



## **Assessment of Heavy Metal Enrichment and Degree of Contamination in Play grounds and market of Duza Twin Village, Anka, Zamfara, Nigeria**

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### **Abstract**

Phase-by-phase Post-remediation exercise of Duza twin village was conducted to determine the success of remediation carried out by Environmental Emergency Response Mission. Present phase in this report boards on the children playground and the village market. Ten samples from playing grounds around the village market and general surrounding in the central of the village were made to assess possibility of contamination by artisanal mining exercises in the locality. Contamination Factor(CF) and Geo-accumulation index were used to determine extent of contamination and relate such to mining ore and extraction chemical used. GeoI values obtained for Pb and Hg respectively at the market location are 1.148 and 5.013, indicating moderate contamination by Lead and extreme contamination by mercury. The output of play grounds yields GeoI of 1.76 and 4.889 for Lead and mercury respectively. This results in similar range for both locations. In conclusion, the villagers have abused the

remediation done by resuming ore processing at what- ever-small magnitude to escape the prying eyes of the village authorities.

**Keywords :** Human health risk assessment, Geo-accumulation index, XRF analysis, Contamination Factor

## **1. Introduction**

In March 2010, an unusually high number of deaths, primarily among children under age 5 in Bukkuyum and Anka Local Government Areas (LGAs) of Zamfara State, northern Nigeria, was reported by Médecins sans Frontières (MSF-Holland) to state health authorities. Further study on blood samples taken by MSF revealed that the increased mortality was the result of acute lead poisoning, determined to be caused by massive environmental contamination from artisanal mining and processing of gold found in lead-rich ore. The grinding of the ore into fine particles resulted in extensive dispersal of lead dust in the villages concerned, including within family compounds. Ingestion and inhalation of the fine lead particles was determined to be the major reason for high blood lead levels in victims' bodies. (UNEP, 2010).

From 20 September through 7 October 2010, the Joint UNEP/OCHA Environment Unit (JEU) led a sampling and analysis mission to investigate the lead pollution emergency in Zamfara State, following requests for assistance from the Federal Ministry of Health of Nigeria and the UN Resident Coordinator. Specifically, the mission focused on determining quantities of lead in ground and surface water, building on investigations already conducted by the CDC, the World Health Organization (WHO), and the National Water Resources Institute of Nigeria (NWRI), and a team from TerraGraphics Environmental Engineering/The Blacksmith Institute, as it was determined that there was insufficient information in these domains. The mission also took the opportunity to look at lead levels in soil, and mercury levels in air, (UNEP, 2010).

## **2. Materials and Methods**

### **2.1 Study Area Description**



**Figure 1. Google earth map of Duza twin village with the primary school located in between them.**

Duza is a twin village, in between which the primary school serving the twin arms is located. Duza is located in Anka local government of Zamfara State in North-Western Nigeria. Duza lies between latitude  $11^{\circ}53'57.30''\text{N}$  and longitude  $6^{\circ}04'46.70''\text{E}$ .

The inhabitants of the area are mostly Hausa-Fulani practicing Islam as their religion. Most of them are peasant farmers. After the rainy season, majority of the young able men dwell into artisanal mining using manual labour and very primitive processing methods. As a result of their level of ignorance to hazards of mining, most of these dwellers do bring gold ores home for continuation of processing in earlier years prior to Lead epidemic that broke out largely in two local government areas of the state; Anka and Bukkuyum. Climatically, the area enjoys a tropical continental climate, largely controlled by two air masses, i.e tropical maritime from the Atlantic Ocean and tropical continental from the Sahara. These give the area a rainy season from May to October and dry season for the remaining period respectively. The region receives an average rainfall of about 1200mm with highest peak in August/ September. The area is very well drained. Most of the streams are tributaries that empty into the main river (River Zamfara). The river is seasonal and dries up for greater period of the year leaving some puddles of water here and there. In terms of vegetative, the area is made up of guinea savannah with medium shrubs and grasses and sparse trees.

## 2.2 Soil sampling

A total of ten soil samples were used for the present study. The collected samples were thoroughly mixed as a composite representative of the compound soil to be analysed in a polythene bag and labelled. The labelled bag was again double-bagged to avoid cross-contamination.

## 2.3 Laboratory Analyses

The analysis was carried out with Mini Pal x-ray system. Mini Pal is a compact energy dispersive x-ray spectrometer designed for the elemental analysis of a wide range of samples. The system is controlled by a computer running the dedicated Mini pal analytical software. The sample for analysis is weighed and grounded in an agate mortar and a binder (PVC dissolved in Toluene) is added to the sample, carefully mixed and pressed in a hydraulic press into a pellet. The pellet was loaded in the sample chamber of the spectrometer and voltage (30kv max.) and a current (1mA max.) is applied to produce the x-rays to excite the sample for a preset time ( of 30minutes is this case). The spectrum from the sample is now analyzed to determine the concentration of the elements in the sample.

## 2.4 Data Analysis

Contamination factor (CF) and geo-accumulation index (GeoI) are quantitative check used to describe concentration trend of metals in soils. Contamination factor (CF) is a quantifier of the degree of contamination relative to either the average crustal composition of the respective metal or to measured background values from geologically similar and uncontaminated area (Tijani *et al.*, 2004). It is expressed as:

$$CF = \frac{C_n}{B_n} \dots\dots\dots \text{eq. 1 ( Mohiuddin et.al. 2010)}$$

Where  $C_n$  is the mean concentration of metal n in soil and  $B_n$  is the background concentration (value) of metal n, either taken from the literature (average crustal abundance) or directly determined from a geologically similar material. In the present study, literature values are used.

$$GeoI = \ln \left[ \frac{C_n \text{ Sample}}{1.5 \times C_n \text{ Background}} \right] \dots\dots\dots \text{eq. 2 ( Mohiuddin et.al. 2010)}$$

Where  $C_n$  and  $B_n$  are as defined above, while 1.5 is a factor for possible variation in the background concentration due to lithologic differences. GeoI is classified into seven descriptive classes as follows:

**Table 1. The degree of metal pollution in terms of seven enrichment classes.**

GeoI Value	GeoI Class	Designation of soil sample Quality
< 0	0	Extremely Uncontaminated
0-1	1	Uncontaminated to moderately contaminated
1-2	2	Moderately Contaminated
2-3	3	Moderately to strongly Contaminated
3-4	4	Strongly Contaminated
4-5	5	Strongly to extremely Contaminated
>5	6	Extremely contaminated

The GeoI class 6 is an open-end class that is indicative of all values greater than 5, and a GeoI of 6 is said to be indicative of 100-fold enrichment of a metal with respect to the baseline value (Mueller, 1979).

### 3. Results

Tables 2 and 3 displays the output result of the XRF analysis conducted of samples obtained from the children’s playground and market place respectively. Tables 4 and 5 represents the output evaluations of corresponding contamination factors(Cf) and Geoaccumulation Indices (GeoI) of the two children activity based areas. These results were plotted to give graphic representations of the observed events in figures 2 and 3.

**Table 2. Duza play ground samples**

DUZA PLAY GROUND SAMPLES								
	DPGS1	DPGS2	DPGS3	DPGS4	DPGS5	Max.	Min.	Mean
Mo	10.377	7.501	9.14	6.869	6.398	10.377	6.398	8.151429
Zr	1035.966	830.51	948.481	656.718	598.265	1035.966	598.265	814.8816
Sr	110.667	92.346	84.733	78.788	97.623	110.667	78.788	93.37314
U	5.81	5.849	6.273	4.499	7.184	7.184	4.499	5.899714
Rb	49.82	48.331	44.96	50.013	54.783	54.783	44.96	49.66429
Th	17.773	11.219	13.476	10.421	8.125	17.773	8.125	12.416
Pb	197.911	173.821	58.428	33.905	159.978	197.911	33.905	122.2656
Au	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

DUZA PLAY GROUND SAMPLES								
	DPGS1	DPGS2	DPGS3	DPGS4	DPGS5	Max.	Min.	Mean
Se	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
As	17.598	7.433	8.223	9.523	2.859	17.598	2.859	9.441857
Hg	17.205	17.077	17.713	16.794	16.016	17.713	16.016	16.93343
Zn	181.189	57.208	27.474	27.65	50.721	181.189	27.474	78.98643
W	20.695	17.209	18.113	13.341	17.798	20.695	13.341	17.31314
Cu	62.6	23.614	28.689	22.311	23.665	62.6	22.311	35.11286
Ni	20.947	18.557	18.944	17.453	17.874	20.947	17.453	18.88214
Co	42.053	48.903	43.292	25.132	44.317	48.903	25.132	39.676
Fe	9147.121	8525.663	8026.229	6053.993	6797.331	9147.121	6053.993	7678.779
Mn	249.307	215.38	207.974	168.748	190.051	249.307	168.748	207.0736

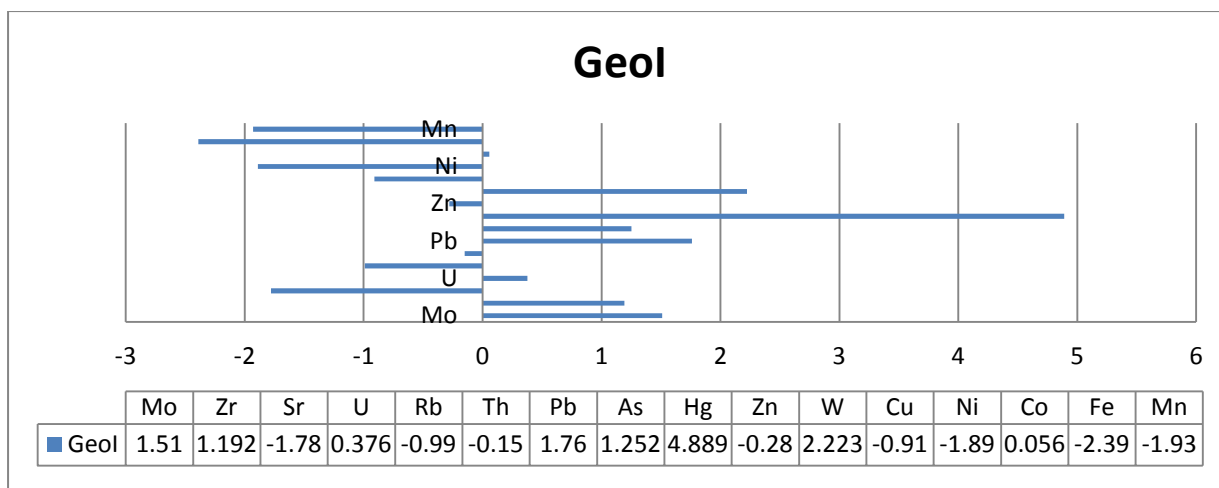
**Table 3. Duza market samples**

DUZA MARKET SAMPLES								
	DMS1	DMS2	DMS3	DMS4	DMS5	Max.	Min.	Mean
Mo	7.137	5.887	6.26	5.43	7.133	7.137	5.43	6.344857
Zr	837.717	882.9	651.935	680.521	1010.412	1010.412	651.935	817.976
Sr	88.249	107.918	94.834	112.526	122.792	122.792	88.249	105.3371
U	5.326	5.35	5.686	7.355	5.895	7.355	5.326	6.041857
Rb	48.562	50.36	48.731	60.243	55.509	60.243	48.562	53.17286
Th	12.299	12.015	8.068	9.833	12.358	12.358	8.068	10.71414
Pb	82.455	58.368	72.67	62.219	52.614	82.455	52.614	66.19929
Au	< LOD	< LOD	< LOD	< LOG	< LOD	< LOD	< LOD	< LOD
Se	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
As	9.514	10.778	6.59	9.642	10.328	10.778	6.59	9.174286
Hg	24.572	18.455	16.382	18.179	16.001	24.572	16.001	19.166
Zn	44.143	38.825	202.113	331.956	92.98	331.956	38.825	154.3997
W	13.031	14.346	16.516	18.324	22.235	22.235	13.031	17.10257
Cu	23.276	24.82	26.791	26.902	28.782	28.782	23.276	26.08986
Ni	12.636	16.841	15.769	23.365	16.899	23.365	12.636	17.35871

DUZA MARKET SAMPLES								
	DMS1	DMS2	DMS3	DMS4	DMS5	Max.	Min.	Mean
Co	34.29	32.927	40.311	48.022	31.447	48.022	31.447	38.06657
Fe	5882.088	6222.41	6903.724	9081.629	7517.748	9081.629	5882.088	7224.474
Mn	153.125	171.406	218.905	220.345	245.903	245.903	153.125	201.2446

**Table 4. Determination of geoaccumulation index of Duza play ground samples using table 2 results.**

Parameters	Max.	Min.	Mean(Cn)	Bn	CF	GeoI	Summary of cont. Level
Mo	10.377	6.398	8.151429	1.2	6.793	1.510	2
Zr	1035.966	598.265	814.8816	165	4.938	1.192	2
Sr	110.667	78.788	93.37314	370	0.252	-1.78	0
U	7.184	4.499	5.899714	2.7	2.185	0.376	0
Rb	54.783	44.96	49.66429	90	0.552	-0.99	0
Th	17.773	8.125	12.416	9.6	1.29	-0.15	0
Pb	197.911	33.905	122.2656	14	8.733	1.76	2
As	17.598	2.859	9.441857	1.8	5.245	1.252	2
Hg	17.713	16.016	16.93343	0.085	199.2	4.889	5
Zn	181.189	27.474	78.98643	70	1.128	-0.28	0
W	20.695	13.341	17.31314	1.25	13.851	2.223	3
Cu	62.6	22.311	35.11286	60	0.585	-0.91	0
Ni	20.947	17.453	18.88214	84	0.225	-1.89	0
Co	48.903	25.132	39.676	25	1.587	0.056	0
Fe	9147.121	6053.993	7678.779	56,300	0.136	-2.39	0
Mn	249.307	168.748	207.0736	950	0.218	-1.93	0

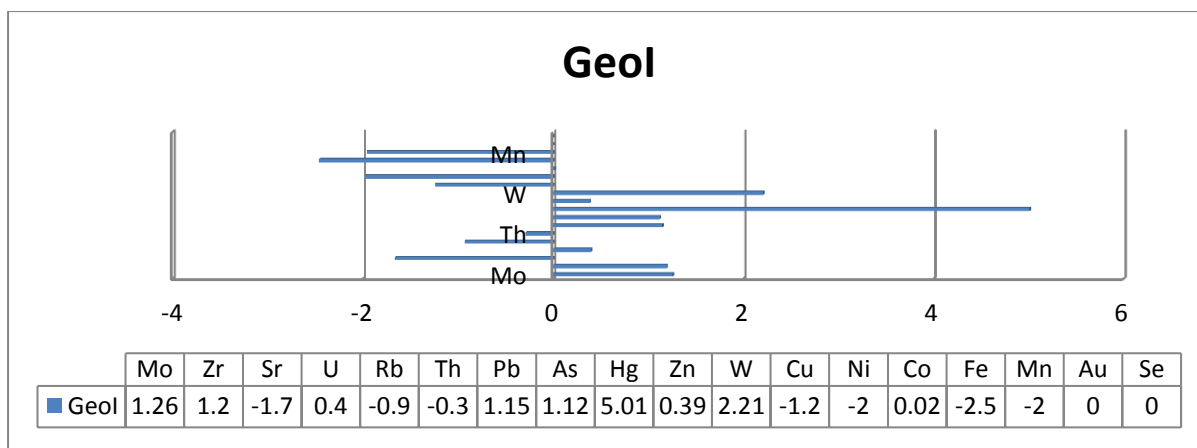


**Figure 2. Output of GeoI values of Duza Play ground elemental concentrations.**

**Table 5. Determination of geoaccumulation index of Duza market samples using table 3 results.**

Parameters	Max.	Min.	Mean(Cn)	Bn	CF	GeoI	Summary of cont. Level
Mo	7.137	5.43	6.344857	1.2	5.287	1.259	2
Zr	1010.412	651.935	817.976	165	4.957	1.195	2
Sr	122.792	88.249	105.3371	370	0.285	-1.66	0
U	7.355	5.326	6.041857	2.7	2.238	0.399	1
Rb	60.243	48.562	53.17286	90	0.590	-0.93	0
Th	12.358	8.068	10.71414	9.6	1.116	-0.29	0
Pb	82.455	52.614	66.19929	14	4.73	1.148	2
As	10.778	6.59	9.174286	1.8	5.096	1.122	2
Hg	24.572	16.001	19.166	0.085	225.5	5.013	6
Zn	331.956	38.825	154.3997	70	2.205	0.386	1
W	22.235	13.031	17.10257	1.25	13.68	2.210	3
Cu	28.782	23.276	26.08986	60	0.435	-1.24	0
Ni	23.365	12.636	17.35871	84	0.206	-1.98	0
Co	48.022	31.447	38.06657	25	1.523	0.015	1
Fe	9081.629	5882.088	7224.474	56,300	0.128	-2.46	0
Mn	245.903	153.125	201.2446	950	0.212	-1.96	0





**Figure 3. Output of GeoI values of Duza Market elemental concentrations.**

#### 4. Discussions

Starting with observable results of the children play grounds; It can be observed that almost all elements assessed occurs at very low concentrations except mercury (Hg) and lead(Pb). The GeoI values of all elements presented recorded no contamination except Pb and Hg.

Pb at any concentration presents health hazard to the populace due to its toxicity. In the present study, the maximum value of pb recorded is 197.911ppm, minimum value yields 33.905 ppm while the mean evaluated output yields 122.27ppm. The GeoI indicates 1.76. From table 1, this implies moderate contamination. This result implies that after remediation the villagers have somehow allowed further contamination to take place by their interaction with the Lead-poisoned Gold mine via lack of adequate safety measures or by deliberately violating the established rules in going about their exercises. Some of the possible un-observed safety rules may include coming back into the village in their mining clothes, shoes or/and mining implements that must have been laden with lead dust and consequently create exposure routes to the play ground where they also do rest in evening hours. Also possibility of some of these miners secretly coming home with ores cannot be ruled out since this has been strongly indicated in the sampled residential compound results in earlier evaluations.

The second observable result equally of great concern is the very high concentration of mercury. The recorded maximum value is 17.713ppm, minimum of 16.016ppm and mean value of 16.93ppm. The GeoI of 4.889 falls to extreme contamination range. This has now proven that there are deliberate cases of ore processing in the village even after remediation periods. Hg is known chemical for gold ore concentration, thus high value of contamination of the element in the village centre strongly indicates that the villagers have deliberately

abandon the safety rules laid down by the remedial team of CDC, MSF and other health authorities.

Observed result of the village market samples analysed yields very similar results to the observed effects of the children play ground; Lead concentrations noted at proportion that cannot be considered negligible and mercury values reflect strong indication of gold ore processing in the village against the remedial established rules. Pb maximum concentration recorded is 82.455ppm, minimum being 52.614ppm and mean result is 66.20ppm. The resulting GeoI of value 2, indicates moderate contamination. At the level of moderate contamination, Pb, value at such sites is already at point of health hazard to the children who are noted for their hand-to-mouth activities. The Hg maximum value is 24.572ppm, minimum of 16.001ppm while the mean value recorded is 19.166ppm. The GeoI recorded of 6 is an indication of extreme contamination.

## 5. Conclusions

The similarity in output of high concentration of mercury in both playground and village market as well as the recurring presence of Pb in all observations about Duza twin village sampled locations have shown strong indications of Gold-ore processing after remediation years. It's clear that the impact of the hazards posed by these chemicals is beyond the understanding of the villagers in spite of safety awareness they were taken through. There is strong chance that the village may still experience epidemics resulting from Pb or other health issues resulting from mercury contamination if the practice is unabated.

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