Sustainability, Agri, Food and Environmental Research, (ISSN: 0719-3726), 7(4), 219: 297-313
http://dx.doi.org/10.7770/safer-V0N0-art1549

EVALUATION OF HEAVY METALS IN AGRICULTURAL SOILS FROM KATSINA STATE NIGERIA

EVALUACIÓN DE METALES PESADOS EN SUELOS AGRÍCOLAS DEL ESTADO DE KATSINA NIGERIA

Aliyu Ibrahim Yaradua*[1], Adamu Jibrin Alhassan[2], Abdullahi Nasir[1], Kabir Ibrahim Matazu[1], Aminu Usman[1], Aminu Idi[2], Abdullahi Imam[2], Nasiru Abdullahi[2], Ibrahim Muhammad Usman[2] and Azik Musa Kanadi[3]

[1]Department of Biochemistry, Faculty of Natural and Applied Sciences, Umaru Musa Yar'adua University, P.M.B. 2218, Katsina, Nigeria

[2]Department of Biochemistry, Faculty of Basic Medical Sciences, Bayero University Kano, P.M.B. 3011, Kano, Nigeria

[3]National Agency for Food and Drug Administration and Control (NAFDAC), P.M.B. 2015, Katsina, Nigeria

*Correspondence Author, Email: aliyuyaradua5@gmail.com

ABSTRACT

This work contributes to the monitoring of Agricultural soil pollution in Katsina State, North western Nigeria by assessing the degree of heavy metal pollution in Agricultural soil samples. The study was conducted in the year 2017 within some catchment areas located within the 3 senatorial zones that constitute to make up the state (Katsina senatorial zone: Birchi, Dutsinma and Katsina; Daura senatorial zone: Daura, Ingawa and Zango; Funtua senatorial zone: Dabai, Funtua, Kafur, Malunfashi and Matazu). Analysis for the concentration of these heavy metals; Cr, Cd, Fe, Ni, Mn, Pb and Zn was conducted by the use of AAS (by Atomic Absorption Spectrophotometry) method. . Several indices were used to assess the metal contamination levels in the Agricultural soil samples, namely; Geo-accumulation Index (Igeo), Enrichment Factor (EF), Contamination Factor (CF), Degree of Contamination (Cd) and Pollution Load Index (PLI). The result of this study has shown that generally among the heavy metals evaluated, the highest concentration was observed for Fe (range: 20.195-38.347 ppm), followed by Zn (range: 0.528-1.134 ppm), Pb (range: 0.256-0.627 ppm), Mn (range: 0.261-0.572 ppm) and Cr (range: 0.093-0.344 ppm). While Cd has the lowest concentration (range: 0.022-0.043 ppm). For all the site sampled the heavy metal Ni was below detection level (BDL). From the results of heavy metals I-geo values, according to Muller's classification, soil samples from Birchi, Daura, Dutsinma, Kafur and Zango were unpolluted (class 0) while soil samples from Dabai, Funtua, Ingawa, Katsina, Malunfashi and Matazu are moderately polluted (class 1). The result for the enrichment factor has shown that with the exception of the heavy metal Fe, which shows significant enrichment for all the sites sampled all the other heavy metals show deficiency to minimal enrichment. Also based on the contamination factors for all soil samples the heavy metal Fe has a CF values range of 1.2861-2.3240, indicating that the Agricultural soil samples are moderately contaminated with Fe. In contrast, the rest of the heavy metals exhibit low contamination in general. The value of PLI ranges from 0.2408 to 0.4935, indicating unpolluted to moderate pollution, with the sampling site for Katsina displaying the highest PLI value while the sampling site of Ingawa has the lowest PLI. The Eri values for all samples are all < 40, presenting low ecological risk. The results suggest that the Agricultural soils samples from Katsina state has low contamination by the heavy metals evaluated.

Key words: Agricultural soils, Heavy metals, Katsina state, Pollution load index, Contamination factor.

RESUMEN

Este trabajo contribuye al monitoreo de la contaminación del suelo agrícola en el estado de Katsina, noroeste de Nigeria, mediante la evaluación del grado de contaminación por metales pesados en muestras de suelo agrícola. El estudio se realizó en el año 2017 dentro de algunas áreas de captación ubicadas dentro de las 3 zonas senatoriales que constituyen el estado (zona senatorial de Katsina: Birchi, Dutsinma y Katsina; zona senatorial de Daura: Daura, Ingawa y Zango; zona senatorial de Funtua: Dabai, Funtua, Kafur, Malunfashi y Matazu). Análisis para la concentración de estos metales pesados; Cr, Cd, Fe, Ni, Mn, Pb y Zn se llevaron a cabo mediante el uso del método AAS (por espectrofotometría de absorción atómica). . Se utilizaron varios índices para evaluar los niveles de contaminación de metales en las muestras de suelo agrícola, a saber; Índice de geoacumulación (Igeo), Factor de enriquecimiento (EF), Factor de contaminación (CF), Grado de contaminación (Cd) e Índice de carga de contaminación (PLI). El resultado de este estudio ha demostrado que, generalmente, entre los metales pesados evaluados, se observó la concentración más alta para Fe (rango: 20.195-38.347 ppm), seguido de Zn (rango: 0.528-1.134 ppm), Pb (rango: 0.256-0.627 ppm), Mn (rango: 0.261-0.572 ppm) y Cr (rango: 0.093-0.344 ppm). Mientras que Cd tiene la concentración más baja (rango: 0.022-0.043

ppm). Para todo el sitio muestreado, el Ni de metales pesados estaba por debajo del nivel de detección (BDL). De los resultados de los valores de I-geo de metales pesados, según la clasificación de Muller, las muestras de suelo de Birchi, Daura, Dutsinma, Kafur y Zango no estaban contaminadas (clase 0), mientras que las muestras de suelo de Dabai, Funtua, Ingawa, Katsina, Malunfashi y Matazu son moderadamente contaminado (clase 1). El resultado del factor de enriquecimiento ha demostrado que, con la excepción del Fe de metales pesados, que muestra un enriquecimiento significativo para todos los sitios muestreados, todos los demás metales pesados muestran una deficiencia de enriquecimiento mínimo. También basado en los factores de contaminación para todas las muestras de suelo, el Fe de metales pesados tiene un rango de valores de CF de 1.2861-2.3240, lo que indica que las muestras de suelo agrícola están moderadamente contaminadas con Fe. En contraste, el resto de los metales pesados exhiben baja contaminación en general. El valor de PLI varía de 0.2408 a 0.4935, lo que indica contaminación no contaminada a moderada, con el sitio de muestreo para Katsina mostrando el valor de PLI más alto, mientras que el sitio de muestreo de Ingawa tiene el PLI más bajo. Los valores de Eri para todas las muestras son <40, presentando bajo riesgo ecológico. Los resultados sugieren que las muestras de suelos agrícolas del estado de Katsina tienen baja contaminación por los metales pesados evaluados.

alabras clave: suelos agrícolas, metales pesados, estado de Katsina, índice de carga de contaminación, factor de contaminación.

INTRODUCTION

Soil is not only a medium for plant growth or pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface water, groundwater, atmosphere and food (Chen *et al*. 1997). The Soil is also a key part of the Earth system as it control the hydrological, erosional, biological, and geochemical cycles (Chen *et al*. 1997). The soil system also offers goods, services, and resources to humankind (Berendse *et al*. 2015; Brevik *et al*. 2015; Decock *et al*. 2015 and Smith *et al*. 2015). Soils have been used to detect the deposition, accumulation, and distribution of heavy metals in different locations (Alirzayeva *et al*. 2006 and Onder *et al*. 2007), this is why it is necessary to research how soils are affected by societies. Pollution is one of these damaging human activities, and we need more information and assessment of soil pollution (Mahmoud and El-Kader 2015; Riding *et al*. 2015; Roy and Mcdonald 2015 and Wang *et al*. 2015). Heavy metal pollution of agricultural soil can result not only in decreased crop output and quality and hurt human health through the food chain, but also further deterioration of air and water environmental quality

(Turkdogan *et al*. 2002; Su and Wong 2003 and Xia *et al*. 2004). Excessive accumulation of heavy metals in agricultural soils can affect the quality and safety of food and further increase the risk of serious diseases (cancer, kidney, liver damage, etc.), as well as impact ecosystems, thus combining environmental chemistry with biological toxicology and ecology (Suresh *et al*. 2012). Literature indicates that studies have been conducted on pollution by heavy metals of some areas in Nigeria (Ahaneku and Sadiq 2014; Opaluwa *et al*. 2012; Abdullateef *et al*. 2014 and Orisakwe *et al*. 2012), but nothing of such has been monitored on the heavy metal levels emanating from Agricultural soils in Katsina state Northwestern Nigeria and their possible effects on the quality of soil and human health. Therefore, it is important to investigate the level of heavy metals in soil to ascertain pollution levels.

MATERIALS AND METHODS

Study area: The study was carried out during 2017 in Katsina State, Nigeria located between latitude $12^0$15′N and longitude of $7^0$30′E in the North West Zone of Nigeria, with an area of 24,192km^2 (9,341 sq metres). The study was conducted within some catchment areas located within the 3 senatorial zones that constitute to make up the state (Katsina senatorial zone: Birchi, Dutsinma and Katsina; Daura senatorial zone: Daura, Ingawa and Zango; Funtua senatorial zone: Dabai, Funtua, Kafur, Malunfashi and Matazu). Katsina State has two distinct seasons: rainy and dry. The rainy season begins in April and ends in October, while the dry season starts in November and ends in March. This study was undertaken during the dry season. The average annual rainfall, temperature, and relative humidity of Katsina State are 1,312 mm, 27.3ºC and 50.2%, respectively. Like most alluvial soils, the soil in Katsina state is the flood plain type and is characterized by considerable variations. The soil has two main types, which are soils with little hazards and soils with good water holding capacity.

Soil sampling: Katsina has been divided into three agro-ecological zones (Guinea Savannah; Sudan Savannah; Sub-Sahel Savannah), with farmers in the state engaged in the production of horticultural crops, such as Maize, Sorghum, Millet, Rice, Beans, Soybeans, Cotton, Cassava, Groundnut, Sweet Potatoes, vegetables and fodder crops (Katsina State investors hand book, 2016). Fifty-five soil samples (Katsina zone; 15 soil samples; Daura zone: 15 soil samples; Funtua zone: 25 soil samples) were collected from 0-20 cm depths (plough layer) of cultivated farmland with a hand auger from the designated sampling areas. Five samples were collected randomly from each location. The distance from one sampling point to another was approximately 50 m at each location. The collected five samples from each location were mixed and about 250-300 g of the soil was sampled and put into a plastic container in accordance with the method adopted by Syed *et al.* (2012). The samples were properly labelled and were taken to the laboratory for analysis.

Chemical analysis of soil samples: Soil samples were dried at room temperature and pebbles, stones, and large debris were removed from the soils before it was passed through a 2 mm polyethylene sieve. All glassware and plastic ware were soaked in 10% nitric acid for 24 hrs and rinsed thoroughly with deionized water. The soil samples were digested by mixed acid ($HCl-HNO_3$) for Mn, Zn, Pb, Cd, Ni, Fe and Cr analyses. The concentrations of the heavy metals were measured by an atomic absorption spectrometer (AA210RAP BUCK Atomic Absorption Spectrometer flame emission spectrometer filter GLA-4B Graphite furnace, East Norwalk USA) according to standard methods (AOAC, 1995) and the results were given in part per million (ppm).

RESULTS AND DISCUSSION

Soil samples from 11 locations within the 3 senatorial zones of Katsina State were analyzed in this study. As shown in Table 1, among the heavy metals evaluated, the highest concentration was observed for Fe (range: 20.195-38.347 ppm), followed by Zn (range: 0.528-1.134 ppm), Pb (range: 0.256-0.627 ppm), Mn (range: 0.261-0.572 ppm) and Cr (range: 0.093-0.344 ppm). While Cd has the lowest concentration (range: 0.022-0.043 ppm) and the concentration range for the heavy metal Ni was BDL in all the soil samples.

The Pb concentration range for the agricultural soil samples in this study is similar to that reported for soils from post office area, Bulunkutu and Bama station in Maiduguri metropolis, Borno state Nigeria (Abdullateef *et al*. 2014) and that reported for soil samples from Lafia metropolis, Nasarawa state, Nigeria with a Pb concentration range of 0.100- 0.530 ppm (Opaluwa *et al*. 2012). But the values are lower than those reported for the Pb concentration in soils in Bosso, Chanchaga, Gidan Kwano, Ogbomosho, Owerri and Ibeno AkwaIbom in Nigeria (Ahaneku and Sadiq, 2014; Oladeji *et al*. 2016; Orisakwe *et al*. 2012 and Udosen *et al.* 2012), and also in Pb levels in soils reported in studies conducted in Birjand city of Iran, Western Rajastan, Faisalabad, Suxian county south China and Thrace region of Turkey and Tarnaveni in Romania (Sayadi *et al.* 2017; Anjula, 2014; Farid *et al*. 2015; Daping *et al*. 2015; Ekmekyapar *et al*. 2012 and Mihaileanu *et al.* 2019). Furthermore the result for the Pb concentration in this study is higher than that reported in a study that evaluates heavy metal concentrations of some selected Dams sediment in Katsina state Nigeria (Yaradua *et al.* 2018).

The Cd concentration range for the soil samples in this study is similar to that reported by Farid *et al*. (2015) for Cd values for soil samples from Madina town of Faisalabad and that reported for Nanxun county Southeast China (Zhou *et al*. 2015), Thrace region of Turkey

(Ekmekyapar *et al*. 2012) and the results for studies conducted in the towns of Bosso, Chanchaga, Gidan Kwano, Lafia metropolis, Maiduguri metropolis and the city of Owerri all in Nigeria (Ahaneku and Sadiq 2014; Opaluwa *et al*. 2012; Abdullateef *et al*. 2014 and Orisakwe *et al*. 2012). But the values are lower than that reported in studies for the Cadmium concentration in soils conducted in Suxian county, western Rajastan, Birjand city in Asia (Daping *et al*. 2015; Anjula 2014 and Sayadi *et al*. 2017) and in some studies conducted in Nigeria (Udosen *et al*. 2012 and Oladeji *et al*. 2016).

Though an essential heavy metal, Fe has the tendency to become toxic to living organisms, even when exposure is low. In the present study, the mean Fe concentration in both the soil samples was higher than that reported for soil samples from Lafia metropolis Nasarawa state, Nigeria (Opaluwa *et al*. 2012) and that of a study conducted by Abdullateef *et al*. (2014) in Maiduguri metropolis Borno state, Nigeria.

The Zn concentration obtained in this study was higher than the report of a study conducted in Lafia, Nasarawa state Nigeria (Opaluwa *et al*. 2012). But the result was lower than the values reported for Zn in soil from western Rajastan (Anjula, 2014), Zn concentration in soil from Thrace region of Turkey (Ekmekyapar *et al.* 2012), the result of Oladeji *et al.* (2016) for Zn in soil from Ogbomoso Nigeria, and the values reported for Zn in soils from Bosso, Chanchaga and Gidan-Kwano Niger state Nigeria (Ahaneku and Sadiq, 2014).

The present study recorded a concentration range of 0.093-0.344 ppm for Cr, values that are lower compared with Cr in soils from western Rajastan and Birjand city of Iran (Anjula *et al*. 2014), Thrace region of Turkey Ekmekyapar *et al.,* (2012), Tarnaveni in Romania (Mihaileanu *et al*. 2019) and the result of Cr in various soil samples from Maiduguri state, Nigeria (Abdullateef *et al*. 2014). But the values were similar to the results of Ahaneku and Sadiq (2014) of Cr in soils from Bosso, Chanchaga and Gidan Kwano in Nasarawa state, Nigeria.

Mn mean concentration obtained in this study was lower than the Mn concentrations in soil near a former chemical manufacturing facility in Tarnaveni, Romania (Mihaileanu *et al.,* 2019).

Table 1: Heavy Metals Concentration in Agricultural Soil Samples from Katsina State (ppm)

Location	Heavy Metal						
	Mn	Zn	Pb	Cd	Ni	Fe	Cr
Birchi	0.300 ± 0.0005	0.641 ± 0.0004	0.448 ± 0.0002	0.033 ± 0.0003	BDL	21.212± 0.0009	0.344 ± 0.0003
Dabai	0.566 ± 0.0015	1.207 ± 0.0002	0.348 ± 0.0003	0.025 ± 0.0001	BDL	24.896 ± 0.0012	0.093 ± 0.0002
Daura	0.287 ± 0.0006	0.968 ± 0.0003	0.529 ± 0.0008	0.043 ± 0.0003	BDL	22.246 ± 0.0002	0.226 ± 0.006
Dutsinma	0.321 ± 0.0004	0.612 ± 0.0004	0.441 ± 0.0006	0.032 ± 0.0004	BDL	23.342 ± 0.0006	0.342 ± 0.0006
Funtua	0.572 ± 0.0004	1.132 ± 0.0006	0.541 ± 0.0015	0.025 ± 0.0006	BDL	28.264 ± 0.0012	0.268 ± 0.0003
Ingawa	0.261 ± 0.0007	1.099 ± 0.0003	0.627 ± 0.0002	0.034 ± 0.0002	BDL	20.195 ± 0.0023	0.143 ± 0.0010
Kafur	0.511 ± 0.0006	1.083 ± 0.0015	0.462 ± 0.0013	0.031 ± 0.0004	BDL	31.716 ± 0.0009	0.241 ± 0.0004
Katsina	0.486 ± 0.0004	0.775 ± 0.0002	0.256 ± 0.0002	0.024 ± 0.0002	BDL	38.347 ± 0.0009	BDL
Malunfashi	0.470 ± 0.0012	1.094 ± 0.0004	0.402 ± 0.0003	0.026 ± 0.0003	BDL	32.985 ± 0.0017	0.285 ± 0.0002
Matazu	0.277 ± 0.0004	1.134 ± 0.0002	0.285 ± 0.0003	0.022 ± 0.0001	BDL	37.442 ± 0.0009	0.099 ± 0.0007
Zango	0.272 ± 0.0015	0.528 ± 0.0006	0.564 ± 0.0002	0.032 ± 0.0004	BDL	24.568 ± 0.0006	0.232 ± 0.0002

Values are expressed as Mean ± Standard deviation

Indices: Several indices were used to assess the metal contamination levels in the Agricultural soil samples, namely; Geo-accumulation index (I-geo), Pollution Load Index (PLI), Enrichment Factors (EF), Contamination Factor (CF) and Degree of Contamination (Cd). World surface rock average data of heavy metals which was used as background values were taken from Martin and Meybeck (1979).

Geo-accumulation index: Geo-accumulation index (I-geo) was employed to evaluate the heavy metals pollution in the Agricultural soil samples. This method has been used by Müller since the late 1960s (Muller 1969). I-geo was calculated using the following equation:

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

Where Cn is the measured content of the examined metal in the sediment samples and Bn is the geochemical background content of the same metal. The constant 1.5 is introduced to minimize the effect of possible variations in the background values, which may be recognized to anthropogenic influences The index of geo-accumulation (Igeo) is characterized according to the Muller seven grades or classes profile of the geo-accumulation index i.e. the value of soil quality is considered as unpolluted (Igeo is ≤0, class 0); from unpolluted to moderately polluted (Igeo is 0 - 1, class 1); moderately polluted (Igeo is 1 - 2, class 2); from moderately to strongly polluted (Igeo is 2 - 3, class 3); Strongly polluted (Igeo is 3 - 4, class 4); from strongly to extremely polluted (Igeo is 4 - 5, class 5) and Extremely polluted (Igeo is >6, class 6) (Muller 1969).) Therefore, from the results of heavy metals I-geo values on table 2, according to Muller's classification, soil samples from Birchi, Daura, Dutsinma, Kafur and Zango were unpolluted (class 0) while soil samples from Dabai, Funtua, Ingawa, Katsina, Malunfashi and Matazu are from unpolluted to moderately polluted (class 1).

Table 2: Heavy Metals Geo-accumulation Values for Agricultural Soil Samples from Katsina State

	I-geo					
Site	Mn	Zn	Pb	Cd	Fe	Cr
Birchi	-3.1549	-2.4685	-1.7282	-0.9586	-0.0680	-2.4949
Dabai	-2.9208	-2.2007	-1.8386	-0.0794	0.0026	-3.0969
Daura	-3.2219	-2.2924	-1.6556	-0.8438	-0.0463	-2.6778
Dutsinma	-3.1549	-2.4949	-1.7352	-0.9718	-0.0254	-2.4949
Funtua	-2.9208	-2.2292	-1.6478	-1.0793	0.0577	-2.6021
Ingawa	-3.2219	-2.2366	-1.5834	-0.9457	0.1077	-2.8861
Kafur	-2.9586	-2.2441	-1.7144	-0.9859	-0.0883	-2.6383
Katsina	-2.9586	-2.4202	-1.9706	-1.0969	0.1902	BDL
M/Fashi	-3.0000	-2.2441	-1.7747	-1.0620	0.1247	-2.5686
Matazu	-3.2219	-2.2219	-1.9245	-1.1350	0.1798	-3.0458

Enrichment factor: Enrichment Factors (EF) were considered to estimate the abundance of metals in the Agricultural soil samples. EF was calculated by a comparison of each tested metal concentration with that of a reference metal (Muller 1981). The normally used reference metals are Mn, Al and Fe (Liu *et al*. 2005). In this study Fe was used as a conservative tracer to differentiate natural from anthropogenic components, following the hypothesis that its content in the earth crust has not been troubled by anthropogenic activity and it has been chosen as the element of normalization because natural sources (98%) greatly dominate its contribution (Tippie 1984). According to Rubio *et al*. (2000), the EF is defined as follows:

$$EF=\frac{\left(\frac{M}{Fe}\right)sample}{\left(\frac{M}{Fe}\right)Background}$$

Where EF is the enrichment factor, $(M/Fe)_{sample}$, is the ratio of metal and Fe concentration of the sample and $(M/Fe)_{background}$ is the ratio of metals and Fe concentration of a background. Five contamination categories are reported on the basis of the enrichment factor (Sutherland 2000). EF <2 deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment, EF>40 extremely high enrichment. As shown in Table 3, with the exception of the heavy metal Fe, which shows significant enrichment for all the sites sampled all the other heavy metals show deficiency to minimal enrichment.

Table 3: Enrichment Factor Values for Soil Samples from Selected Agricultural Sites in Katsina State

	Enrichment Factor (EF)					
site	Mn	Zn	Pb	Cd	Fe	Cr
Birchi	0.2007	0.4288	0.2828	0.0221	14.1949	0.2301
Dabai	0.3403	0.7257	0.2092	0.0150	14.6681	0.0559
Daura	0.1784	0.6017	0.3288	0.0267	13.8280	0.1405
Dutsinma	0.1989	0.3793	0.2733	0.0205	14.4649	0.2119
Funtua	0.2610	0.5166	0.2469	0.0114	12.8989	0.1223
Ingawa	0.0181	0.0761	0.0433	0.6024	13.9750	0.0099
Kafur	0.2410	0.5108	0.2179	0.0146	14.9586	0.1137
Katsina	0.1969	0.3140	0.1037	0.0097	15.535	BDL
M/Fashi	0.2168	0.5046	0.1854	0.0120	15.2138	0.1315
Matazu	0.1150	0.5054	0.1270	0.0098	16.6854	0.0441
Zango	0.1607	0.3119	0.33320.	0.0189	14.5124	0.1370

Contamination factor: Contamination Factor (CF) was used to determine the contamination status of the Agricultural soils in the current study. CF was calculated according to the equation described below (Pekey *et al*. 2004):

$$C=\frac{Mc}{Bc}$$

Where Mc Measured concentration of the metal and Bc is the background concentration of the same metal. Four contamination categories are documented on the basis of the contamination factor (Hakanson 2000). CF<1 low contamination; 1≤CF≥3 moderate contamination; 3≤CF<6 considerable contamination; CF>6 very high contamination, while the degree of contamination (Cd) was defined as the sum of all contamination factors. The following terms is adopted to illustrate the degree of contamination: Cd<6: low degree of contamination; 6≤Cd<12: moderate degree of contamination; 12≤Cd<24: considerable degree of contamination; Cd>24: very high degree of contamination indicating serious anthropogenic pollution. The result of the contamination factors for the evaluated heavy metals is shown on table 4. From the table, the relative distributions of the contamination factor among the samples are: Fe > Cd >Pb> Zn > Cr >Mn. Soils have been used as environmental indicators, and this ability to identify heavy metal contamination sources and monitor contaminants is also well documented. Thus, the accumulation of metals in the soils is strongly controlled by the nature of the substrate as well as the physicochemical conditions controlling dissolution and precipitation (Venkatramanan et al. 2012). For all soil samples the heavy metal Fe has a CF values range of 1.2861-2.3240, indicating that the Agricultural soil samples are moderately contaminated with Fe. In contrast, the rest of the heavy metals exhibit low contamination in general.

Table 4: Contamination Factor for Agricultural Soil Samples from Katsina State

	Contamination Factor (EF)					
Site	Mn	Zn	Pb	Cd	Fe	Cr
Birchi	0.0010	0.0051	0.0280	0.1690	1.2861	0.0049
Dabai	0.0018	0.0095	0.0218	0.1250	1.5089	0.0013
Daura	0.0009	0.0076	0.0331	0.2150	1.3482	0.0032
Dutsinma	0.0010	0.0048	0.0276	0.1600	1.4147	0.0048
Funtua	0.0019	0.0089	0.3380	0.1250	1.7130	0.0038
Ingawa	0.0008	0.0086	0.0392	0.1700	1.2239	0.0020
Kafur	0.0017	0.0085	0.0289	0.1550	1.9220	0.0034
Katsina	0.0016	0.0061	0.0160	0.1200	2.3240	BDL
M/Fashi	0.0015	0.0086	0.0251	0.1300	1.9990	0.0040
Matazu	0.0009	0.0089	0.0178	0.1100	2.2692	0.0014
Zango	0.0009	0.0042	0.0353	0.1600	1.4890	0.0033

Degree of Contamination and Pollution Load Index: The degree of contamination (Cd) was defined as the sum of all contamination factors. The following terms is adopted to illustrate the degree of contamination: Cd<6: low degree of contamination; 6≤Cd<12:

moderate degree of contamination; 12≤Cd<24: considerable degree of contamination; Cd>24: very high degree of contamination indicating serious anthropogenic pollution. Pollution Load Index (PLI) was used to evaluate the extent of pollution by heavy metals in the environment. The range and class are same as Igeo. PLI for each sampling site has been calculated following the method planned by Tomlinson *et al*. (1980) as follows:

$$\text{PLI} = (CFI + CF2 + CF3 \ldots \ldots \ldots CFn)^{\frac{1}{n}}$$

Where n is the number of metals and CF is the contamination factor. The value of PLI ranges from 0.2408 to 0.4935 (Table 5), indicating unpolluted to moderate pollution. However, the sampling site for Katsina displayed the highest PLI value while the sampling site of Ingawa has the lowest PLI.

Table 5: Degree of Contamination and Pollution Load Index of Agricultural Soil samples from Katsina State

Site	Degree of Contamination	Pollution Load Index
Birchi	1.4941	0.2490
Dabai	1.6633	0.2772
Daura	1.6080	0.2680
Dutsinma	1.6129	0.2688
Funtua	2.1906	0.3651
Ingawa	1.4445	0.2408
Kafur	2.1195	0.3533
Katsina	2.4677	0.4935
M/Fashi	2.1682	0.3614
Matazu	2.4082	0.4014
Zango	1.6927	0.2821

Potential Ecological Risk Index: This research employed the Potential Ecological Risk Index (PERI) proposed by Hakanson (1980) to evaluate the potential ecological risk of heavy metals. This method comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals (Nabholz 1991; Singh *et al*. 2010 and Douay *et al*. 2013). PERI is formed by three basic modules: degree of contamination (CD), toxic-response factor (TR) and potential ecological risk factor (ER).The ecological risk index (Eri) evaluates the toxicity of trace elements in sediments and has been extensively applied to soils (Liang *et al*. 2015). Soils contaminated by heavy metals can cause serious ecological risks and negatively impact human health due to various forms of interaction (agriculture, livestock, etc.) where highly toxic heavy metals can enter the food chain. To calculate the Eri for individual metals, the following Equation was used;

$$Eri = Tri \times Cfi$$

Where Tr is the toxicity coefficient of each metal whose standard values are Cd = 30, Ni = 5, Pb = 5, Cr = 2, and Zn = 1, Mn = 1 (Hakanson 1980 and Xu 2008) and Cfi is the contamination factor. To describe the ecological risk index the following terminology was used: Er< 40, low; 40 ≤ Er< 80, moderate; 80 ≤ Er< 160, considerable; 160 ≤ Er< 320, high; and Er ≥ 320, very high. The risk factor was used as a diagnostic tool for water pollution control, but it was also successfully used for assessing the contamination of soils in the environment by heavy metals (Mugosa *et al*. 2016). The results suggest that the potential ecological risk of the tested heavy metals in the soil samples was mainly caused by the heavy metal Cd. Based on these calculations, the order of the single ratio of the tested heavy metals for the total potential ecological hazard is Cd>Pb>Cr>Zn>Mn for Birchi; Cd>Pb>Zn>Cr>Mn for Dabai; Cd>Pb>Zn>Cr>Mn for Daura; Cd>Pb>Cr>Zn>Mn for Dutsinma; Cd>Pb>Zn>Cr>Mn for Funtua; Cd>Pb>Zn>Cr>Mn for Ingawa; Cd>Pb>Zn>Cr>Mn for Kafur; Cd>Pb>Zn>Mn for Katsina; Cd>Pb>Zn>Cr>Mn for Malunfashi; Cd>Pb>Zn>Cr>Mn for Matazu; Cd>Pb>Cr>Zn>Mn for Zango soil samples. The Eri of all the heavy metals were all below 40, placing these metals at low ecological risk level (Table 6).

Table 6: Ecological Risk Index of Agricultural Soil Samples from Katsina State

	Ecological Risk Index (Eri)				
Site	Mn	Zn	Pb	Cd	Cr
Birchi	0.0010	0.0051	0.1400	5.0700	0.0098
Dabai	0.0018	0.0095	0.1090	3.7500	0.0026
Daura	0.0009	0.0076	0.1655	6.4500	0.0064
Dutsinma	0.0010	0.0048	0.1380	4.8000	0.0096
Funtua	0.0019	0.0089	0.1690	3.7500	0.0076
Ingawa	0.0008	0.0086	0.1960	5.1000	0.0040
Kafur	0.0017	0.0085	0.1445	4.6500	0.0068
Katsina	0.0016	0.0061	0.0800	3.6000	BDL
M/Fashi	0.0015	0.0086	0.1255	3.9000	0.0080
Matazu	0.0009	0.0089	0.0890	3.3000	0.0028

Zango	0.0009	0.0042	0.1765	4.8000	0.0066

In conclusion, The study reveals that generally among the heavy metals evaluated, the highest concentration was observed for Fe (20.195-38.347 ppm), followed by Zn (0.528-1.134 ppm), Pb (0.256-0.627 ppm), Mn (0.261-0.572 ppm) and Cr (0.093-0.344 ppm), while Cd showed the lowest concentration (0.022-0.043 ppm) and Ni showed BDL in all the soil samples. From the results of heavy metals I-geo values, according to Muller's classification, soil samples from Birchi, Daura, Dutsinma, Kafur and Zango were unpolluted (class 0) while soil samples from Dabai, Funtua, Ingawa, Katsina, Malunfashi and Matazu are from unpolluted to moderately polluted (class 1). The result for the enrichment factor has shown that with the exception of the heavy metal Fe showed significant enrichment for all the sites sampled all the other heavy metals showed deficiency to minimal enrichment. Based on the contamination factors for all soil samples, Fe has a CF values range from 1.2861-2.3240, indicating that the Agricultural soil samples are moderately contaminated with Fe. In contrast, the rest of the heavy metals exhibit low contamination in general. The value of PLI ranged from 0.2408 to 0.4935, indicating unpolluted to moderate pollution. However, the sampling site for Katsina displayed the highest PLI value while the sampling site of Ingawa has the lowest PLI. The Eri values of heavy metals for all samples are < 40, presenting low ecological risk.

REFERENCES

Abdullateef, B., Kolo, B. G., Waziri, I and Idris, M.A., 2014, Levels Of Heavy Metals in Soil as Indicator Of Environmental Pollution in Maiduguri, Borno State, Nigeria. *Bull. Env. Pharmacol. Life Sci.,* Vol 3 (11): 133-136

Ahaneku I.E., and Sadiq B.O., 2014, Assessment of Heavy Metals in Nigerian Agricultural Soils *Pol. J. Environ. Stud*. Vol. 23, No. 4, 1091-1100

Alirzayeva, E.G., Shirvani, T.S., Yazici, M.A., Alverdiyeva, S.M., Shukurov, E.S., Ozturk, L., Ali-Zade, V.M., and Cakmak, I., 2006, Heavy Metal accumulation in Artemisia and Foliaceous Lichen species from the Azerbaijan flora, Forest Snow and Landscape *Research*, 80, 339–348.

Anjula, A., 2014 Toxic Metal Contamination of Staple Crops (Wheat and Millet) in Periurban Area of Western Rajasthan. *International Refereed Journal of Engineering and Science* (IRJES) ISSN (Online) 2319-183X, (Print) 2319-1821 Volume 3, Issue 4, PP.08-18

Berendse, F., van Ruijven, J., Jongejans, E., and Keesstra, S., 2015, Loss of plant species diversity reduces soil erosion resistance, *Ecosystems*, 18: 881–888.

Brevik, E. C., Cerdà, A., Mataix-Solera, J., Pereg, L., Quinton, J. N., Six, J., and Van Oost, K., 2015, The interdisciplinary nature of soil, *SOIL*, 1, 117–129, doi:10.5194/soil-1-117.

Chen, T.B. Wong, J.W., Zhou, H.Y., and Wong, M.H., 1997, Assessment of trace metal distribution and contamination in surface soils in Hong Kong. *Environmental Pollution*, 96: 61-68

Decock, C., Lee, J., Necpalova, M., Pereira, E.I.P., Tendall, D.M., and Six, J., 2015. Mitigating N_2O emissions from soil: from patching leaks to transformative action, *Soil*, 1: 687–694

Douay, F., Pelfrêne, A., Planque, J., Fourrier, H., Richard, A., Roussel, H., and Girondelot, B., 2013, Assessment of potential health risk for inhabitants living near a former lead smelter, Part 1: metal concentrations in soils, agricultural crops, and homegrown vegetables, *Environmental Monitoring Assessment*, 185: 3665–3680

Ekmekyapar T.F., Şabudak G., and Şeren G., 2012, Assessment of heavy metal contamination in soil and wheat (*Triticum aestivum L*.) plant around the Çorlu–Çerkezkoy highway in Thrace region. *Global NEST Journal*, 14: 496-504

Farid G., Sarwar N., Saifullah, Ahmad A., and Ghafoor A., 2015, Heavy Metals (Cd, Ni and Pb) Contamination of Soils, Plants and Waters in Madina Town of Faisalabad Metropolitan and Preparation of Gis Based Maps. *Advanced Crop Sciences Technology;* 4: 199. doi:10.4172/2329-8863.1000199

Hakanson, L., 1980. An Ecological Risk Index for Aquatic Pollution Control a Sedimentological Approaches, *Water Research,* 14: 975-1001

Katsina State investor's handbook, Yaliam Press Ltd 2016: 12-15

Liang, J. Liu, Yuan, J.Y., Zeng, X.Z., Lai, G.M., Li, X., Wu, X.D., Yuan, H.P., and Li, F., 2015 Spatial and temporal variation of heavy metal risk and source in sediments of Dongting Lake wetland, mid-south China. *Journal of Environmental Sciences and Health* 50: 100–108

Liu, W.H., Zhao, J Z., Ouyang, Z.Y., Söderlund, L. and Liu, G.H., 2005. Impacts of Sewage Irrigation on Heavy Metal Distribution and Contamination in Beijing, China, *Environmental International*, 31: 805-812

Mahmoud, E. and Abd El-Kader, N., 2015. Heavy metal immobilization in contaminated soils using phosphogypsum and rice straw compost, *Land Degradation Development*, 26: 819–824

Martin, J. and Meybeck, M., 1979, Elemental Mass-Balance of Material Carried by Major World Rivers. *Marine Chemistry*, 7: 173-206

Mihaileanu RG, Neamtiu IA, Fleming M, Pop C, Bloom MS, Roba C, Surcel M, Stamatian F, Gurzau E. 2019 Assessment of heavy metals (total chromium, lead, and manganese) contamination of residential soil and homegrown vegetables near a former chemical manufacturing facility in Tarnaveni, Romania. *Environmental Monitoring Assessment*, 191:8 https://doi.org/10.1007/s10661-018-7142-0

Mugoša, B., Đurović D., Nedović-Vuković M., Barjaktarović-Labović S., and Vrvić, M., 2016, Assessment of Ecological Risk of Heavy Metal Contamination in Coastal Municipalities of Montenegro. International *Journal of Environmental Research and Public Health* 13: 393

Müller, G., 1969. Index of Geoaccumulation in Sediments of the Rhine River, *Geojournal* 2(3), 108-118

Muller, G., 1981, The Heavy Metal Pollution of the Sediments of Neckars and Its Tributary, A Stocktaking *Chemische Zeit*, 150, 157-164

Nabholz, J.V., 1991. Environmental hazard and risk assessment under the United States Toxic Substances Control Act, *Sci. Total Environ*., 109, 649–665, doi:10.1016/0048-9697(91)90218-4, 1991

Oladeji, J.T., Adetola, S.O. and Ogunsola, A.D., 2016, Heavy metal concentrations of soil in Ogbomosho and its environs *Merit Research Journal of Environmental Science and Toxicology*, 4: 1-5

Onder, S., Dursun, S., Gezgin, S. and Demirbas, A., 2007, Determination of heavy metal pollution in grass and soil of City Centre Green areas (Konya, Turkey) *Polish Journal of Environmental Studies*, 16: 145 – 154

Opaluwa, O.D., Aremu, M.O., Ogbo, L.O., Abiola, K.A., Odiba, I.E., Abubakar, M.M. and Nweze, N.O., 2012 Heavy metal concentrations in soils, plant leaves and crops grown around dump sites in Lafia Metropolis, Nasarawa State, Nigeria. *Advances in Applied Science Research,* 3:780-784

Orisakwe O.E., Nduka J.O., Amadi C.N., Dike D.O., and Bede O., 2012. Heavy metals health risk assessment for population via consumption of food crops and fruits in Owerri, South Eastern, Nigeria; *Chemistry Central Journal* 6:77 DOI: 10.1186/1752-153X-6-77

Pekey, H., Karakas, D., Ayberk, S., Tolun, L. and Bakoglu, M., 2004, Ecological Risk Assessment using Trace Elements from Surface Sediments of Izmit Bay (Northeastern Marmara Sea) Turkey, *Marine Pollution Bulletin*, 48: 946-953

Riding, M.J., Martin, F.L., Jones, K.C., and Semple, K T., 2015, Carbon nanomaterials in clean and contaminated soils: environmental implications and applications, *Soil*, 1: 1–21, doi:10.5194/soil-1-1

Roy, M., and Mcdonald, L.M., 2015, Metal uptake in plants and health risk assessments in metal-contaminated smelter soils, *Land Degradation Development*, 26: 785–796

Rubio, R. and Vilas, F., 2000, Geochemistry of Major and Trace Elements in Sediments of the Ria de Vigo (NW Spain) an Assessment of Metal Pollution, *Marine Pollution Bulletin*, 40: 968-980.

Saleem M.S., Haq M.U., Memon K.S., 2005. Heavy metals contamination through industrial effluent to irrigation water and soil in Korangi area of Karachi (Pakistan); *International Journal of Agriculture and Biology*, 7: 646-648

Sayadi M.H., Rezae A., .Sayyed M.R.G., 2017, Grain size fraction of heavy metals in soil and their relationship with land use. Proceedings of the International Academy of Ecology and Environmental Sciences; 7: 1-11

Singh, A., Sharma, R.K., Agrawal, M., and Marshall, F.M., 2010, Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. *Food Chemistry Toxicology*, 48, 611–619

Smith, P., Cotrufo, M.F., Rumpel, C., Paustian, K., Kuikman, P.J., Elliott, J.A., McDowell, R., Griffiths, R.I., Asakawa, S., Bustamante, M., House, J. I., Sobocká, J., Harper, R., Pan, G., West, P.C., Gerber, J.S., Clark, J.M., Adhya, T., Scholes, R.J., and Scholes, M.C., 2015. Biogeochemical cycles and biodiversity as key drivers of ecosystem services provided by soils, Soil, 1, 665–685

Su D.C., Wong Y.S., 2003.Chemical speciation and Phytoavailability of Zn, Cu, Ni and Cd in soils amended with fly ash stabilized sewage sludge. *Environment International*, 1060, 1

Suresh, G., Sutharsan, P., Ramasamy, V., and Venkatachalapathy, R., 2012, Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veranam lake sediments, India. *Ecotoxicology Environmental Safety,* 84; 117–124

Sutherland, R.A., 2000. Bed Sediment Associated Trace Metals in an Urban Stream, Oahu, Hawaii, *Environmental Geology*, 39: 611-627

Syed H.R., Dilara K., Tanveer M.A., Mohammad S.I., Mohammad A.A., Mohammad A.A., 2012. Assessment of heavy metal contamination of agricultural soils around Dhaka

Export processing zone (DEPZ), Bangladesh: Implication of seasonal variation and Indices. *Applied Science* 2, 583

Tippie, V.K., 1984. An Environmental Characterization of Chesapeake Bay and a Frame Work for Action, In: V. Kennedy, Ed., The Estuary as a Filter, Academic Press, New York

Tomlinson, D.L., Wilson, J.G., Harris, C.R. and Jeffney, D.W., 1980. Problems in the Assessment of Heavy-Metal Levels in Estuaries and the Formation of a Pollution Index; *Helgoland Marine Research*, 33: 566-72

Turkdogan M.K, Kilicel F., and Kara K., 2002, Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. *Journal of Environmental Toxicity and Pharmacology,* 13: 175, 2002

Udosen E.D., Ukpong, M.E., and Etim E.E., 2012, Concentrations of Heavy Metals in Soil Samples within Mkpanak in Ibeno Coastal Area of Akwa Ibom State, Nigeria. *International Journal of Modern Chemistry*, 2012, 3: 74-81

Venkatramanan, S., Ramkumar, T., Anithamary, I. and Vasudevan, S., 2012, Heavy Metal Distribution in Surface Sediments of the Tirumalairajan River Estuary and the Surrounding Coastal Area, East Coast of India, *Arabian Journal of Geosciences*, 7: 123-130

Wang, H.Q., Zhao, Q., Zeng, D.H., Hu, Y.L., and Yu, Z.Y., 2015. Remediation of a magnesium-contaminated soil by chemical amendments and leaching, *Land Degradation and Development*, 26, 613–619

Xia Y., Li F., Wan H., Ma J., Yan G., Zhang T., and Luo W., 2004. Spatial distribution of heavy metals of agricultural soils in Dongguan, China; *Journal of Environmental Sciences*, 16: 912

Xu, Z., Ni, S., Tuo, X., and Zhang, C., 2008, Calculation of Heavy Metals Toxicity Coefficient in the Evaluation of Potential Ecological Risk Index. *Environmental Sciences and Technology,* 31: 112–115

Yaradua, A.I., Alhassan, A.J., Nasir, A., Matazu, K.I., Muhammad, I., Idi, A., Muhammad, I.U. and Aliyu, S.M., 2018 Evaluation of heavy metals in sediment of some selected Dams from Katsina state Nigeria. *International Journal of Scientific and Technical Research in Engineering (IJSTRE)* Volume 3 Issue 2, 13-19

Zhao, K., Fu, W., Ye, Z., and Zhang, C., 2015, Contamination and Spatial Variation of Heavy Metals in the Soil-Rice System in Nanxun County, Southeastern China; *International Journal of Environmental Research and Public Health,* 12: 1577-1594