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# Impact of mining activities on ground water quality status, Dareta Village, Zamfara, Nigeria

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## ABSTRACT

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Medecins Sans Frontieres (MSF) in March 2010 discovered an epidemic of Lead poisoning in Zamfara state, Northern Nigeria. The source was traced to environmental exposure to Lead from the processing of Lead-rich ore mined by artisans in the state for Gold extraction which necessitated an immediate remediation of the affected villages. Dareta village was remediated between June and July 2010. The remediation was a simple process of taking off five centimeters of the contaminated top soil and replacing it with clean soil having confirmed from previous investigations that the contamination was superficial, followed by burial of the contaminated surface soil in land fill which may have far reaching consequences on the ground water quality. Water sample collected from randomly sampled hand dug wells in Dareta at the onset of the remediation exercise were analyzed for selected physicochemical parameters and metal concentrations using standard analytical techniques. Mean level of the parameters examined were Temperature (29.08±0.22°C), pH (6.34±0.26), Electrical Conductivity (370.83±179.16), Total Dissolved Solids (174.33±100.02), Nickel (0.06±0.05m), Chromium (0.17±0.07), Manganese (o.14±0.10), and Magnesium (2.48±0.27). The implications of the findings to public health are also discussed.

Key words: Lead poisoning, Dareta, Remediation, Physico-chemical parameters, Water Quality.

## INTRODUCTION

The need for better environment and health cannot be over emphasized. With increasing industrialization, urbanization, population growth, agricultural and mining activities, the global environment has become fragile and has been a cause for concern [1]. In his quest to satisfy his needs and aspirations for better living conditions through resource exploitation man has created an increasing number of environmental problems. He exploit nature, and in so doing upset the natural equilibrium which in turn have been proved to be harmful to man himself. Following each use of water and the exploitation of land and water resources, various forms of pollution contributes to the degradation of the environmental quality [2]. Recently, there is growing awareness of impact on environment of effluents and solid wastes of anthropogenic origin and serious concern on the use of water as a receptacle for such waste. The notion therefore that water; one of nature's, greatest gift to man is inexhaustible and can assimilate and diffuse anything put into it is fast fading out [3]. Water is indispensable. It is not only essential for the survival of man but also for other living organism [4]. It is an essential nutrient that is involved in every function of the human body and constitutes about two-third of the human body. The importance of water in our daily life makes it imperative that thorough microbiological and physio-chemical examinations be conducted on water. Potable water is

that water that is free from disease producing microorganisms and chemical substances that are dangerous to health [5].

Freshwater quality and availability is one of the most critical environmental and sustainability issues of the present century. Of all sources of freshwater on the Earth, groundwater constitutes over 90% of the world's readily available freshwater resources [6]. Groundwater represents an important source of drinking water and its quality is currently threatened by a combination of over-abstraction and microbiological and chemical contamination [7]. The presence of metals in groundwater and soils can pose a significant threat to human health and ecological systems. The chemical form of the metal contaminant influences its solubility, mobility, and toxicity in ground-water systems and depends on the source of the metal waste, the soil and ground-water chemistry at the site. Metals differ from other toxic substances in that they are neither created nor destroyed by humans. Ground water may be contaminated with metals from wastewater discharges or by direct contact with metals-contaminated soils, sludge's, mining wastes, and debris. Metal-bearing solids at contaminated sites can originate from a wide variety of sources in the form of airborne emissions and process solid wastes [8]. Water for human consumption must be free from microorganisms and chemical substances in concentrations large enough to cause environmental imbalance and disease [9]. The World Health Organization (WHO) estimated in 1996 that every eight seconds a child dies from a water-related disease and that each year more than five million people died from illnesses linked to unsafe drinking water or inadequate sanitation [1]. Contamination of groundwater has severe implications for public health, particularly in small communities and developing countries where groundwater is often the preferred source of drinking water.

Zamfara State, Nigeria, has a lot of untapped mineral resources. The natives tap these minerals crudely with so many mining mills scattered all over the State [8]. Dareta village is one of such mining fields. The uncontrolled and illegal mining activities have left a lot of environmental hazards, enormous amount of wastes and different types of pollutants on the mining communities. Many deaths are being recorded in different communities of the state. These deaths have been traced to environmental exposure to lead from the processing of lead-rich ore mined by artisans for gold extraction which necessitated an immediate remediation of the affected villages. Dareta village (Perhaps most troubling of all) was remediated between June and July 2010. [10, 11, 12 and 13]. Studies have confirmed high Lead, Cadmium, and Zinc levels in human blood and hand-dug wells in Dareta village at the onset of the remediation exercise [14, 15]. Elevated levels of Lead, Cadmium and Copper in Dareta soil was reported [10]. It is possible that the Lead contaminated gold ore mined by artisans in the state contain other toxic metals. This study is focused on the assessment of Chromium, Nickel, Magnesium, Manganese levels and physicochemical parameters of water quality of hand wells in Dareta village, Zamfara, Nigeria at the onset of the remediation exercise. This study will therefore serve as baseline for assessing the impact of the exercise on ground water quality. The implications of the findings to public health are also discussed.

### MATERIALS AND METHODS

Sample containers were thoroughly washed with detergent, rinsed with water followed by distilled water before soaking in 5% HNO<sub>3</sub> for about 24 hours. Water Samples were collected from hand dug wells using plastic drawers into 4-litre acid washed polypropylene sample containers. Electrical conductivity, temperature and total dissolved solids were determined on site using HACH conductivity / TDS meter (model 44600.00), pH was also determined on site electronically using Hanna instrument pH 210 micro processor pH meters. The samples were then kept on ice in ice-chest and transported to the Environmental laboratory of National Research Institute for Chemical Technology, (NARICT) Zaria, Nigeria, at temperature of < 4°C. The samples were digested according to Standard methods for the examination of water and wastewater, American Public Health Association [16]. Metal analyses were carried out using flame Atomic Absorption Spectrophotometer (AA-6800, Shimadzu, Japan) after wet digestion. The calibration curves were prepared separately for each of the metal by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks. The values obtained were subjected to statistical analysis. The elements determined included Chromium, Nickel, Manganese and Magnesium.

## DATA ANALYSIS

Data collected were subjected to statistical analysis. The descriptive statistics were computed and Correlation coefficient used to determine the association between the heavy metals under study at 95% confidence level. All statistical analyses were done by SPSS software for windows

#### VALIDATION OF ANALYTICAL PROCEDURE

In order to check the reliability of the analytical methods employed for metals determination, Standard Reference Material, Lichens coded IAEA-336 was also digested and then analyzed following the same procedure.

### **RESULTS AND DISCUSSION**

A standard reference material of lichens coded IAEA-336 was analyzed in like manner to our samples. The values determined and the certified values of the five (5) elements determined were very close (table 1) suggesting the reliability of the analytical method employed.

TABLE 1. Shows the results of analysis of reference material (Lichen IAEA -336) compare to the reference value

Element (Mg/l)	Pb	Cd	Cu	Mn	Zn		
A Value	5.25	0.140	4.00	55.78	29.18		
R value	4.2-5.5	0.1-2.34	3.1-4.1	56-70	37-33.8		
A Value = Analyzed value, R value = Reference value							

Twelve hand dug wells were randomly picked for the study. Physico-chemical parameters and heavy metal concentration of individual sample are presented in Table 2. The mean concentrations, range of the metals and physico-chemical parameters across the different hand dug wells are summarized in table 3 and compared with World Health Organization (WHO), European Union (EU) and the Nigerian Standards for Drinking Water Quality (NSDWQ) guidelines for potable water. The spatial distribution of physico-chemical parameters and metals across the various hand dug wells are presented in figures 2 and 3 respectively. Metals concentration follows the trend Magnesium > Chromium > Manganese > Nickel.

TABLE 2: Concentration of Metals in Wells within Dareta Village, Anka, Nigeria. (Values are in Mg/l Except Otherwise Stated)

S/No Ni	NI:	Cr	Mg	Mn	EC us/om	Tempt (°C)	лU	TDS
	INI				EC µs/cm		рп	mg/l
1	0.050	0.199	2.499	0.068	100	29.0	5.82	60
2	0.013	0.242	2.909	0.323	240	29.3	6.13	12
3	0.004	0.164	2.352	0.099	420	29.2	6.53	210
4	0.083	0.045	2.435	0.139	540	28.9	6.56	270
5	0.026	0.141	2.727	0.047	350	29.01	6.43	170
6	0.013	0.184	2.792	0.098	290	29.2	6.5	140
7	0.057	0.091	2.524	0.098	440	29.4	6.41	220
8	0.101	0.229	1.949	0.271	770	28.8	6.34	380
9	0.164	0.153	2.659	0.106	460	29.0	6.55	230
10	0.150	0.098	2.35	0.072	380	28.7	6.5	180
11	0.041	0.232	2.442	0.070	310	29.3	6.46	150
12	0.053	0.299	2.13	0.289	150	29.2	5.84	70

As reflected in Table 2, the temperatures which ranged from  $28.7^{\circ}$ C to  $29.40^{\circ}$ C were found outside the WHO standard of  $25^{\circ}$ C for domestic water supply. Increase in temperature leads to increase in solubility. At high temperatures total dissolved solid is increased as more solute goes into solution. The temperatures recorded in this study were also above the EU acceptable limit (table 3, figure 2.). Similar findings were reported for wells in Kubwa, Bwari Area Council, FCT, Nigeria [9], and a mean value of  $26.33\pm0.89^{\circ}$ C. was reported for samara, zaria, Nigeria [17]

TABLE 3. Mean concentration of Nickel, chromium, Magnesium, Manganese and physicochemical parameters in Hand dug wells, Dareta village, Anka, Nigeria

	Ni	Cr	Mg	Mn	EC (µs/cm)	Tempt	pН	TDS
Range	0.00-0.16	0.05-0.30	1.95-2.91	0.05-0.32	100-770	30-35	5.8-6.6	12-380
Mean	0.06	0.17	2.48	0.14	370.83	29.08	6.34	174.33
Std. Dev.	0.05	0.07	0.27	0.10	179.16	0.22	0.26	100.02
WHO Std	0.02	0.05	0.20	0.2	250	25	6.5-8.5	500
NSDWQ	0.02	0.05	0.20	0.2	1000	-	6.6-8.5	500
EU std	0.02	0.05	Na	0.05	250	25	6.5-8.5	

Na= not available. EU = European Union. WHO = world Health Organization.

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The pH of water is very important in the determination of water quality since it affects other chemical reactions such as solubility and metal toxicity. The groundwater samples in this study were found to be acidic with a mean pH value of 6.34 which is below the World Health Organization (WHO), European Union (EU) and the Nigerian Standard for Drinking Water Quality (NSDWQ) guidelines for potable water (table 3). In Mubi, Nigeria, a pH range of 4-7.3 was recorded for hand dug wells [18]. pH range of 5.68-5.72 was reported for groundwater Supplies in Akure, Nigeria [19] and 6.61- 694 for wells in Kubwa, Bwari Area Council, FCT, Nigeria [9]. A mean pH value of 6.13 was recorded by Longe in lagos [20]. Metals tend to be more soluble and more reactive at lower pH. Lead sticks to soil particles and enters drinking water only if the water is acidic or soft [9]. It should be recalled that Acute mass lead poisoning epidemics was discovered in zamfara state in 2010 and following requests for assistance from the Federal Ministry of Health of Nigeria and the UN Resident Coordinator, The joint UN Office for the Coordination of Humanitarian Affairs (OCHA) and UN Environment Programme (UNEP) Environment unit led the investigation of lead pollution emergency in the state. OCHA testing indicates that well water in the affected villages (Dareta inclusive) range from 10 to 50ug/l Pb. The US standard for delivered potable water is 15ug/l Pb. Measurements showed that 25-30% of wells in the villages assessed did not meet the WHO guideline for lead in drinking water, although in most wells, the limit of 10 ug/l was exceeded by no more than several  $\mu$ g/l. However, in some wells, concentrations of up to 10-15 times the guideline were found [11 and 21]. With the pH recorded in this study slow movement of metals to the ground water aquiver cannot be excluded. It is also worthy to note that the remediation exercise in Dareta village was a simple process of taking off five centimeters of the contaminated top soil and replacing it with clean soil having confirmed from previous investigations that the contamination was superficial, followed by burial of the contaminated surface soil in landfills. Figure 3 shows that the landfill sites were already filled with water even before the burial of the contaminated top soils.





One of the Landfill sites where contaminated top soil are buried in Dareta village

Low pH of such waters will enhance solubility of metal which may have far reaching consequences on the ground water quality. Lead and Copper levels in many areas of Dareta village, including residential compounds, around drinking water sources and grinding mills exceeded the acceptable limit for residential areas [10].



The spatial distribution of physico-chemical parameters in Hand dug wells, Dareta village, Anka, Nigeria.

The electrical conductivity (EC) of all water samples ranged between 100-770  $\mu$ s/cm. The EC of water sample reveals that levels of dissolved ionic substance in hand dug wells in Daretta were generally within the World Health Organization (WHO), European Union (EU) and the Nigerian Standard for Drinking Water Quality (NSDWQ) guidelines for potable water (table 3). Only one out of twelve wells sampled (8.3%) had electrical conductivity value above the maximum permissible limit (table 2, fiqure 2). A mean value of 0.41 $\mu$ s/cm was reported for wells in Kubwa, Bwari Area Council, FCT, Nigeria [9] and 597.60 ± 229.32  $\mu$ s/cm for samara, zaria, Nigeria [17]. Mean values of 901.40 ±50.26 and 884.45 ± 61.28 were reported for groundwater in West Thrace, Turkey [7]. Conductivity of water is a measure of its ability to conduct electricity due to the presence of ionic solutes. The magnitude of the conductivity therefore is a useful indication of the total concentration of ionic solute [22].

The amount of total dissolved solids (TDS) in a given water sample indicates the general nature of salinity of that water. The water that contains more than 500mg/l TDS is not considered suitable for drinking water supply. In the present investigation all twelve samples from different hand dug well contains acceptable value of TDS and they were ranged from 12mg/l to 380mg/l (table 2, Figure 2). TDS contents of hand dug wells were therefore within permissible limits. Similar values (18mg/l - 342mg/l) were reported for groundwater Supplies in Akure, Nigeria [19]. A range of 208 – 370mg/l was reported for wells in Kubwa, Bwari Area Council, Fct, Nigeria [9]. Mean values of  $456.60\pm24.31$ mg/l and  $450.65\pm30.80$ mg/l were reported for groundwater in West Thrace, Turkey [7]. The total dissolved solids of dug well water ranging from a minimum of  $100.91\pm12.14$  mg/l to a maximum of  $120.78\pm0.40$  mg/l was recorded for Bargarh District, Orissa, India [23]. World Health Organization does not directly consider electrical conductivity in guidelines for drinking water quality [24], but it does give recommendations for dissolved solids because of taste considerations [17].

Chromium occurs naturally in the Earth's crust and can be detected in all environmental media. The continental dust flux is the main natural source of Chromium in the atmosphere, but much larger amounts are released by human activities. Chromium is an important mineral the body must have to function properly. It's responsible for stimulating the activities of insulin in the body and also help controls blood cholesterol levels. The acceptable daily intake of chromium is 50-200µg/day. The body stores chromium in blood and in hair [25]. The toxicity of chromium depends on its oxidation state. Hexavalent chromium is more toxic than the trivalent form [26]. Chromium (Cr) is considered an essential nutrients and a health hazard. Hexavalent Chromium is considered harmful even in small intake quantity (dose) whereas trivalent Chromium is considered essential for good health at moderate intake. The highest and lowest concentrations of Cr in this study were 0.05mg/l and 0.30mg/l respectively. The mean value was 0.17mg/l (table 3). When compared with World Health Organization (WHO), European Union (EU) and the

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Nigerian Standard for Drinking Water Quality (NSDWQ) guidelines for potable water (table 3 figures 3), it was found to be 3.4 times the acceptable limit for Cr in Drinking water (0.05mg/l). Eleven out of twelve hand dug wells representing 91.67% had values above the acceptable limits (table 2). The results of statistical analysis reveal a positive correlation between Chromium and magnesium, chromium and Nickel, and between chromium and Manganese. Only the correlation between chromium and magnesium was statistically significant at 95% confidence level. From the above, it could be suggested that same source could be responsible for the presence of Chromium and manganese at the concentrations discovered in this study across the different sample locations. A range of 0.05mg/l to 0.22mg/l was reported for wells in Kubwa, Bwari Area Council, FCT, Nigeria [9]. Mean values of 0.45mg/l was reported for groundwater near municipal landfill in Lagos Nigeria [20]. Chromium is a toxic human carcinogen that can cause or increase the rates of certain cancers. Ingestion of high concentrations of Cr (VI), often results in lung function and blood system problems, gastrointestinal burns, hemorrhage, generalized oedema, pulmonary oedema, liver damage, and kidney damage. Symptoms are diarrhea, abdominal pain, indigestion, and vomiting. Death may be the result of pulmonary or cardiac arrest. Skin contact causes a number of skin problems, including rashes and sores. The American environmental Agency gave the cancer potency factor as 42mg/kg body weight. The acceptable daily intake of chromium is 50-200µg/day [15, 24, 26 and 27,]



FIGURE 3

The spatial distribution of Nickel, Chromium, Magnesium and Manganese concentration in hand dug wells, Dareta village, Anka, Nigeria.

Manganese is an essential nutrient that is important for normal processes in the human body. It helps in food digestion, supports the immune system, regulates blood sugar level and is involved in the production of energy and cell reproduction. Manganese is important for bone growth, works with vitamin K to support blood clothing and with the B- complex vitamins to control the effect of stress. The estimated safe and adequate Daily Dietary intake of manganese is 2-5mg/day for adults and 2.5-25µg per kilogram bodyweight for infants. Manganese is a mineral element that is both nutritionally essential and potentially toxic [28]. In the present study, Mn ranged from 0.05-0.32mg/l with a mean value of 0.14mg/l (table 3, figure 3), thus exceeding the European Union acceptable limit of 0.05mg/l but within the World Health organization and National Standards for Drinking Water Quality of limits of 0.2mg/l. Three out of twelve samples (25%) exceeded the World Health Organization and National Standards for Drinking Water Quality. A positive correlation was observed between Chromium and manganese, Nickel and manganese, and between magnesium and Manganese. The correlations were not statistically significant at 95% confidence level. A range of 0.01mg/l to 0.05mg/l was reported for wells in Kubwa, Bwari Area Council, Fct, Nigeria [9]. Mean values of 0.09mg/l was reported for groundwater near municipal landfill in Lagos Nigeria [19]. Manganese toxicity can result in a permanent neurological disorder with symptoms similar to those of Parkinson's disease, including; tremors, difficulty walking, and facial muscle spasms. Individuals with chronic liver disease are uniquely susceptible to Manganese toxicity. Thus, impaired liver function may lead to decreased Manganese

excretion. Manganese accumulation in individuals with liver problems may contribute to neurological problems and its associated symptoms which are often preceded by psychiatric symptoms, such as irritability, aggressiveness and even hallucinations. Manganese is eliminated from the body mainly in bile. [29]. Manganese passes from mother to infant across the placenta and in breast milk. Moreover, Manganese crosses the blood-brain barrier and enters the brain much more easily in infants than in adults. [10].

Nickel occurs naturally in soils as a result of the weathering of the parent rock. The underlying rocks and soilforming processes strongly influence the amount of Nickel in soils. Anthropogenic activities have resulted in the widespread atmospheric deposition of Nickel. Small amounts of Nickel are needed by the human body to produce red blood cells, however, when the concentration exceeds a certain threshold, it elicits toxic effect. The concentration of Ni ranged from 0.00 - 0.16mg/l with a mean value of 0.06mg/l. Nine out of the twelve hand dug wells (75%) had nickel levels above the World Health Organization, European Union and the Nigerian Standards for Drinking water Quality limits of 0.02mg/l for nickel in drinking water (table 2, 3 and figure 3). The mean value for nickel in this study was found to be three times higher than the acceptable limit. Similar values were recorded by Aremu for wells in Kubwa, Bwari Area Council, Fct, Nigeria with a mean value of 0.71 [9]. The results of statistical analysis reveal a positive correlation between Chromium and Nickel, magnesium and Nickel, and between Nickel and Manganese. The correlations were not statistically significant at 95% confidence level. Chronic exposure can cause decreased body weight, heart and liver damage, thyroid disease, cancer and skin irritation. Other toxic effects of Nickel observed following chronic exposure include chronic bronchitis, emphysema, reduced vital capacity and asthma [27]. Nickel values obtained in this study pose serious cause for concern considering the fact that consumers are at risk of exposure exceeding the Oral tolerable daily intake (TDI oral) of 12µg/kg body weight per day.

Magnesium functions as an essential constituent for bone structure, for reproduction and for normal functioning of the nervous system. It is also a part of the enzyme system with a recommended dietary allowance of 6mg/kg/day. Table 2 presents Mg as the metal with the highest concentration in this study, magnesium values ranged from 1.95 mg/l to 2.01 mg/l with a mean value of 2.48mg/l which is over 12 time the World Health Organization and the Nigerian Standards for Drinking water Quality limits of 0.02mg/l for magnesium in drinking water (table 2, 3 and figure 2). A positive correlation was observed between magnesium and manganese, magnesium and Nickel, and between magnesium and chromium. The correlations were not statistically significant at 95% confidence level. Higher values ranging from 1.94mg/l to 64.56mg/l was reported for wells in Kubwa, Bwari Area Council, FCT, Nigeria with a mean value of 0.71 [9].

## CONCLUSION

Physicochemical parameters of water quality and selected metals-chromium, manganese Nickel and magnesium were investigated at the onset of the remediation exercise in Dareta village. Temperature was found to be above the WHO limit of 25°C for domestic water supply. The samples under study were generally acidic with a mean pH value of 6.34 which is below the World Health Organization (WHO), European Union (EU) and the Nigerian Standard for Drinking Water Quality (NSDWQ) guidelines values of 6.5 -8.5 for potable water. The Electrical Conductivity reveals that levels of dissolved ionic substance were generally within the World Health Organization (WHO), European Union (EU) and the Nigerian Standard for Drinking Water Quality (NSDWQ) permissible limits. All twelve hand dug wells sampled had TDS values within the acceptable limit. Nickel, Chromium and Magnesium were seriously implicated in this study. The mean magnesium concentration was over twelve times the permissible limits while Nickel and Chromium were about three times the limit. The mean value of manganese was found to be within the World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) permissible limits though 25% of the wells sampled actually had manganese level above these limits.

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