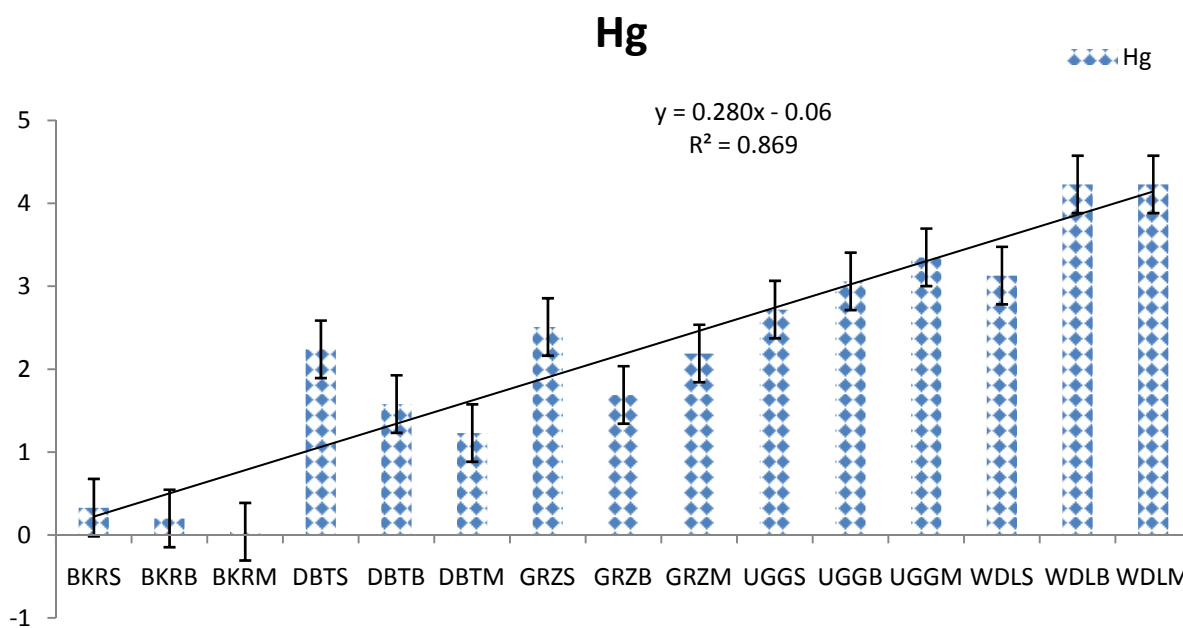
168

169 *Figure 1: Non-linear distribution of mean Hg levels in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG)*

7

171

172   Figure 2 displays weak linear correlations for the distribution of mean Pb levels in samples

173   around Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL)

174   local government of Kano state Nigeria, as indicated by the value of linear coefficient (r). The

175   measure of the total variation in the dependent variable (R^2) further justifies that.

176

177

178   *Figure 2: Non-linear distribution of mean Pb concentration in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo*
179   *(UGG) and Wudil (WDL) local government of Kano state Nigeria.*
180

181   Strong non – linear correlation (r = 0.0015) for the distribution of mean Cd levels in samples

182   around Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL)

183   local government of Kano state Nigeria is shown on Figure 3 with a reasonable measure of the

184   total variation in the dependent variable (R^2).

Cd

y = 0.001x + 0.021
R² = 0.687
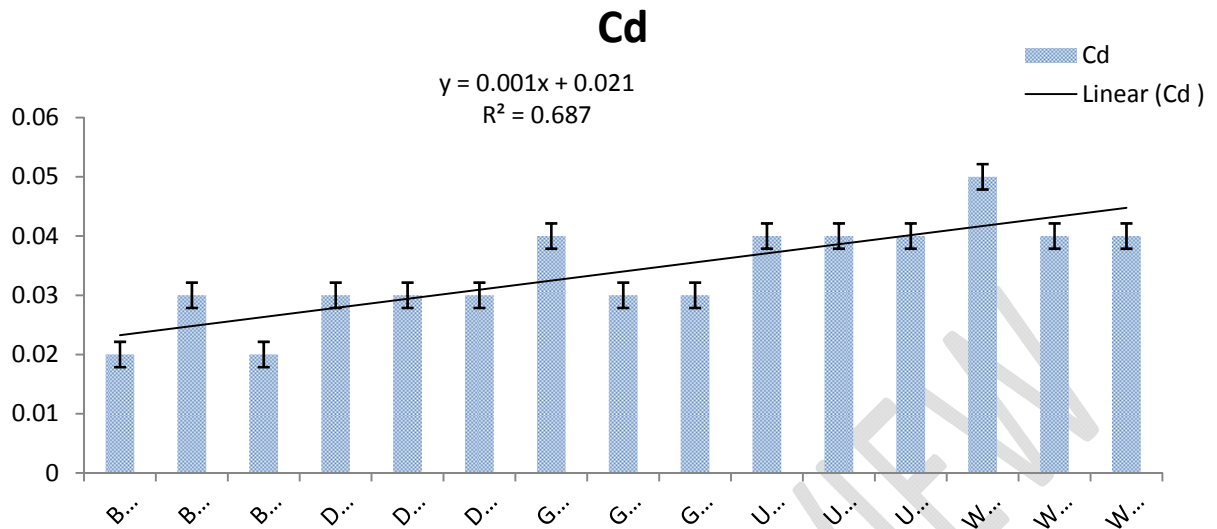
185

186 *Figure 3: imperfect linear distribution of mean Cd value in sample of Bunkure (BKR), Danbatta (DBT), Gwarzo (GRZ), Ungogo (UGG) and*
187 *Wudil (WDL) local government of Kano state Nigeria.*
188

189   Figure 4 shows an imperfect linear distribution of Cr in samples of Bunkure (BKR), Danbatta

190   (DBT), Gwarzo (GRZ), Ungogo (UGG) and Wudil (WDL) local government of Kano state

191   Nigeria. The near zero linear coefficient (r) correlation is suggesting the distribution of the Cr

192   across the local governments is not perfectly correlated. This is further substantiated by the value

193   of the square of coefficient of multiple variations (R^2), which gave a measure of the total

194   variation in the dependent variable.
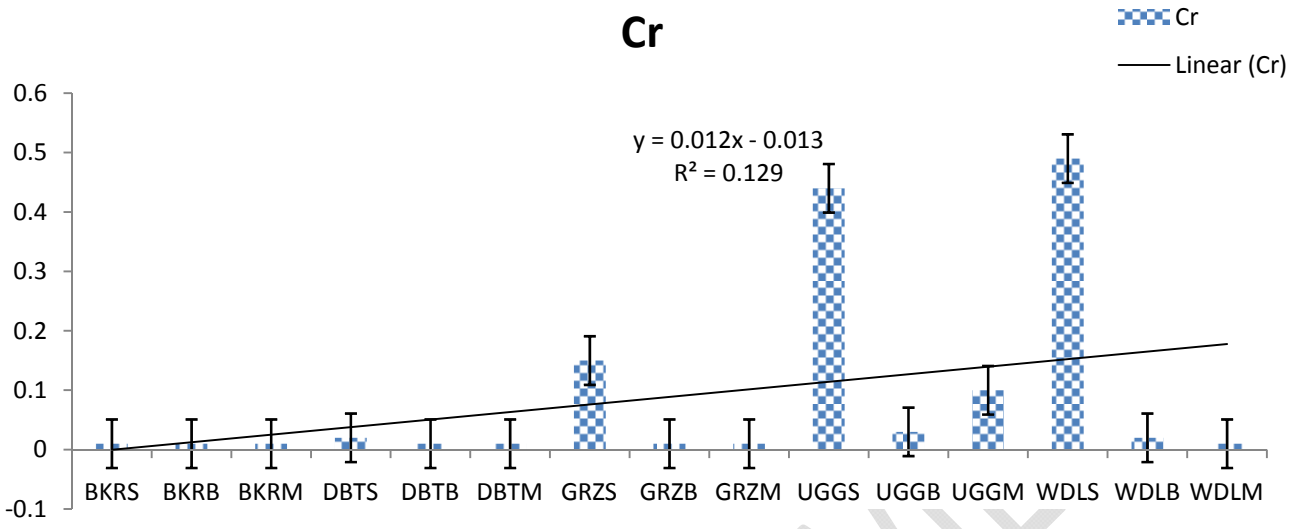
195

196

9

Cr

y = 0.012x - 0.013
R² = 0.129

197

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.

198
199
200

201

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 showed 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 imperfect 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 the coefficient correlation of Lead (Pb) distribution in soil, and farm produces (beans and maize) in five local government areas of the study. The lead distributions show a significant negative correlation (P<0.01) between the soil in DBT and the farm produce, maize in BKR and beans in WDL. In some instances, it shows a 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 the 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 shows the coefficient correlation for the distribution of Cd in the <mark>Local Government Area under the</mark> study. <mark>It showed a significant</mark> 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 shows a negative correlation with that of maize except for UGG that shows a significant positive correlation (P<0.01). The <mark>distribution showed a positive correlation</mark> 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

The coefficient correlation of Chromium (Cr) distribution in the local government areas under study was shown on Table 4. It shows a 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 a significant negative correlation (P<0.01) in some instances Table 4. A positive correlation exists in each local government between soil and farm produce except in BKR and beans in GRZ and WDL that shows a 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 <mark>State, Nigeria was shown in Table 5.</mark> The <mark>result showed that the</mark> 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. <mark>Ungogo showed the highest</mark> soil PL of Lead ($5.6\times10^{-3}\pm0.04$) while the lowest soil Lead PL was in Bunkure ($0.93\times10^{-3}\pm0.08$). Also, <mark>Wudil showed the highest</mark> PL of Cadmium ($1.6\times10^{-2}\pm0.01$) and PL of Chromium ($4.9\times10^{-3}\pm0.01$).

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

Study area	Hg	Pb	Cd	Cr
Bunkure	0.33 ± 0.44	$0.93\times10^{-3} \pm 0.08$	$0.67\times10^{-2}\pm 0.00$	$0.1\times10^{-3}\pm 0.02$
Danbatta	2.24 ± 1.30	$1.66\times10^{-3} \pm 0.13$	$1.0\times10^{-2}\pm 0.00$	$0.2\times10^{-3}\pm 0.02$
Gwarzo	2.51 ± 0.46	$1.9\times10^{-3} \pm 0.05$	$1.3\times10^{-2}\pm 0.00$	$1.5\times10^{-3}\pm 0.03$
Ungogo	2.72 ± 0.48	$5.6\times10^{-3} \pm 0.04$	$1.3\times10^{-2}\pm 0.00$	$4.4\times10^{-3}\pm 0.04$
Wudil	3.13 ± 0.16	$3.3\times10^{-3} \pm 0.01$	$1.6\times10^{-2}\pm 0.01$	$4.9\times10^{-3}\pm 0.01$

Table 6 shows the transfer factor of toxic metals from soil to grains in the five Local Government Areas under study. <mark>From this study, all</mark> the grains within the study zones exhibited a positive transfer factor, with the exception of Chromium in Bunkure, Danbatta and Gwarzo, <mark>where transfer factor</mark> 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 was presented in Table 8. From the results beans and maize from Wudil had the highest health risk index due to 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.

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

5. DISCUSSION

The 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 were within the respective limits of 150mg/Kg, 3mg/kg and 100 mg/Kg set by International Standard tolerable limits (2001). However, with the 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 were within the 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 was significantly ($P < 0.01$) correlated with levels in the farm produce. The significant ($P < 0.01$) negative correlation may indicate uptake/removal of the toxic metals from soil into the crops, while the instances of positive significant ($P < 0.01$) correlation may indicate additional point sources of these metals, possible from the application of agrochemicals (fertilizers, pesticides and herbicides) and/or from non-point sources such as runoff from environmental waste deposits of organic manure of animal origin, this is in line with the findings of Alhassan *et al* (2012) who established a higher reference value of some of these toxic metals in road-side 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 the food chain. It may, therefore, serve as a means of exposing the human population to these toxic metals. This may be convinced by

considering the outstanding characteristics of elements "non-destroyable and bioaccumulating".

The findings of the study established alarming concentration of Hg in most of the samples 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 its 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 with 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

19

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 groundwater but, they are very persistent in sediments in the 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 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 the 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 an 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 the 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 in environmental pollution. However, from this study, the results Show that all metals are below the limit tolerated by the legislation. However, it is imperative to note that chronic exposure to these even at low concentrations should be avoided.

REFERENCES

Alloway B.J (1995). Heavy metals in soils 2nd edition, Blackie academic and professional,

Glasgow. pp. 500.

Alhassan, A.J. Sule, M.S. Atiku, M.K., Wudil, A.M., Dangambo, M.A., Mashi, J.A. And Ibrahim, N.A. (2012). Study of Correlation between Heavy Metal Concentration, Street Dust and Level of Traffic in Major Roads of Kano Metropolis, Nigeria.

Al-Saleh I and Shinwari N. (2001). Report on the levels of cadmium, lead and mercury in imported rice grain samples. *Biol Trace Elements Health Research*, 83 (1):91-96.

AOAC. (2005). Official Methods of Analysis, association of analytical Chemists. Washington DC, 15 edition. Pp 11-14.

Alabdulaaly, A. I., & Khan, M. A. (2009). Heavy metals in cooler waters in Riyadh, Saudi Arabia. *Environmental Monitoring and Assessment.* 157, 23-28.

Carpenter D.O. (2001). Effects of metals on the nervous system of Humans and metals. *International Journal of Occupational medicine and Environmental Health.* 14(3); 209-218.

Davidson PW, Myers GJ, Weiss B (2004). "Mercury exposure and child development outcomes". *Pediatrics* **113**: 1023–9.

Emsley, J (2011). Nature's Building Blocks. Oxford University Press. ISBN 9780199605637. Pp 34.

Garrett N.E, Garrett R.J.B, Archdeacon J.W. (1992). Placental transmission of mercury to foetal rat. *Toxicological Application pharmacological.* 22; 649-654.

Gray C.W, Mclaren R.C, Roberts A.H.C. (2003). Atmospheric accessions of heavy metals to some New Zealand pastoral soils. *The science of the total Environment.* 305; 105-115.

Holding BV (2004). Heavy Metals (http: www. Lenntech. Com/heavy metals.htm).

International Standard Tolerable Limits (2001). Maximum levels of heavy metals in soil and foods. ISBN 9780123970268.

Liu, W. H., Zhao, J. Z., Soderlund, L., and Liu, G. H. (2005). Impacts of sewage irrigation on heavy metal distribution and contamination in Beijin, China. *Environment international journal.* 31: 313-812.

Lynch, E., and Braithwaite, R. (2005). A Review Of The Clinical And Toxicological Aspects of "Traditional" (Herbal) Medicines Adulterated With Heavy Metals. Sand Well and West Birmingham Nhs. In: UK Trust Regional Laboratory for Toxicology City Hospital Birmingham UK, pp. 769-778.

Madyiwa S. (2006). Modeling lead and cadmium uptake by star Grass under irrigation with

treated waste water. Published philosophiae. Doctor Thesis, University of Pretoria, South Africa. pp. 44-51

Peter, B. W. (2005). Municipal Solid Waste Compositing: Potential Effect of Heavy Metals in Municipal Solid Waste Composts on Plants and Environment. Boyce Thompson Institute for Plant Research at Cornell University: 1-5.

Pirzada, H., Ahmad, S. S., Rashid, A., & Shah, T. (2009). Multivariate analysis of selected roadside plants (Dalbergia sissoo and Cannabis sativa) for lead pollution monitoring. *Pakistan Journal Bot*, 41, 1729-1736.

Sabine Martin and Wendy Griswold. (2009). Centre for hazardous substances Research. Kansas University. U.S.

Schumacher, M., Bosgue, M. A., Domingo, J. L., &Corbella, J. (1991). Dietary Intake of Lead and Calcium from Foods in Tarragora Province, Spain. Bull Environ Contaminants and Toxicology, 46, 320-328.

Somers, E. (1983). The Toxic Potential of Trace Metals in foods. A Review. *Journal of Food Science*. 39, 215-217.

Srivastava, S; Goyal, P (2010). Novel Biomaterials: Decontamination of Toxic Metals from Wastewater. Springer-Verlag. ISBN 978-3-642-11329-1.

Stilwell, Sean (2000). "Power, Honour and Shame: The Ideology of Royal Slavery in the Sokoto Caliphate". Africa: Journal of the International African Institute (Edinburgh University Press) 70 (3): 394–421.

USEPA, IRIS. (2002).United State, Environmental Protection Agency, Integrated Risk Information System. http://www.epa.gov/iris/subs. Accessed 25 February 2010.

Vallero, DA; Letcher, TM (2013). Unravelling environmental disasters. Elsevier.

Wang, S. T. (2005). Study on predicting effects of the soil polluted with heavy metals on vegetables and method of assessing quality of the soil in vegetable plot irrigated with a sewage-a case study on Baoding suburb. Agricultural University of Hebei, China. Pp 1-43.

World Health Organization (WHO). (2014) Joint FAO/WHO Food Standards Programme. Codex Committee on Food Additives and Contaminants. Thirty-second session. Draft Maximum levels of lead. Prepared by Denmark pp 389.

World Health Organization (WHO), (2007). *Exposure to mercury: A major public health concern*. Geneva, Switzerland, World Health Organization (http://www.who.int/phe/news/Mercury-flyer.pdf, accessed 10 May 2010).

Zhan-Jun Xue, Shu-Qing Liu, Yan-Ling Liu and Yong-Lu Yan (2012). Health risk assessment of

heavy metals for edible parts of vegetables grown in sewage-irrigated soils in suburbs of Baoding city, china. *Environmental Monitoring Assess* 184:3503-3513.

Rajeswari, T. R., & Sailaja, N. (2014). Impact of heavy metals on environmental pollution. *Journal of Chemical and Pharmaceutical Sciences*, *3*, 175-181.