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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).

Index terms— agricultural soils, heavy metals, katsina state, pollution load index, contamination factor.

1 Introduction

oil 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. It is 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;Smith et al., 2015). Soils have been used to detect the deposition, accumulation, and distribution of heavy metals in different locations ??Alirzaye vaet al., 2006;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;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; ??u and Wong, 2003;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;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 Katsina agricultural soil to ascertain pollution levels.

2 II.

3 Material and Methods

4 a) Study Area

The study was carried out during 2017 in Katsina State, Nigeria located between latitude 12°15'N and longitude of 7°30'E in the North West Zone of Nigeria, with an area of 24,192 km² (9,341 sq meters). 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, 27.3°C 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.

5 b) Soil Sampling

Fifty-five 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 polyethylene container in accordance with the method adopted by (Syed et al., 2012). The samples were properly labeled and were taken to the laboratory for analysis.

6 c) 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-HNO₃) 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).

7 III.

8 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). 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. But the result is lower than the Fe concentration in soil from Ibeno Akwa Ibom state Nigeria (Udosen et al., 2012).

The heavy metal Zn concentration obtained in this study is higher than the report of a study conducted in Lafia, Nasarawa state Nigeria (Opaluwa et al., 2012). But the result is lower than that that reported for Zn in soil from western Rajasthan (Anjula, 2014).

9 b) 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 (Müller, 1969). I-geo was calculated using the following equation: $I\text{-geo} = \log_2 (C_n / 1.5 B_n)$

Where C_n is the measured content of the examined metal in the sediment samples and B_n 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 (I-geo) 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). The Igeo values seen in the present study similar to the values. (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: $EF = (M/Fe)_{\text{sample}} / (M/Fe)_{\text{Background}}$

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. 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): $CF = M_c / B_c$

Where M_c Measured concentration of the metal and B_c 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 3. 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. 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: $PLI = (CF_1 + CF_2 + CF_3 + \dots + CF_n)^{1/n}$

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. 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; 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;

10 $Eri = Tri \times Cfi$

Where, Tri 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; 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 Eri values for all samples are all < 40 (Table 6), presenting low ecological risk.

11 Conclusion

The main goal of this research is to assess the levels of some heavy metals in Agricultural soils of Katsina state, north western Nigeria, in order to determine the impact of anthropogenic heavy metal pollution arising from Agricultural activities. Several indices were used to assess the metal contamination levels in the Agricultural soil samples, namely Geoaccumulation index (I-geo), Pollution Load Index (PLI), Enrichment Factors (EF), Contamination Factor (CF) and Degree of Contamination (Cd). The result of this study reveals 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) and the heavy metal Ni 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, which shows significant enrichment for all the sites sampled all the other heavy metals show deficiency to minimal enrichment. 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. 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 all < 40 , presenting low ecological risk.

Figure 1:

1

Location	Heavy Metal						
	Mn	Zn	Pb	Cd	Ni	Fe	Cr
Birchi	0.300	0.641	0.448	0.033	BDL	21.212	0.344
	± 0.0005	\pm	\pm	\pm		\pm	\pm
Dabai		0.0004	0.0002	0.0003		0.0009	0.0003
	0.566	1.207	0.348	0.025	BDL	24.896	0.093
Daura	± 0.0015	\pm	\pm	\pm		\pm	\pm
		0.0002	0.0003	0.0001		0.0012	0.0002
Dutsinma	0.287	0.968	0.529	0.043	BDL	22.246	0.226
	± 0.0006	\pm	\pm	\pm		\pm	\pm
Funtua		0.0003	0.0008	0.0003		0.0002	0.006
	0.321	0.612	0.441	0.032	BDL	23.342	0.342
Ingawa	± 0.0004	\pm	\pm	\pm		\pm	\pm
		0.0004	0.0006	0.0004		0.0006	0.0006
Kafur	0.572	1.132	0.541	0.025	BDL	28.264	0.268
	± 0.0004	\pm	\pm	\pm		\pm	\pm
Katsina		0.0006	0.0015	0.0006		0.0012	0.0003
	0.261	1.099	0.627	0.034	BDL	20.195	0.143
Malunfashi	± 0.0007	\pm	\pm	\pm		\pm	\pm
		0.0003	0.0002	0.0002		0.0023	0.0010
Matazu	0.511 \pm	1.083	0.462	0.031	BDL	31.716	0.241
	0.0006	\pm	\pm	\pm		\pm	\pm
Zango		0.0015	0.0013	0.0004		0.0009	0.0004
	0.486	0.775	0.256	0.024	BDL	38.347	BDL
Zango	± 0.0004	\pm	\pm	\pm		\pm	
		0.0002	0.0002	0.0002		0.0009	
Zango	0.470	1.094	0.402	0.026	BDL	32.985	0.285
	± 0.0012	\pm	\pm	\pm		\pm	\pm
Zango		0.0004	0.0003	0.0003		0.0017	0.0002
	0.277	1.134	0.285	0.022	BDL	37.442	0.099
Zango	± 0.0004	\pm	\pm	\pm		\pm	\pm
		0.0002	0.0003	0.0001		0.0009	0.0007
Zango	0.272 \pm 0.0015	0.528 \pm 0.0006	0.564 \pm 0.0002	0.032 \pm 0.0004	BDL	24.568 \pm 0.0006	0.2

Values are expressed as Mean \pm St

a) 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).

Figure 2: Table 1 :

2

Site	Mn	Zn	I-geo 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

c) 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

Figure 3: Table 2 :

3

Enrichment Factor (EF)

Figure 4: Table 3 :

4

Site	Mn	Contamination Zn	Factor Pb	(CF) 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

e) Degree of Contamination and Pollution Load Index

Figure 5: Table 4 :

5

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

Figure 6: Table 5 :

6

	Ecological	Risk (Eri)	Index		
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

IV.

Figure 7: Table 6 :

.1 Competing Interests

Authors have declared that no competing interests exist.

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