



## Distribution and Forms of Heavy Metals in Dan-Company Mining Soils, Anka, Nigeria

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### ABSTRACT

Lead poisoning crisis that crystallized in Bukkyum and Anka local governments of Zamfara State, Nigeria, gave birth to this research works in line with recommendations by Médecins sans Frontières (MSF-Holland) to Zamfara state health authorities. (UNEP/OCHA, 2010). The work consist of Soil sampling and XRF analysis of selected mining stages as well as a host village residential compounds, Dan-company. The concentration levels of Fe, Ni, Cu and Cr are elevated while that of other heavy metals is present within regulatory limits. The elevated levels of metals by their nature do rarely portend hazards to health. The relationship of mining cave values, tailings and residential compounds shows that the villagers of the mining environment might have been educated from the earlier years of the British settlers that flagged off mining in the area.

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### Introduction

North-western part of Nigeria is a region that is notably blessed with many forms of mineral deposits such as Gold, copper, tantalite, chalk and many other minerals of monetary value. Largely considered, the State and Federal governments have not given any serious focus to exploration of these minerals as a form of revenue base for national development due to distractions from black oil deposits; the petroleum. The result of this lack of focus generates the growth and development of risk-laden artisanal mining activities.

Soil plays a vital role in human life as the very survival of mankind is tied to the preservation of soil productivity (Kabata-Pendies and Mukherjee, 2007). According to Chen et al. (1997) soil is apart from being a medium for plants to grow is also a transmitter of many pollutants including potentially toxic metals into the atmosphere, biosphere and water resources. A major contaminant source soil, especially when it comes to the dry deposition of heavy metals, is smelting of ore minerals. Managing contaminated soil in different environments requires an understanding of heavy metals concentrations, the scale of contamination and the source of the heavy metals in that particular environment (Luo et al., 2007). At low concentrations, some PTMs (e.g. Cu, Cr, Mo, Se and Zn) are essential to healthy functioning and reproduction of microorganisms, plants and animals (Alloway 1995). However, at high concentrations, these essential elements may cause direct toxicity or reproduction effects. Although soil total concentration of metals is commonly used in establishing environmental quality standards, its usefulness to predict soil-to-plant transfer is often questioned, since the speciation and bioavailability of the metals in soils vary greatly depending upon soil physicochemical properties (Wang et al. 2006).

#### Aim and objectives

The immediate and latent environmental and health effects of these method of mining forms the motivating factor behind the need to carry out survey and research in some of the mining locations in Anka that are not affected by lead poisoning with

the aim of fishing out other possible health related problems associated with the mining method which has not been brought under focus. This particular zone under investigation is not officially documented by the doctors without borders chelating team that worked and still working on lead poisoned mining localities in the Anka zone as having been investigated. This research team thus has the following objectives in mind;

- I. To determine the types of heavy metals and metalloids present in the mining locality,
- II. To evaluate the concentrations of such metals and compare them to regulatory benchmark concentrations for health safety considerations of the workers and the general populace in the locality.
- III. To establish preliminary toxicological data for the area under consideration upon which further survey will be built in attempt to attain baseline health safety data with regards to soils in the environment.

Dan –Company is name of settlement derived from the earlier British mining company establish since the period that precedes the Nigerian independence from the colonial masters. History has it that in the Anka zone, Dan-Company is noted to have been one of the seats of the first known British miners that introduces panning and sedimentation methods of mineral processing in the north-west zone of the country. The location being an un-occupied space prior to commencement of mining later grew to a village as a result of the activities lend hands to the name of the village as Dan-Company; literary meaning "Off-shoot of company".

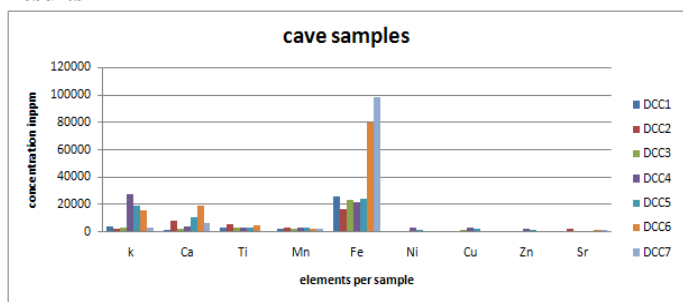
With the continuous artisanal mining exercises being carried out by the villagers it became a necessity for the environmental and health impacts of the exercise to be investigated. The necessity become more urgent since the name of the village do not surface on the list investigated zones by medicine frontiers (Doctors without borders) that investigated mining locations in Zamfara over Lead poison cases in 2010.

**Methodology**

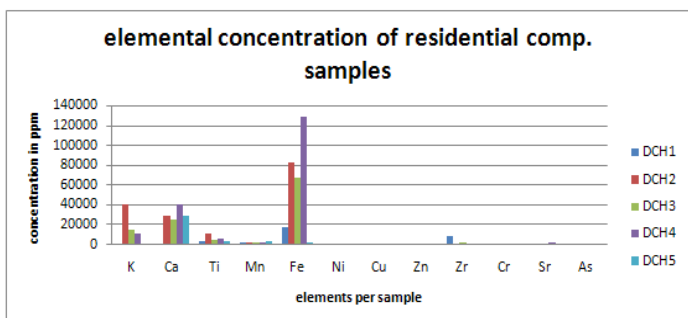
The soil and tailing samples were collected from different mining stages and the compounds of the villagers with the aid of sterilized plastic container, the samples were pulverized with the aid of agate mortar and pestle into a fine powder. The powders were prepared into a thick pellet of 13mm diameter. The analysis was carried out at the Center for Energy Research and Development (CERD), Obafemi Awolowo University, Ife, Nigeria with the aid of the center's XRF machine.

The elemental analyses of the soil and tailing samples were carried out using the Energy Dispersive X-ray Fluorescent (EDXRF) spectrometer. The spectrometer an ECLIPSE III, supplied by AMTEK INC. MA; USA, is a self-contained miniature X-ray tube system. It features a 30 kV/100 μA power supply, silver (Ag) transmission target, and a beryllium end window. In order to facilitate the use of this spectrometer, a portable controller is attached to it which generates all the voltages needed to operate the X-ray tube and provides both the voltage (kV) and current (μA) display and control. All our measurements were taken using the voltage 25 kV and current 50 μA. Each sample was irradiated for 1,000 seconds. The dead time was less than 5% using Teflon filters before the detector. The detection system for all the measurements is a Model XR-100CR which is a high performance X-Ray Detector with preamplifier and a Cooler System which uses a thermoelectrically cooled Si-PIN Photodiode as an X-Ray detector. The power to the XR-100CR is provided by the PX2CR power supply. The detector is coupled to the Pocket MCA 8000A Multichannel Analyzer. The resolution of the detector for the 5.9 keV peak of 55Fe is 220 eV FWHM with 12 μs shaping time constant for the standard setting and 186 eV FWHM with 20 μs time constant for the optional setting. The optional setting was used for our measurements with the resolution of 186 eV for the 5.9 Peak of 55Fe. The quantitative analyses of samples were carried out using the Quantitative Analysis Software package. It converts elemental peak intensities to elemental concentrations and/or film thicknesses.

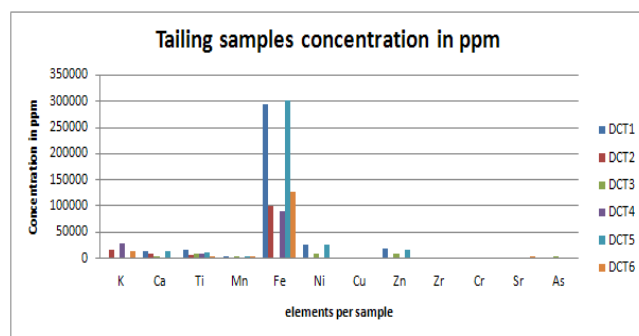
**Results**



**Figure 1. Chart of elemental characteristics of cave samples**



**Figure 2. Chart of elemental characteristics of residential samples**



**Figure 3. Chart of elemental characteristics of cave samples**

Tables 1,2 and 3 shows the concentration spectra of identified heavy metals in the soil and tailing samples in the mining caves, the residential compound and the tailings examined. Table 4 shows a compacted summary of concentration levels along with United States Environmental Protection Agency (US EPA) benchmarks. A glance at the benchmark column against the elemental concentrations readily shows that Iron, Fe, Nickel, Ni and Chromium, Cr, are the metals in elevated concentrations in the sections under consideration. Potassium and Calcium falls to no screening level category. The value of Potassium (K) ranges from 1866ppm to 27413ppm, 10227 to 40013ppm and 130 to 26632 for cave, residential and tailing samples respectively. The maximum concentration of the observed stages for Potassium (40013ppm) was recorded in the residential compounds, while minimum concentration (130ppm) was registered in the tailing samples. The mean low observation at the tailing zone can be related to solubility of potassium in water. With respect to Table 4, there is no screening level for potassium from EPA registry, but the United States National Library of Medicine hinted that excessive potassium can cause serious complications in the heart. Although potassium has a variety of important functions within the body, it can be extremely dangerous when levels become too high. The lowest concentration (2699ppm) of Ca was observed in the tailing samples while the maximum value is recorded in the residential compounds with a threshold level of 40455ppm. It can be observed that the wide range between the maximum and minimum value can be adduced to its solubility in water. Calcium is the most abundant metal in the human body: is the main constituent of bones and teeth and it has keys metabolic functions. It is an essential component for the preservation of the human skeleton and teeth. It also assists the functions of nerves and muscles. The intake of more than 2,5 grams of calcium per day without a medical necessity can lead to the development of kidney stones and sclerosis of kidneys and blood vessels. ( Lenntech B.V., 2014). Similar to Potassium, EPA do not have screening level for Calcium, this can be linked to overwhelming importance to the body compared to possibility of intake exceeding recommended levels. The screening limit soil concentration level of Tin for human health safety is 47000ppm by EPA, when compared to obtained results for the three examined stages that yield 15306ppm at the residential compounds as maximum value, it is seen from the table that for the site under consideration, Tin constitutes no threat to the local populace and workers by the overall concentration levels. Manganese, Mn, is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability.

Element	DCC1	DCC2	DCC3	DCC4	DCC5	DCC6	DCC7	Mean	Max.	Min.
k	3423	1866	3174	27413	18529	14968	2165	10219.71	27413	1866
Ca	1142	7834	2165	3442	9845	18762	6123	7044.714	18762	1142
Ti	2940	4730	2940	2940	2940	4519	2	3001.571	4730	2
Mn	2160	2317	2160	2160	2160	1317	1308	1940.286	2317	1308
Fe	25622	16151	23495	21326	23555	79126	97773	41006.86	97773	16151
Ni	482	26	1109	2246	1082	26	26	713.8571	2246	26
Cu	669	11	1808	2215	1628	11	11	907.5714	2215	11
Zn	418	239	779	1402	926	381	228	624.7143	1402	228
Sr	N.D	1861	N.D	N.D	N.D	829	696	1128.667	1861	696

Element	DCH1	DCH2	DCH3	DCH4	DCH5	Mean	Max.	Min.
K	N.D	40013	13780	10227		21340	40013	10227
Ca	N.D	28900	24236	40455	28900	30622.75	40455	24236
Ti	2940	10444	4358	4844	2940	5105.2	10444	2940
Mn	2160	977	850	1270	2160	1483.4	2160	850
Fe	16900	82762	67705	128281	1651	59459.8	128281	1651
Ni	518	555	26	26	8	226.6	555	8
Cu	880	260	11	11	40	240.4	880	11
Zn	573	682	322	304	23	380.8	682	23
Zr	8321	218	1472	185	348	2108.8	8321	185
Cr	N.D	528	2	N.D	N.D	265	528	2
Sr	N.D	N.D	N.D	1260	N.D	1260	1260	1260
As	N.D	N.D	N.D	13	N.D	13	13	13

Element	DCT1	DCT2	DCT3	DCT4	DCT5	DCT6	Mean	Max.	Min.
K	N.D	15309	N.D	26632	N.D	13075	18338.67	26632	13075
Ca	11294	8357	2699	N.D	13104	N.D	8863.5	13104	2699
Ti	15306	4020	6975	7739	10821	2470	7888.5	15306	2470
Mn	3324	1135	2786	1230	2896	1559	N.D	2896	N.D
Fe	294507	98332	33.7409	88027	300749	124808	151076.1	300749	33.7409
Ni	25299	26	8651	773	24692	26	9911.167	25299	26
Cu	N.D	11	N.D	363	N.D	11	128.3333	363	11
Zn	17267	306	6387	793	14739	258	6625	17267	258
Zr	N.D	N.D	N.D	73	N.D	N.D	73	73	73
Cr	N.D	N.D	N.D	36	N.D	N.D	36	36	36
Sr	N.D	N.D	N.D	N.D	N.D	2107	2107	2107	2107
As	N.D	N.D	2092	N.D	N.D	N.D	2092	2092	2092

Element	Mining café(PPM)		Residential compound(ppm)		Tailings(PPM)		References
	Max.	Min.	Max.	Min.	Max.	Min.	
K	27413	1866	40013	10227	26632	130	Soil Screening Levels (OFNL, 2008)
Ca	18762	1142	40455	24236	13104	2699	No Screening Level (OFNL, 2008)
Ti	4730	2	10444	2940	15306	2470	47000(OFNL, 2008)
Mn	2317	1308	2160	850	2896	1135	3200(OFNL, 2008)
Fe	97773	16151	128281	1651	300749	33.74	55000(OFNL, 2008)
Ni	2246	26	555	8	25299	26	1600(OFNL, 2008)
Cu	2215	11	880	11	363	11	2900(OFNL, 2008)
Zn	1402	228	682	23	17267	258	23000(OFNL, 2008)
Zr	N.D	N.D	8321	185	73	73	No Screening Level (OFNL, 2008)
Cr	N.D	N.D	528	2	36	36	210(OFNL, 2008)
Sr	1861	696	1260	1260	2107	2107	47000(OFNL, 2008)
As	N.D	N.D	13	13	2092	2092	NEPC (2003), ANZECC (2000)
EPA*	United States Environmental Protection Agency(ONFCI, 2008)						

Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of Manganese compounds. (Lenntech B.V., 2014). With reference to the site under investigation, Manganese concentration is found to be at maximum mean concentration at the tailing units with a top value of 2896ppm, followed by the cave value at a mean concentration of 2317ppm and finally at residence with a value of 2160 at mean concentration level. This recorded value indicates a general within-safe-range Manganese concentration for soil by comparing with the EPA limit of 3200ppm.

The acceptable environmental limit of Copper in soil is 2900ppm. The observed events in this examination revealed that Cu has its maximum concentration recorded at the mines section with a threshold value of 2213ppm. This is not close to the environmental limit. It can be stated safely that the workers as well as the local populace are not at risk by the level of copper contamination assessed. The output investigation of Zinc shows a maximum mean concentration at the tailing sites with a mean value of 17267ppm, followed closely by 1402ppm level of concentration at the mine cafes. The mean maximum value obtainable at the residential compounds is 682ppm, which is at variance with the observed scenario at the mine and tailing sections. It can be inferred that the observed level at the compound is an indicator that the settlements under investigation had either been educated about the hazards of allowing or processing the mineral in their residences, thus level observed may just represent the natural event at the compound of the soil formation.

The mean concentration of Iron (Fe) content was highest in the tailing samples with a value of 300749ppm, followed by another high concentration reading at the residence at 128281ppm and 97773ppm mean values at the mine cafes. The benchmark by EPA indicates a top limit of 55000ppm. This raised level of Iron concentration in all the stages is a call for concern because high intake of iron through any of the pathways when an individual is exposed, may result into hepatic megalia, cardiac infraction and nephric malfunction. In the present study, based on the observation, the value of Fe was found to be well rose, which is significant due to iron-rich soil of the area. The concentration noted for Nickel is found to be of overall mean high values at the tailing sections having 25299ppm, followed by 2246ppm in the cave samples and a mean low concentration at the residences with computed value at 555ppm. In all the stages, there exists wide range between minimum and maximum values of recorded concentrations for the Nickel level studied. Based on the acceptable limit of 1600ppm endorsed by United States Environmental Protection Agency, nickel concentration in the mining and processing stages present health risks to the mine workers that work without face mask. The recorded value at the residence shows no correlation between the artisanal activities and the local populace. Excess intake leads to hypoglycemia, asthma, nausea, headache, and epidemiological symptoms like cancer of nasal cavity and lungs.

An interesting scenario is presented by chromium in the assessment; a very low concentration was observed at the tailing section and not even detected at all in the mining cafes, while much raised level was noted at the residence output with a mean value of 528ppm against the regulatory limit of 210ppm. This particular scene can be related to transport of contaminant from source well different from the locality of study. The toxicity of chromium depends on the oxidation state, chromium (VI) being more toxic than the trivalent form chromium (III). In addition,

chromium (VI) is the more readily absorbed by both inhalation and oral routes. The respiratory tract is the primary target for inhaled chromium following acute exposure, although effects on the kidney, gastrointestinal tract and liver have also been reported. Acute ingestion of high doses of chromium (VI) compounds, the exact quantity of which is not usually known, results in acute, potentially fatal, effects in the respiratory, cardiovascular, gastrointestinal, hepatic, renal, and neurological systems. Due to the corrosive nature of some chromium (VI) compounds, dermal exposure can lead to dermal ulcers and at high doses, systemic toxicity leading to effects on the renal, haematological and cardiovascular system and death. (Assem, L., Zhu, H., 2007).

### Conclusions and Recommendation

The concentration levels of Fe, Ni, Cu and Cr in soil around Dan-Company mining settlement are considered elevated above natural concentration level. Other heavy metals are present within regulatory limits. The observed elevated levels of metals by their nature do rarely portend immediate hazards to health and this could have explained the absence of any notable emergence of the stated health effects at large notable scale within the community. A close investigation between the relationship of mining cave values, tailings and residential compounds shows that the villagers of the mining environment might have been educated from the earlier years of the British settlers that flagged off mining in the area in the colonial days. Since this area has hardly been investigated and documented prior to this study, this study thus forms preliminary data on the zone assessed. The preliminary concentration data will serve as monitoring benchmark as mining and ore processing operations continue with time in case of future events. There is a necessity for formation of an environmental monitoring and management program for heavy metals and other elements in the area. This is in order to monitor any on-set of heavy metal pollution that could endanger the immediate environment.

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