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6 **Abstract**

7 This work contributes to the monitoring of Agricultural soil pollution in Katsina State, North
8 western Nigeria by assessing the degree of heavy metal pollution in Agricultural soil samples.
9 The study was conducted in the year 2017 within some catchment areas located within the 3
10 senatorial zones that constitute to make up the state (Katsina senatorial zone: Birchi,
11 Dutsinma and Katsina; Daura senatorial zone: Daura, Ingawa and Zango; Funtua senatorial
12 zone: Dabai, Funtua, Kafur, Malunfashi and Matazu). Analysis for the concentration of these
13 heavy metals; Cr, Cd, Fe, Ni, Mn, Pb and Zn was conducted by the use of AAS (by Atomic
14 Absorption Spectrophotometry) method. Several indices were used to assess the metal
15 contamination levels in the Agricultural soil samples, namely; Geo-accumulation Index (Igeo),
16 Enrichment Factor (EF), Contamination Factor (CF), Degree of Contamination (Cd) and
17 Pollution Load Index (PLI).

18

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

20 **1 Introduction**

21 oil is not only a medium for plant growth or pool to dispose of undesirable materials, but also a transmitter
22 of many pollutants to surface water, groundwater, atmosphere and food. It is a key part of the Earth system
23 as it control the hydrological, erosional, biological, and geochemical cycles (Chen et al., 1997). The soil system
24 also offers goods, services, and resources to humankind (Berendse et al., 2015;Brevik et al., 2015;Decock et al.,
25 2015;Smith et al., 2015). Soils have been used to detect the deposition, accumulation, and distribution of heavy
26 metals in different locations ??Alirzayeva et al., 2006;Onder et al., 2007), this is why it is necessary to research how
27 soils are affected by societies. Pollution is one of these damaging human activities, and we need more information
28 and assessment of soil pollution (Mahmoud and El-Kader, 2015;Riding et al., 2015;Roy and McDonald, 2015;Wang
29 et al., 2015). Heavy metal pollution of agricultural soil can result not only in decreased crop output and quality
30 and hurt human health through the food chain, but also further deterioration of air and water environmental
31 quality (Turkdogan et al., 2002; ??u and Wong, 2003;Xia et al., 2004). Excessive accumulation of heavy metals
32 in agricultural soils can affect the quality and safety of food and further increase the risk of serious diseases
33 (cancer, kidney, liver damage, etc.), as well as impact ecosystems, thus combining environmental chemistry with
34 biological toxicology and ecology (Suresh et al., 2012).Literature indicates that studies have been conducted on
35 pollution by heavy metals of some areas in Nigeria (Ahaneku and Sadiq, 2014;Opaluwa et al., 2012;Abdullah et al.,
36 2014;Orisakwe et al., 2012), but nothing of such has been monitored on the heavy metal levels emanating
37 from Agricultural soils in Katsina state Northwestern Nigeria and their possible effects on the quality of soil and
38 human health. Therefore, it is important to investigate the level of heavy metals in Katsina agricultural soil to
39 ascertain pollution levels.

40 **2 II.**

41 **3 Material and Methods**

42 **4 a) Study Area**

43 The study was carried out during 2017 in Katsina State, Nigeria located between latitude 12015'N and longitude
44 of 7030'E in the North West Zone of Nigeria, with an area of 24,192km² (9,341 sq meters). The study was
45 conducted within some catchment areas located within the 3 senatorial zones that constitute to make up the
46 state (Katsina senatorial zone: Birchi, Dutsinma and Katsina; Daura senatorial zone: Daura, Ingawa and Zango;
47 Funtua senatorial zone: Dabai, Funtua, Kafur, Malunfashi and Matazu). Katsina State has two distinct seasons:
48 rainy and dry. The rainy season begins in April and ends in October, while the dry season starts in November
49 and ends in March. This study was undertaken during the dry season. The average annual rainfall, temperature,
50 and relative humidity of Katsina State are 1,312 mm, 27.3°C and 50.2%, respectively. Like most alluvial soils,
51 the soil in Katsina state is the flood plain type and is characterized by considerable variations. The soil has two
52 main types, which are soils with little hazards and soils with good water holding capacity.

53 **5 b) Soil Sampling**

54 Fifty-five soil samples were collected from 0-20 cm depths (plough layer) of cultivated farmland with a hand auger
55 from the designated sampling areas. Five samples were collected randomly from each location. The distance
56 from one sampling point to another was approximately 50 m at each location. The collected five samples from
57 each location were mixed and about 250-300 g of the soil was sampled and put into a polyethylene container in
58 accordance with the method adopted by (Syed et al., 2012). The samples were properly labeled and were taken
59 to the laboratory for analysis.

60 **6 c) Chemical Analysis of Soil Samples**

61 Soil samples were dried at room temperature and pebbles, stones, and large debris were removed from the soils
62 before it was passed through a 2 mm polyethylene sieve. All glassware and plastic ware were soaked in 10%
63 nitric acid for 24 hrs and rinsed thoroughly with deionized water. The soil samples were digested by mixed
64 acid (HCl-HNO₃) for Mn, Zn, Pb, Cd, Ni, Fe and Cr analyses. The concentrations of the heavy metals were
65 measured by an atomic absorption spectrometer (AA210RAP BUCK Atomic Absorption Spectrometer flame
66 emission spectrometer filter GLA-4B Graphite furnace, East Norwalk USA) according to standard methods
67 (AOAC, 1995) and the results were given in part per million (ppm).

68 **7 III.**

69 **8 Results and Discussion**

70 Soil samples from 11 locations within the 3 senatorial zones of Katsina State were analyzed in this study. As
71 shown in Table 1, among the heavy metals evaluated, the highest concentration was observed for Fe (range:
72 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-
73 0.572 ppm) and Cr (range: 0.093-0.344 ppm). While Cd has the lowest concentration (range: 0.022-0.043 ppm)
74 and the concentration range for the heavy metal Ni was BDL in all the soil samples.

75 The Pb concentration range for the agricultural soil samples in this study is similar to that reported for soils
76 from post office area, Bulunkutu and Bama station in Maiduguri metropolis, Borno state Nigeria (Abdullahi et al., 2014) and that reported for soil samples from Lafia metropolis, Nasarawa state, Nigeria with a Pb
77 concentration range of 0.100-0.530 ppm (Opaluwa et al., 2012) Though an essential heavy metal, Fe has the
78 tendency to become toxic to living organisms, even when exposure is low. In the present study, the mean Fe
79 concentration in both the soil samples was higher than that reported for soil samples from Lafia metropolis
80 Nasarawa state, Nigeria (Opaluwa et al., 2012) and that of a study conducted by Abdullahi et al., (2014) in
81 Maiduguri metropolis Borno state, Nigeria. But the result is lower than the Fe concentration in soil from Ibendo
82 Akwa Ibom state Nigeria (Udosen et al., 2012).

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

87 **9 b) Geo-Accumulation Index**

88 Geo-accumulation index (I-geo) was employed to evaluate the heavy metals pollution in the Agricultural soil
89 samples. This method has been used by Müller since the late 1960s ??Muller, 1969). I-geo was calculated using
90 the following equation: $I\text{-geo} = \log 2 / (C_n / 1.5B_n)$

91 Where C_n is the measured content of the examined metal in the sediment samples and B_n is the geochemical
92 background content of the same metal. The constant 1.5 is introduced to minimize the effect of possible variations
93 in the background values, which may be recognized to anthropogenic influences The index of geo-accumulation
94 (I_{geo}) is characterized according to the Muller seven grades or classes profile of the geo-accumulation index i.e.

95 the value of soil quality is considered as unpolluted (Igeo is ?0, class 0); from unpolluted to moderately polluted
96 (Igeo is 0 -1, class 1); moderately polluted (Igeo is 1 -2, class 2); from moderately to strongly polluted (Igeo is
97 2 -3, class 3); Strongly polluted (Igeo is 3 -4, class 4); from strongly to extremely polluted (Igeo is 4 -5, class
98 5) and Extremely polluted (Igeo is >6, class 6) ??Muller, 1969.) Therefore, from the results of heavy metals
99 I-geo values on table 2, according to Muller's classification, soil samples from Birchi, Daura, Dutsimma, Kafur
100 and Zango were unpolluted (class 0) while soil samples from Dabai, Funtua, Ingawa, Katsina, Malunfashi and
101 Matazu are from unpolluted to moderately polluted (class 1). The Igeo values seen in the present study similar
102 to the values. (Muller, 1981). The normally used reference metals are Mn, Al and Fe (Liu et al., 2005). In this
103 study Fe was used as a conservative tracer to differentiate natural from anthropogenic components, following the
104 hypothesis that its content in the earth crust has not been troubled by anthropogenic activity and it has been
105 chosen as the element of normalization because natural sources (98%) greatly dominate its contribution (Tippie,
106 1984). According to Rubio et al. (2000), the EF is defined as follows: $EF = (M/Fe)_{\text{sample}} / (M/Fe)_{\text{Background}}$

107 Where EF is the enrichment factor, $(M/Fe)_{\text{sample}}$ is the ratio of metal and Fe concentration of the sample and
108 $(M/Fe)_{\text{background}}$ is the ratio of metals and Fe concentration of a background. Five contamination categories
109 are reported on the basis of the enrichment factor (Sutherland, 2000). $EF < 2$ deficiency to minimal enrichment,
110 $EF = 2-5$ moderate enrichment, $EF = 5-20$ significant enrichment, $EF = 20-40$ very high enrichment, $EF > 40$
111 extremely high enrichment. As shown in Table 3, with the exception of the heavy metal Fe, which shows
112 significant enrichment for all the sites sampled all the other heavy metals show deficiency to minimal enrichment.
113 Contamination Factor (CF) was used to determine the contamination status of the Agricultural soils in the
114 current study. CF was calculated according to the equation described below (Pekey et al., 2004): $C = M_c / B_c$

115 Where M_c Measured concentration of the metal and B_c is the background concentration of the same metal.
116 Four contamination categories are documented on the basis of the contamination factor ??Hakanson, 2000).
117 $CF < 1$ low contamination; $1 \leq CF \leq 3$ moderate contamination; $3 \leq CF < 6$ considerable contamination; $CF > 6$ very
118 high contamination, while the degree of contamination (Cd) was defined as the sum of all contamination factors.
119 The following terms is adopted to illustrate the degree of contamination: $Cd < 6$: low degree of contamination;
120 $6 \leq Cd < 12$: moderate degree of contamination; $12 \leq Cd < 24$: considerable degree of contamination; $Cd > 24$: very
121 high degree of contamination indicating serious anthropogenic pollution. The result of the contamination factors
122 for the evaluated heavy metals is shown on table 3. From the table, the relative distributions of the contamination
123 factor among the samples are: $Fe > Cd > Pb > Zn > Cr > Mn$. Soils have been used as environmental indicators,
124 and this ability to identify heavy metal contamination sources and monitor contaminants is also well documented.
125 Thus, the accumulation of metals in the soils is strongly controlled by the nature of the substrate as well as the
126 physicochemical conditions controlling dissolution and precipitation (Venkatraman et al., 2012). For all soil
127 samples the heavy metal Fe has a CF values range of 1.2861-2.3240, indicating that the Agricultural soil samples
128 are moderately contaminated with Fe. In contrast, the rest of the heavy metals exhibit low contamination in
129 general. The degree of contamination (Cd) was defined as the sum of all contamination factors. The following
130 terms is adopted to illustrate the degree of contamination: $Cd < 6$: low degree of contamination; $6 \leq Cd < 12$:
131 moderate degree of contamination; $12 \leq Cd < 24$: considerable degree of contamination; $Cd > 24$: very high degree
132 of contamination indicating serious anthropogenic pollution. Pollution Load Index (PLI) was used to evaluate
133 the extent of pollution by heavy metals in the environment. The range and class are same as Igeo. PLI for each
134 sampling site has been calculated following the method planned by Tomlinson et al. (1980) as follows: $PLI = (CF$
135 $I + CF_2 + CF_3 + \dots + CF_n)^{1/n}$

136 Where n is the number of metals and CF is the contamination factor.

137 The value of PLI ranges from 0.2408 to 0.4935 (Table 5), indicating unpolluted to moderate pollution. However,
138 the sampling site for Katsina displayed the highest PLI value while the sampling site of Ingawa has the lowest
139 PLI. Hakanson (1980) to evaluate the potential ecological risk of heavy metals. This method comprehensively
140 considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals
141 (Nabholz, 1991; Singh et al., 2010; Douay et al., 2013). PERI is formed by three basic modules: degree of
142 contamination (CD), toxic-response factor (TR) and potential ecological risk factor (ER). The ecological risk
143 index (Eri) evaluates the toxicity of trace elements in sediments and has been extensively applied to soils (Liang
144 et al., 2015). Soils contaminated by heavy metals can cause serious ecological risks and negatively impact human
145 health due to various forms of interaction (agriculture, livestock, etc.) where highly toxic heavy metals can enter
146 the food chain. To calculate the Eri for individual metals, the following Equation was used;

147 10 $Eri = Tri \times Cfi$

148 Where, Tri is the toxicity coefficient of each metal whose standard values are $Cd = 30$, $Ni = 5$, $Pb = 5$, $Cr = 2$,
149 and $Zn = 1$, $Mn = 1$ (Hakanson, 1980; Xu, 2008) and Cfi is the contamination factor. To describe the ecological
150 risk index the following terminology was used: $Er < 40$, low; $40 \leq Er < 80$, moderate; $80 \leq Er < 160$, considerable;
151 $160 \leq Er < 320$, high; and $Er \geq 320$, very high. The risk factor was used as a diagnostic tool for water pollution
152 control, but it was also successfully used for assessing the contamination of soils in the environment by heavy
153 metals ??Mugosa et al., 2016). The Eri values for all samples are all < 40 (Table 6), presenting low ecological
154 risk.

11 Conclusion

155 The main goal of this research is to assess the levels of some heavy metals in Agricultural soils of Katsina state,
156 north western Nigeria, in order to determine the impact of anthropogenic heavy metal pollution arising from
157 Agricultural activities. Several indices were used to assess the metal contamination levels in the Agricultural
158 soil samples, namely Geoaccumulation index (I-geo), Pollution Load Index (PLI), Enrichment Factors (EF),
159 Contamination Factor (CF) and Degree of Contamination (Cd). The result of this study reveals that generally
160 among the heavy metals evaluated, the highest concentration was observed for Fe (range: 20.195-38.347 ppm),
161 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
162 (range: 0.093-0.344 ppm). While Cd has the lowest concentration (range: 0.022-0.043 ppm) and the heavy metal
163 Ni BDL in all the soil samples. From the results of heavy metals I-geo values, according to Muller's classification,
164 soil samples from Birchi, Daura, Dutsinma, Kafur and Zango were unpolluted (class 0) while soil samples from
165 Dabai, Funtua, Ingawa, Katsina, Malunfashi and Matazu are from unpolluted to moderately polluted (class 1).
166 The result for the enrichment factor has shown that with the exception of the heavy metal Fe, which shows
167 significant enrichment for all the sites sampled all the other heavy metals show deficiency to minimal enrichment.
168 Based on the contamination factors for all soil samples the heavy metal Fe has a CF values range of 1.2861-2.3240,
169 indicating that the Agricultural soil samples are moderately contaminated with Fe. In contrast, the rest of the
170 heavy metals exhibit low contamination in general. The value of PLI ranges from 0.2408 to 0.4935, indicating
171 unpolluted to moderate pollution. However, the sampling site for Katsina displayed the highest PLI value while
172 the sampling site of Ingawa has the lowest PLI. The Eri values of heavy metals for all samples are all < 40,
173 presenting low ecological risk.

Figure 1:

1

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 0.285
Malunfashi	0.470 ± 0.0012	1.094 ± 0.0004	0.402 0.0003	0.026 0.0003	BDL	32.985 0.0017	0.099 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	0.2

Values are expressed as Mean ± 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 :

11 CONCLUSION

2

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

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	Zn	Contamination Factor	(CF)	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

Site	Ecological	Risk Index					
		(Eri)	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 :

11 CONCLUSION

175 .1 Competing Interests

176 Authors have declared that no competing interests exist.

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