



Human Health Risk Assessment of Some Toxic Metals in Groundwater Resources in Four Selected Towns of Delta State, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Author KN designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors KN and REJ managed the analyses of the study. Author REJ managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: The health risk assessment of some toxic metals in groundwater in four selected towns of Delta State, Nigeria was confirmed by this study.

Methodology: Ninety six groundwater samples were obtained from sixty four hand-dug wells and thirty two boreholes between December 2016 and May 2017. Samples were analyzed for heavy metals using standard procedures. Data collected was subjected to descriptive and inferential statistics using the Statistical Package for Social Sciences (SPSS) for Windows version 22.0. Health Risk Assessment for Non cancer hazard and carcinogenic effects were determined.

Results: The HQ of Cr, Mn and Ni were below 1.0 indicating no threat to the water consumers while the HQ values for Pb, Cd and Cu were above 1.0 indicating risk to human health. The HI value was found to be greater than 1.0, indicating noncarcinogenic adverse effects. The estimated Lifetime of Carcinogenic Risks (LTCR) for Pb, Cr, Cd and Ni exceeded the predicted lifetime risk for carcinogens of 10^{-6} from ingestion pathway. The groundwater had higher risks of Cr and Cd as

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LTCR value in most sites were $>10^{-4}$. The high LTCR should be given high priority as public health is concerned.

Conclusions: This study indicated possible non-carcinogenic and carcinogenic human health hazard from groundwater consumption in study area through oral consumption.

Keywords: Health risk assessment; Hazard Quotient (HQ); Hazard Index (HI); Lifetime of Carcinogenic Risk (LTCR).

1. INTRODUCTION

The Niger Delta Region of Nigeria thrives in oil and gas deposits, and exploration and exploitation activities have been on for several decades now. It is known that oil and gas activities could contribute solid, liquid and gaseous contaminants to the environment and that these toxicants could infiltrate the soil profile and contaminate aquifers [1,2,3]. The problems of groundwater contamination include outbreaks of water-borne diseases, as well as unsuitability of water for both agricultural and industrial uses. Groundwater pollution by heavy metals have also been implicated to cause human health hazards as a result of bioaccumulations. Persistent, Bioaccumulative and Toxic substances (PBTs) such as lead and cadmium have high mobility in the environment and high toxicity. PBTs have been observed to have a high order of bioaccumulation and biomagnification with very long retention times in various media, and widespread distribution across the earth.

Toxic metals are usually present in industrial, municipal and urban runoff, which can be harmful to humans and biotic life. Increased urbanization and industrialization (including petroleum exploitation) are to be blamed for an increased level of trace metals, especially heavy metals, in our waters [4]. Many dangerous chemical elements if released into the environment, bioaccumulate in organisms, soil and sediments of water bodies [5]. There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be very toxic and relatively accessible [4]. Toxicity level depends on the type of metal, its biological role and the type of organisms that are exposed to it. Heavy metals have a marked effect on the aquatic flora and fauna which through biomagnification enters the food chain and ultimately affect the human beings as well [6]. The heavy metals in drinking water that are toxic to humans include lead, iron, cadmium copper, zinc, chromium etc.

The known fatal effects of toxic metals in drinking water include damaged or reduced mental and central nervous function and lower energy level. They also cause irregularity in blood composition, badly effect vital organs such as kidneys and liver. [7]. The long term exposure of these metals result in physical, muscular, neurological degenerative processes that cause Alzheimer's disease (brain disorder), Parkinson's disease (degenerative disease of the brain), muscular dystrophy (progressive skeletal muscle weakness), multiple sclerosis (a nervous system disease that affects brain and spinal cord), Also ,lead is one of the most common heavy metal in drinking water ,if occurred more than its permissible limit shows general metabolic poison and enzyme inhibitor [8]. Lead has the ability to replace calcium in bone to form sites for long term replacements. Heavy metals like copper are the essential trace elements but show toxicity in excess. Toxicity can result from any of the heavy metals if they are present more or less from its original limits in drinking water.

Majority of PBTs in the environment are either created through industry [9]. Lead reduces intelligence quotient in children and lead poisoning in adults can affect the peripheral and central nervous systems, the kidneys and liver failure, brain damage, headache, vomiting, loss of memory, gastrointestinal tract, anemia, nausea, insomnia, loss of appetite, irritability, convulsions, blood pressure, anorexia, both male and female reproduction, animal carcinogen, hypertension along with renal failure, lung and stomach cancer [10,11]. Chromium can also cause liver and kidney damage, skin irritation and ulceration as well as circulatory and nerve tissue [12].

Cadmium bioaccumulation in body causes serious health problem such as skeletal and testicular tissue damage, kidney dysfunction (hinder filtering mechanism) as well as damage to red blood cells [13]. Nickel toxicity has been linked with cancer of the lungs, nose, and bone and skin irritation [14].

Table 1. List of some toxic/heavy metals, sources and health effects

Heavy metals	Sources	Health effects
Lead (Pb)	Lead is released into the atmosphere from industrial processes such as gasoline, house paint, as well as from vehicle exhausts. Corrosion of old plumbing pipes	Lead is a cumulative poison. The presence of lead in the drinking water can cause damage to the kidney, nervous system, and learning difficulties.
Chromium (Cr)	Petroleum and coal, chromium steel, pigment oxidants, fertilizers, catalyst, oil well drilling and metal plating tanneries.	Chromium may cause lung tumors when inhaled
Manganese (Mn)	Gasoline as methylcyclopentadienyl manganese tricarbonyl (MMT) and thus, gasoline fumes contain a very toxic form of manganese.	Manganese in large doses causes headaches, apathy, irritability, insomnia, and weakness of the legs. Long-term heavy exposure may result in a nervous system disorder.
Cadmium (Cd)	Cadmium is emitted through industrial processes eg production of paints, pigments alloys, coatings, batteries as well as plastics and from cadmium smelters into sewage sludge, fertilizers, and groundwater	Cadmium can potentially cause damage to kidney, bone (osteoporosis), liver and blood in case of continuing exposure at levels that are higher than the maximum contaminant level.
Nickel (Ni)	It is used in the production of batteries, nickel-plated jewelry, machine parts, nickel plating on metallic objects, manufacture of steel.	Long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation.
Copper (Cu)	Anthropogenic and industrial activities.	Copper in large doses is dangerous to infants and people with certain metabolic disorders. Causes liver cirrhosis

However, excessive amount intake of these metals causes health problems: Copper can cause anemia, liver and kidney damages, stomach and intestinal irritation [12].

Generally, high concentrations of Manganese and Copper in drinking water can cause mental diseases such as Alzheimer's and Manganism [15]. High Mn contamination in drinking water also affects the intellectual functions of 10-year-old children [16]. The list of some toxic metals, sources and their health effects are shown in Table 1.

This study will determine the concentrations of some toxic metals in groundwater of the study area and also assesses the potential health risks associated with the heavy metals.

2. MATERIALS AND METHODS

2.1 Study Area

The study was carried out in four major towns in Delta Central District, Delta state, Nigeria, at

Latitude 5.50° and 5.80°N and Longitude 5.84° and 5.98°E (Fig. 1). The area is central to most major towns and communities in the district and experiences less oil pollution than most parts of the Niger Delta [17].

Delta Central is directly underlain by a Quaternary formation, the Somebreiro-Warri Deltaic Plain Sand [18]. This formation consists of a fine to medium and coarse-grained unconsolidated sands with occasional intercalations of gravelly beds, peat or lenses of plastic clay. The sandy and gravelly horizons constitute prolific aquifers that are tapped by shallow wells in the area. This formation is generally in excess of 100 metres in thickness. Below the Somebreiro- Warri Deltaic Plain Sands are the three stratigraphic units that constitute the Niger Delta. These include the Benin, Agbada and Akata formations in order of increasing age.

Oil exploration and exploitation operations have been ongoing for over 40 years in the area and

the major source of water of the inhabitants is groundwater, which is abstracted for several domestic, agricultural, and industrial purposes [3]. Delta Central is made up of eight local councils which include: Ethiope East, Ethiope West, Okpe, Sapele, Udu, Ughelli North, Ughelli South and Uvwie (Fig. 1).

2.2 Sample Collection and Analysis

A total of ninety six groundwater samples were obtained from sixty four hand-dug wells and thirty two boreholes between December 2016 and May 2017. Samples were analyzed for heavy metals using standard procedures [19].

The determination of heavy metals was performed with a bulk scientific 205 atomic

absorption spectrophotometer (AAS). The instrument's setting and operational conditions were done in accordance with manufacturer's specifications. The instrument was calibrated with analytical-grade metal standard stock solutions (1 mg/L) in replicate. 150 ml of sample was transferred to a beaker, 5 mL concentrated HNO₃ was added and the mixture evaporated almost to dryness on a hot plate. Two mL of concentrated HNO₃ was added to dissolve the residues on the walls of the beaker. The distilled, digested sample was filtered and made up to 50 mL and analyzed using AAS. Blank was prepared by carrying distilled deionized water through the whole procedure above. Sample was prepared for analysis, following the methods described earlier [20].

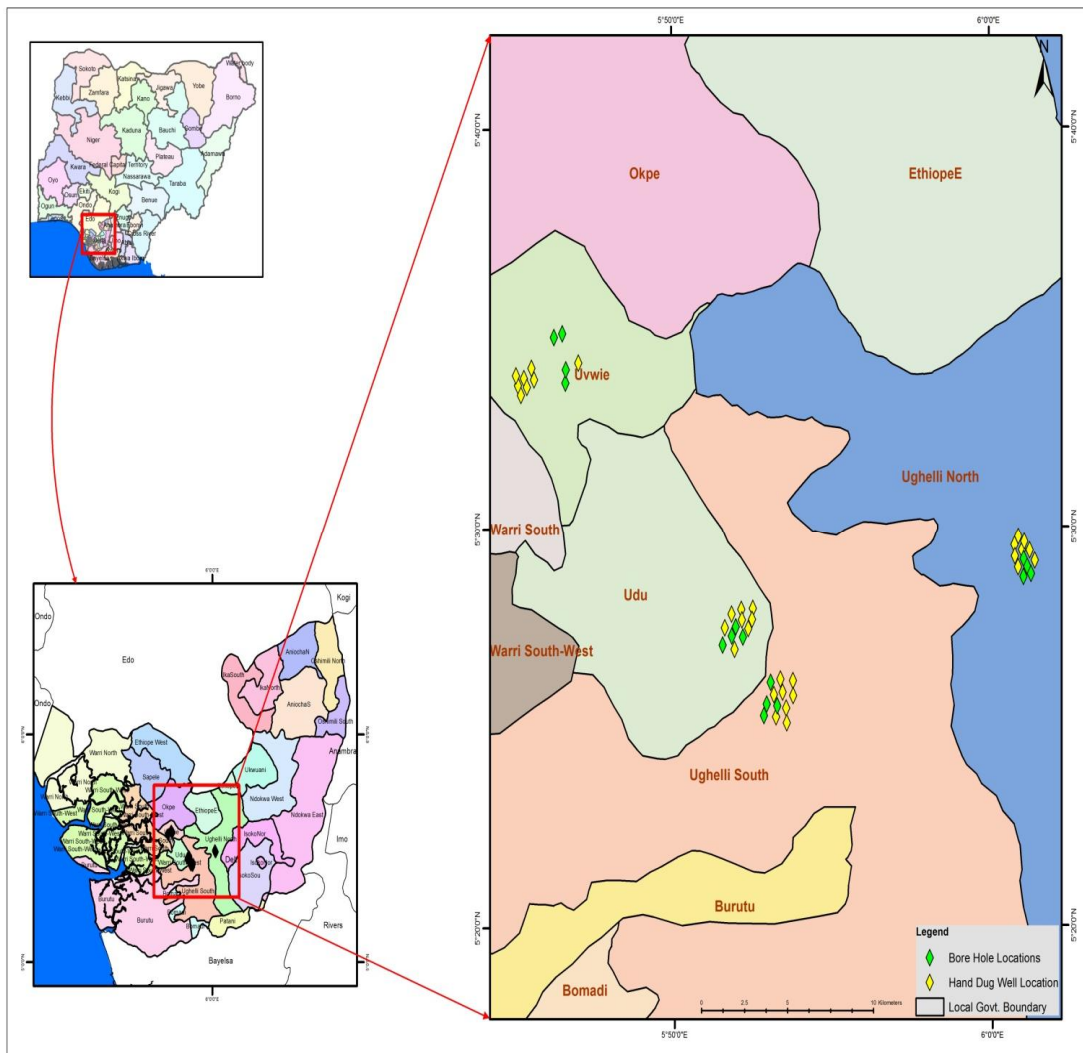


Fig. 1. Map of Delta State showing sampling locations

2.4 Health Risk Assessment

Health Risk Assessment was calculated for Non cancer hazard and carcinogenic effects as follows [21].

$$(1.) \text{ Average Daily Dose (mg/L/day)} = \frac{C * IR * EF * ED}{BW * AT}$$

C = Concentration of metals in water (mg/L)
 IR = Ingestion Rate (2 L for adult, 1 L for a child and 0.75 L for an infant)
 ED = Exposure duration (years)

30 * 365 days for non-carcinogenic adverse effects and 50 years for carcinogenic effects for adult while ED = 6 * 365 days for a child and 1 * 365 days for infant [22].

EF = Exposure frequency (day/year)
 = 250 days/ year [23].
 AT = Averaging time = life expectancy
 AT = ED for non-Carcinogenic effects

While AT = 54.5 * 365 days for Carcinogenic effects on adult [24] and 6 * 365 days for children and 1 * 365 days for infant [25]

BW = Body weight, 60 kg for adult. 10 kg for a child and 5 kg for an infant [26].

$$(2.) \text{ Non cancer hazard index} = HI = \sum_{i=1}^n HQ_i$$

$$\text{Hazard Quotient (HQ)} = \frac{ADD}{RfD}$$

ADD = Average Daily Dose
 RfD = Oral Reference Dose

A summation of the hazard quotients for all chemicals to which an individual is exposed was used to calculate the hazard index [21].

$$HI = HQ_A + HQ_B + \dots + HQ_n$$

Health risk assessment of toxicant was interpreted based on the values of HQ and HI. Values less than one (HQ or HI <1) means no risk and the greater the values above one, the greater is the level of risk of the toxicants manifesting long term health hazards effects increasing [27].

$$(3.) \text{ Cancer Risk} = ADD * SF$$

SF = Slope Factor

Where RfD is the oral reference dose or tolerable daily intake which was obtained from United State Environmental Protection Agency table [28] and refers to the maximum amount of toxicant which does not translate to adverse effect on the one ingesting the toxicants.

Risk is therefore a unit less of chances of an individual developing cancer when exposed over a lifetime and SF is the carcinogenicity slope factor (per mg/kg/day).

Risks values exceeding 1×10^{-4} are regarded as intolerable, risks less than 1×10^{-6} are not regarded to cause significant health effects, and risks lying between 1×10^{-4} and 1×10^{-6} are regarded generally as satisfactory range, but circumstances and condition of exposure determine the range of the value of the circumstance [29].

3. RESULTS AND DISCUSSION

3.1 Toxic Metal Concentration in Groundwater Samples

Table 2 shows the average seasonal concentrations of heavy metals in groundwater samples. Lead had a mean concentration of 0.02 ± 0.03 mg/L which was higher than the WHO [32] and NSDWQ [33] standards of 0.01 mg/L for drinking water. This elevation of lead content in groundwater might not be unconnected with the aged long adoption of lead compound such as tetra ethyl lead as anti-knock agent in petrol to ensure smooth burning in internal combustion engines and the presence of heavy metals in crude oil [34]. The high Pb level may also be attributed to activities of exploration and exploitation of crude oil in the study area [35].

Cr and Mn recorded low mean concentrations of 0.003 ± 0.01 mg/L and 0.02 ± 0.02 mg/L respectively, which were below the allowable limits of the regulatory bodies [32,33]. Cd recorded an average concentration of 0.04 ± 0.05 mg/L which was higher than the WHO (2011) and NSDWQ (2007) permissible limits of 0.003 mg/L [32,33]. However, there were low average values for Ni and Cu of 0.003 ± 0.01 mg/L and 0.02 ± 0.02 mg/L respectively.

Table 2. Oral reference dose for the investigated heavy metals [30]

	Pb	Cr	Mn	Cd	Ni	Cu
Oral reference dose (mg/kg/day)	0.004	0.003	0.033*	0.001	0.02	0.04*

* [31]

Table 3. Mean concentrations of heavy metals in groundwater samples

Variables	WHO (2011)	NSDWQ (2007)	Dry Season	Wet Season	Mean \pm SD
Pb(mg/L)	0.01	0.01	0.02 \pm 0.02	0.02 \pm 0.03	0.02 \pm 0.02
Cr(mg/L)	0.05	0.05	0.004 \pm 0.02	0.002 \pm 0.004	0.003 \pm 0.01
Mn(mg/L)	0.05	0.2	0.02 \pm 0.02	0.01 \pm 0.01	0.02 \pm 0.02
Cd(mg/L)	0.003	0.003	0.04 \pm 0.05	0.03 \pm 0.04	0.04 \pm 0.05
Ni(mg/L)	0.07	0.02	0.01 \pm 0.02	0.001 \pm 0.003	0.003 \pm 0.01
Cu(mg/L)	2	1	0.02 \pm 0.02	0.02 \pm 0.02	0.02 \pm 0.02

Source: Field work, 2016 and 2017

3.2 Health Risk Assessment

The potential non-carcinogenic risk assessment (toxicity) for the study area for adult, children and infant for both hand-dug wells and boreholes were estimated through the non-cancer hazard quotient (HQ) and hazard index (HI). The calculated Average daily dose (ADD) of these heavy metals for the sampling locations are shown in Table 3. ADD values (mg/kg/day) for lead in adult ranged from 1.2E-04 to 2.3E-03 for hand-dug well and from 7.2E-05 to 8.0E-04 for boreholes. The dosage of Lead in children ranged from 3.6E-04 to 7.3E-03 mg/kg/day for hand-dug wells and from 2.2E-04 to 2.4E-03 mg/kg/day for boreholes, and lead in infant varied between 5.4E-04 and 1.1E-02 mg/kg/day for hand-dug wells and between 3.2E-04 and 3.6E-03 mg/kg/day for borehole waters. Chromium ADD values (mg/kg/day) in adult varied between 2.6E-05 and 2.1E-04 for hand-dug wells and between 2.4E-05 and 2.5E-04 for boreholes. Chromium in children ranged from 7.8E-05 to 6.4E-04 for hand-dug well and from 7.2E-05 to 7.4E-04 for boreholes. Chromium in infant ranged from 1.2E-04 to 9.6E-04 for hand-dug wells and from 1.1E-04 to 1.1E-03 for borehole waters. Manganese ADD values (mg/kg/day) in adult ranged from 2.7E-05 to 2.2E-03 for hand-dug well waters and from 2.0E-05 to 8.0E-04 for boreholes. Manganese in children ranged from 8.0E-05 to 6.5E-03 for hand-dug well and from 6.0E-05 to 2.4E-03 for boreholes. Manganese in infant varied between 1.2E-04 and 9.7E-03 for hand-dug wells and between 9.0E-05 and 3.6E-03 for boreholes (Table 3).

Cadmium ADD values (mg/kg/day) in adult ranged from 8.7E-05 to 4.9E-03 for hand-dug

wells and from 1.6E-05 to 4.4E-05 for boreholes. Cadmium in children ranged from 2.6E-04 to 1.5E-02 for hand-dug wells and from 4.8E-05 to 1.3E-04 for boreholes, while Cadmium in infant varied between 3.9E-04 and 2.2E-02 for hand-dug well waters and between 7.2E-05 and 2.0E-04 for borehole waters. Cadmium ADD values corroborated with the works of Nwachukwu *et al.* [36] which reported cadmium ADD values of between 0.0194 and 0.02042 mg/kg/day for shallow hand dug wells in different water sources in rural areas in South East Nigeria. Nickel ADD values (mg/kg/day) in adult varied between 1.6E-05 and 7.2E-04 for hand-dug wells and between 1.6E-05 and 2.4E-05 for boreholes. Nickel in children ranged from 4.8E-05 to 2.2E-03 for hand-dug wells and from 4.8E-05 to 7.2E-05 for boreholes, while nickel in infant ranged from 7.2E-05 to 3.3E-03 for hand-dug wells and from 7.2E-05 to 1.1E-04 for boreholes. Copper ADD values (mg/kg/day) in adult ranged from 4.8E-05 to 1.6E-03 for hand-dug wells and from 1.6E-05 to 1.0E-03 for boreholes. Copper in children varied between 1.4E-04 and 4.7E-03 for hand-dug wells and between 4.8E-05 and 3.1E-03 for borehole waters. Copper in infant ranged from 2.2E-04 to 7.0E-03 for hand-dug wells and from 7.2E-05 to 4.7E-03 for boreholes.

3.3 Non-Cancer Hazard Quotient (HQ) and Hazard Index (HI)

The non-cancer hazard quotient (HQ) and hazard index (HI) of all six metals in the study area for adults, children and infants are presented in Table 4. The hazard quotients of lead in hand-dug wells for adults, children and infants were 5.15, 15.46 and 23.19 respectively. The hazard quotient of lead for boreholes was 2.87 for adults, 8.61 for children and 12.91 for

infants, which was greater than 1. The same applies to cadmium, with the hazard quotient of 2.62 for adults, 7.87 for children and 11.80 for infants. Thus, the HQs were greater than unity which posed a risk. For copper, the calculated HQ for adults, children and infants was 0.682,

2.045 and 3.067 respectively for hand-dug wells, which was less than 1 for adult value, and the others were higher than unity. As for manganese and nickel, hazard quotient of less than unity was estimated for adult, children and infants in hand-dug wells. This indicated that they pose no risk.

Table 4. Average Daily Dose (ADD) values in the study area

	Well				Borehole			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Adult								
Lead	7.2E-04	9.7E-04	1.2E-04	2.4E-03	4.0E-04	2.7E-04	7.2E-05	8.0E-04
Chromium	1.1E-04	7.4E-05	2.6E-05	2.1E-04	6.8E-05	7.7E-05	2.4E-05	2.5E-04
Manganese	5.8E-04	8.0E-04	2.7E-05	2.2E-03	2.6E-04	3.2E-04	2.0E-05	8.0E-04
Cadmium	1.3E-03	2.0E-03	8.7E-05	4.9E-03	3.0E-05	1.1E-05	1.6E-05	4.4E-05
Nickel	1.5E-04	2.4E-04	1.6E-05	7.2E-04	1.7E-05	3.0E-06	1.6E-05	2.4E-05
Copper	7.5E-04	6.1E-04	4.8E-05	1.6E-03	2.8E-04	4.7E-04	1.6E-05	1.0E-03
Child								
Lead	2.2E-03	2.9E-03	3.6E-04	7.3E-03	1.2E-03	8.1E-04	2.2E-04	2.4E-03
Chromium	3.4E-04	2.2E-04	7.8E-05	6.4E-04	2.0E-04	2.3E-04	7.2E-05	7.4E-04
Manganese	1.7E-03	2.4E-03	8.0E-05	6.5E-03	7.7E-04	9.7E-04	6.0E-05	2.4E-03
Cadmium	3.9E-03	6.0E-03	2.6E-04	1.5E-02	9.0E-05	3.3E-05	4.8E-05	1.3E-04
Nickel	4.5E-04	7.2E-04	4.8E-05	2.2E-03	5.2E-05	8.9E-06	4.8E-05	7.2E-05
Copper	2.2E-03	1.8E-03	1.4E-04	4.7E-03	8.4E-04	1.4E-03	4.8E-05	3.1E-03
Infant								
Lead	3.2E-03	4.3E-03	5.4E-04	1.1E-02	1.8E-03	1.2E-03	3.2E-04	3.6E-03
Chromium	5.1E-04	3.3E-04	1.2E-04	9.6E-04	3.1E-04	3.5E-04	1.1E-04	1.1E-03
Manganese	2.6E-03	3.6E-03	1.2E-04	9.7E-03	1.2E-03	1.5E-03	9.0E-05	3.6E-03
Cadmium	5.9E-03	9.0E-03	3.9E-04	2.2E-02	1.3E-04	5.0E-05	7.2E-05	2.0E-04
Nickel	6.7E-04	1.1E-03	7.2E-05	3.3E-03	7.9E-05	1.3E-05	7.2E-05	1.1E-04
Copper	3.4E-03	2.7E-03	2.2E-04	7.0E-03	1.3E-03	2.1E-03	7.2E-05	4.7E-03

SD-Standard deviation, Min-Minimum, Max-Maximum

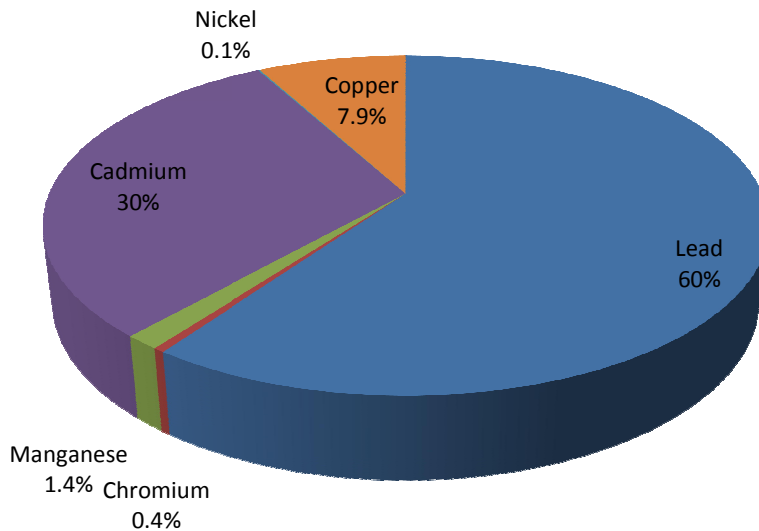


Fig. 2. Summary of % contribution of metals to non-carcinogenic health effects in well water samples

However, the hazard quotients (HQs) of Cr, Mn, Cd, Ni, and Cu in boreholes for adult, children and infants were below the recommended HQ threshold of 1.0, indicating no adverse health effects from the borehole water consumption in most of the sampling areas. In addition HQ for copper in infants (HQ=1.14) was above unity, an indication of moderate risk. Children are more susceptible to the impact of pollutants than adults (Sadovska,)[37]. The computed HI values for adults, children and infants in hand-dug wells were 8.62, 25.85 and 38.78 respectively, and 3.26, 9.77 and 14.66 respectively for borehole waters (Table 4). Like the THQ, a HI > 1 represents a potential for adverse health outcomes. However, long-term daily consumption of the groundwater in the study area could cause chronic negative health effects since the maximum HI values for ingestion were far greater than 1.0.

The contribution of individual metal HQ values to the HI was also evaluated and the results showed Pb, Cd and Cu to be dominant contaminants that together contributed over 97.9% (Fig. 1) of the HI through drinking of hand-dug well waters. The potential health risks of Cr, Mn and Ni were minimal and were in the order: 0.4%, 1.4% and 0.1% for well waters. More attention should therefore be paid to Pb, Cd and Cu pollution in urban environments. The contribution of individual metal HQ values to the HI showed Pb, Cu, and Cd to be dominant contaminants that together contributed over 98%

(Fig. 2) of the HI through drinking of borehole waters. Other metals were in the order: Cr=Mn (1% =1%), Ni (0.03%) and had minimal potential risks.

3.4 Cancer Risk Indices

The calculated cancer risk indices were compared with the United States Environmental Protection Agency (USEPA) guidelines for maximum cancer risk of $1E-06$. In general, US-EPA considers excess cancer risks that are below about 1 chance in 1,000,000 (1×10^{-6} or $1E-06$) to be so small as to be negligible, and risks above 1 in 10,000 (1×10^{-4}) to be sufficiently large that some sort of remediation is desirable. An incremental lifetime cancer risk (ILCR) greater than one in ten thousand ($ILCR > 10^{-4}$) is benchmark for gathering additional information whereas 1/1000 or greater ($ILCR > 10^{-3}$) is moderate increased risk and should be given high priority as a public health concern [37]. Cadmium, Pb and Cr are classified by the International Agency for Research on Cancer (IARC) as being carcinogenic (Tchounwou *et al.*)[38]. Chronic exposure to low doses of Cd and Pb could therefore result into many cancers (Järup,)[11]. The toxicity of chromium, on the other hand, depends on its chemical form with Cr (VI) compounds having a toxic, mutagenic and even carcinogenic nature [39]. However, Cr (III) which prevails in foodstuffs has no associated toxicity and is essential for good health in moderate intake.

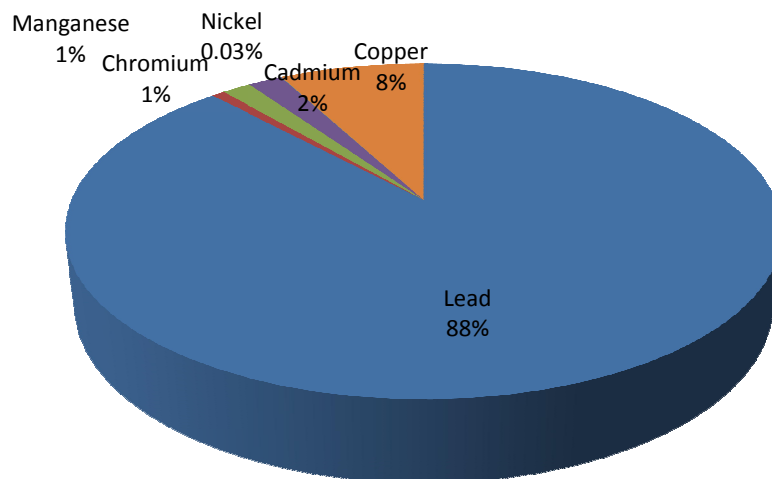


Fig. 3. Summary of % contribution of metals to non-carcinogenic health effects in borehole water samples

Table 5. HQ and HI values of metals in groundwater in the study area

	Well				Borehole			
	Mean	SD	Min	Max	Mean	SD	Min	Max
	Adult							
Lead	5.152	6.903	0.863	17.410	2.868	1.929	0.514	5.708
Chromium	0.038	0.025	0.009	0.071	0.023	0.026	0.008	0.083
Manganese	0.116	0.160	0.005	0.432	0.052	0.065	0.004	0.160
Cadmium	2.622	3.984	0.174	9.798	0.060	0.022	0.032	0.088
Nickel	0.007	0.012	0.001	0.036	0.001	0.000	0.001	0.001
Copper	0.682	0.553	0.044	1.422	0.254	0.429	0.015	0.948
HI	8.618				3.257			
	Child							
Lead	15.457	20.710	2.588	52.231	8.605	5.787	1.541	17.125
Chromium	0.113	0.074	0.026	0.214	0.068	0.077	0.024	0.248
Manganese	0.349	0.480	0.016	1.295	0.155	0.195	0.012	0.480
Cadmium	7.867	11.952	0.522	29.393	0.180	0.067	0.096	0.264
Nickel	0.022	0.036	0.002	0.108	0.003	0.000	0.002	0.004
Copper	2.045	1.660	0.131	4.267	0.761	1.286	0.044	2.844
HI	25.853				9.772			
	Infant							
Lead	23.186	31.064	3.882	78.347	12.908	8.680	2.312	25.688
Chromium	0.169	0.111	0.039	0.321	0.102	0.116	0.036	0.372
Manganese	0.524	0.720	0.024	1.942	0.232	0.292	0.018	0.719
Cadmium	11.801	17.927	0.783	44.090	0.270	0.100	0.144	0.396
Nickel	0.034	0.054	0.004	0.163	0.004	0.001	0.004	0.005
Copper	3.067	2.490	0.196	6.401	1.142	1.929	0.065	4.266
HI	38.780				14.658			

SD-Standard deviation, Min-Minimum, Max-Maximum, HI-Hazard index

Based on this guideline, some cancer risk values of lead (Pb) were within recommended standard of 1×10^{-6} or $1 \text{E-}06$ in adults for both hand-dug wells and boreholes (Table 5). For children and infants, the cancer risks were slightly higher with mean cancer value of $1.8 \text{E-}05$ in children for ingestion pathway with maximum value of $6.2 \text{E-}05$ for hand-dug wells and $1.0 \text{E-}05$ with maximum value of $2.0 \text{E-}05$ for boreholes. For infants the mean cancer risk values were estimated to be $2.8 \text{E-}05$ with maximum value of $9.3 \text{E-}05$ for hand-dug wells and $1.5 \text{E-}05$ with maximum value of $3.1 \text{E-}05$ for boreholes. It was found that the values of cancer risks for Cr were seriously above the limits for ingestion in adults, children and infants implying that these population ages are at serious risk of developing cancer in their lifetime due to Cr exposure. The mean cancer risk value of Cr was found to be $2.5 \text{E-}04$ in adults via ingestion pathway with maximum value of $4.8 \text{E-}04$ for hand-dug wells and that of boreholes was $1.5 \text{E-}04$ with maximum value of $5.6 \text{E-}04$. For children the mean cancer risk values were estimated to be $1.4 \text{E-}03$ for ingestion pathway with maximum value of $2.6 \text{E-}03$ for hand-dug wells and for boreholes, $8.4 \text{E-}04$ with maximum value of 3.0E-

03 was estimated. For infants the mean cancer risk values were estimated to be $2.1 \text{E-}03$ for ingestion pathway with maximum value of $3.9 \text{E-}03$ for hand-dug wells and $1.3 \text{E-}03$ with maximum value of $4.6 \text{E-}03$ was estimated for borehole waters.

For Cd the cancer risk values were found to be too high in some samples and should be given high priority as a public health concern. The mean cancer risk value of Cd was estimated to be $4.4 \text{E-}03$ in adults via oral pathway with maximum value of $1.6 \text{E-}02$ for hand-dug wells and that of boreholes was $1.0 \text{E-}04$ with maximum value of $1.5 \text{E-}04$. The mean cancer risk values for children were estimated to be $2.4 \text{E-}02$ for oral pathway with maximum value of $9.0 \text{E-}02$ for hand-dug wells and $5.5 \text{E-}04$ with maximum value of $8.0 \text{E-}04$ was estimated for borehole waters. For infants the mean cancer risk values were estimated to be $3.6 \text{E-}02$ for oral pathway with maximum value of $1.3 \text{E-}01$ for hand-dug wells and $8.2 \text{E-}04$ with maximum value of $1.2 \text{E-}03$ was estimated for boreholes.

The mean cancer risk value of nickel (Ni) was found to be $6.9 \text{E-}05$ in adults via oral pathway

with maximum value of 3.3E-04 for hand-dug wells and boreholes value was 8.1E-06 with maximum value of 1.1E-05. The mean cancer risk values for children were estimated to be 3.8E-04 for oral pathway with maximum value of 1.8E-03 for hand-dug wells and 4.4E-05 with

maximum value of 6.0E-05 was estimated for borehole waters. For infants the mean cancer risk values were estimated to be 5.7E-04 for oral pathway with maximum value of 2.7E-03 for hand-dug wells and 6.6E-05 with maximum value of 9.1E-05 was estimated for boreholes.

Table 6. Cancer risk values of metals in groundwater in the study area

	Well				Borehole			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Adult								
Lead	3.4E-06	4.5E-06	5.7E-07	1.1E-05	1.9E-06	1.3E-06	3.4E-07	3.7E-06
Chromium	2.5E-04	1.7E-04	5.9E-05	4.8E-04	1.5E-04	1.7E-04	5.4E-05	5.6E-04
Cadmium	4.4E-03	6.7E-03	2.9E-04	1.6E-02	1.0E-04	3.7E-05	5.4E-05	1.5E-04
Nickel	6.9E-05	1.1E-04	7.4E-06	3.3E-04	8.1E-06	1.4E-06	7.4E-06	1.1E-05
CR	4.7E-03				2.6E-04			
Child								
Lead	1.8E-05	2.5E-05	3.1E-06	6.2E-05	1.0E-05	6.9E-06	1.8E-06	2.0E-05
Chromium	1.4E-03	9.1E-04	3.2E-04	2.6E-03	8.4E-04	9.5E-04	2.9E-04	3.0E-03
Cadmium	2.4E-02	3.6E-02	1.6E-03	9.0E-02	5.5E-04	2.0E-04	2.9E-04	8.0E-04
Nickel	3.8E-04	6.0E-04	4.0E-05	1.8E-03	4.4E-05	7.5E-06	4.0E-05	6.0E-05
CR	2.6E-02				1.4E-03			
Infant								
Lead	2.8E-05	3.7E-05	4.6E-06	9.3E-05	1.5E-05	1.0E-05	2.8E-06	3.1E-05
Chromium	2.1E-03	1.4E-03	4.8E-04	3.9E-03	1.3E-03	1.4E-03	4.4E-04	4.6E-03
Cadmium	3.6E-02	5.5E-02	2.4E-03	1.3E-01	8.2E-04	3.0E-04	4.4E-04	1.2E-03
Nickel	5.7E-04	9.1E-04	6.0E-05	2.7E-03	6.6E-05	1.1E-05	6.0E-05	9.1E-05
CR	3.9E-02				2.2E-03			

SD-Standard deviation, Min-Minimum, Max-Maximum, CR-Cancer risk

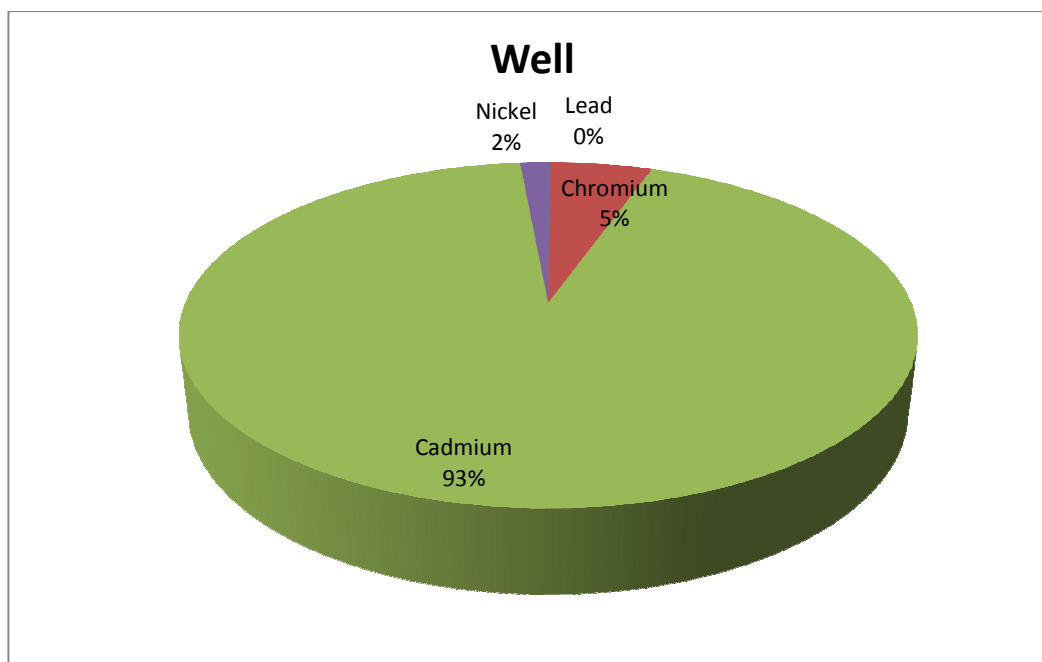


Fig. 4. Summary of % contribution of cancer risk of metals in well water samples

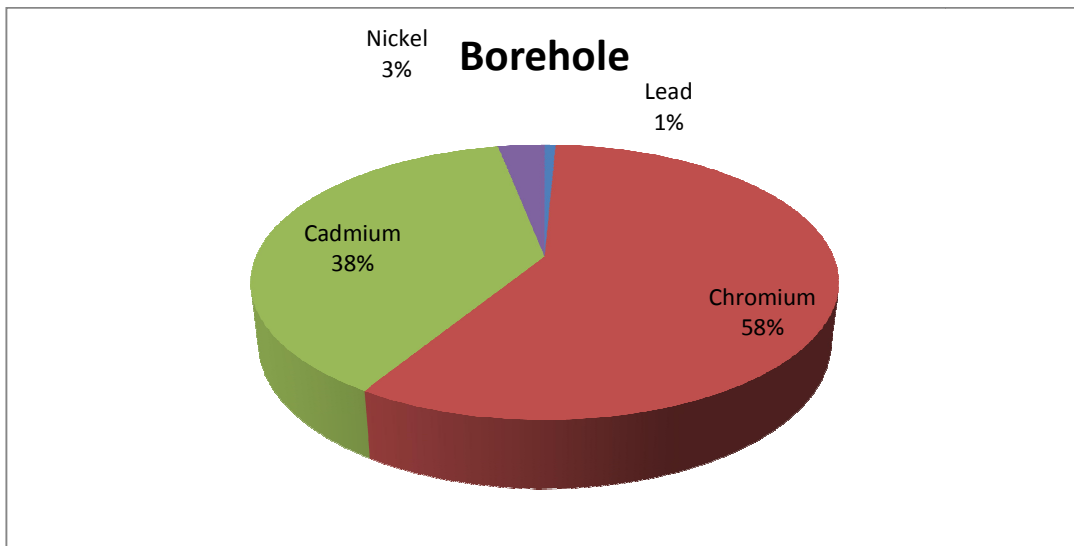


Fig. 5. Summary of % contribution of cancer risk of metals in borehole water samples

The total excess lifetime cancer risk was found to be $4.7E-03$, $2.6E-02$ and $3.9E-02$ for adults, children and infants respectively in hand-dug well water samples. For borehole the total excess lifetime cancer risk was estimated to be $2.6E-04$, $1.4E-03$ and $2.2E-03$ for adults, children and infants respectively (Table 5). The total cancer risk values due to ingestion pathway in adults, children and infants were found to be above the requirement and were majorly contributed by Pb, Cr and Cd in adults, children and infants. The percentage contribution of cancer risk of metals in well water samples showed Cd to be dominant contaminant that contributed 93% (Fig. 3), followed by Cr, Ni and Pb with percentage distributions of 5%, 2% and 0% respectively. In borehole water samples, Cd and Cr were dominant contaminants that together contributed over 96% (Fig. 4). Nickel (Ni) and Pb contributed 3% and 1% respectively with minimal cancer risk potentials.

4. CONCLUSION

The hazards quotient (HQ) of Cr, Mn and Ni were below 1.0 indicating no threat to the water consumers, while the HQ values for Pb, Cd and Cu were above 1.0 indicating risk to the human health. The hazard index value was found to be greater than 1.0, indicating noncarcinogenic adverse effects. This study also established that infants were at the greatest risk of noncarcinogenic effects despite their low body weight. The estimated Lifetime of Carcinogenic Risks (LTCR) for Pb, Cr, Cd and Ni exceeded the

predicted lifetime risk for carcinogens of 10^{-6} from ingestion pathway. Furthermore, there were more appreciable risks from Cr and Cd in the groundwater as LTCR value in most sites were $>10^{-4}$. The high LTCR should be given high priority as public health is concerned. This study indicated possible non-carcinogenic and carcinogenic human health hazard from groundwater consumption in study area through oral consumption. Based on the results of the study, the authors made the following recommendations:

1. Groundwater sources of the towns should be treated for Pb, Cd and Cr pollutants, using the extraction treatment and re-injection (ETR) technology; recirculating well technology (RWT) and natural attenuation methods to remove heavy metals pollutants for public health reasons.
2. Regular flushing of boreholes for removal of mineralized deposits and regular monitoring and hydrogeochemical studies is advocated to detect future deterioration of water quality in the study area.
3. The hand dug wells should be protected with a concrete ring to avoid storm waters and other leachates from dumpsites and other industrial waste.

CONSENT

All authors declare that 'written informed consent was obtained from all individual participants (or

other approved parties) for publication of this case report and accompanying images.

ETHICAL APPROVAL

All authors hereby declare that all experiments have been examined and approved by the appropriate ethics committee and have therefore been performed in accordance with the ethical standards laid down in the 1964 Declaration of Helsinki.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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