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# Health Risk Assessment of Heavy Metal Contamination of Groundwater Around Nnewi Industrial Area, Anambra State, Nigeria

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**Abstract:** The influence of water quality from boreholes situated around the Nnewi industrial area was evaluated by assessing the heavy metal concentrations and health risks associated with human exposure. Water samples were collected from 16 different boreholes around eight industries at a monthly interval from May – October 2019 and November 2019 – April 2020 to cover the rainy and dry seasons, respectively. Water samples were analyzed for copper (Cu), lead (Pb), iron (Fe), zinc (Zn), chromium (Cr), and arsenic (As) using atomic absorption spectrophotometer (AAS). The results were compared with the World Health Organization (WHO) standards. Data obtained for both seasons indicate Cu had a mean value of (0.268±0.136 mg/L), Pb (0.014±0.013 mg/L), Fe (0.119±0.133 mg/L), Zn (0.572±0.220 mg/L), Cr (0.051±0.011 mg/L), and As (0.013±0.001 mg/L) respectively. All the heavy metal concentrations of the sampled water were within their various WHO permissible limits except As, Cr and Pb. The pollution index of As, Cr and Pb were greater than 1, showing heavy contamination of the water. Carcinogenic risk assessment of water via ingestion and dermal route for Cr and As were above the recommended safe limit of $1\times10^{-6}$ which posed a cancer risk. The results show that borehole waters were contaminated with heavy metals in both seasons. It is, therefore, recommended that borehole water from the study areas should be treated before being used for various domestic purposes.

**Keywords:** Health Risk, Heavy Metals, Water Quality, Contamination, Borehole Water

## 1. Introduction

Groundwater is the major source of water in the Nnewi urban area but due to the high rate of waste disposal in different forms into water bodies, it contaminates other water sources. However, solid wastes and wastewater from residential and industrial areas find their way into the groundwater through leaching [1].

Borehole water is potable and accessible; it is sometimes free from unpleasant odours and has a good taste. Although borehole water is safe for consumption, many researchers have shown that borehole waters are susceptible to contamination [2]. The climate, anthropogenic activities and geology of the aquifer are factors that affect the borehole water quality [3]. Due to rapid growth in population and industrialization, the use of borehole water sources has increased in many countries. Borehole water is used for drinking, bathing, washing, cooking, industrial processes and irrigation. In Nigeria, the use of borehole waters is very common [4]. It serves as the most important source of water supply which is potable and accessible [5, 6]. This is because it possesses a purification capacity [7]. Groundwaters are contaminated through the leaching of chemicals from industrial activities, seepage from dumpsites and soil erosion from underground leachate. The degree of contamination may be a result of the structures of the topsoil, borehole water depth, percolation rate and the precipitation pattern [8]. The quality of water is unknown to many communities that depend on borehole water sources;

they assume that borehole water is potable.

Borehole water may be contaminated by the animal, human and industrial wastes in the aquifer [9]. This could be through the discharge of domestic and industrial wastewater and the grazing of animals [10]. Most of the borehole water is not properly maintained; it takes some time to notice when the water is contaminated due to its invisible nature. The water quality cannot be restored immediately by stopping the contaminants from the source [11]. In peri-urban and rural areas, most of the borehole water supplies are not properly treated because; it is very expensive to treat [12]. The use of unknown-quality borehole water sources might put the users at risk of water-borne infections [4].

Heavy metals can be absorbed into soils and water bodies and from there, enter the human body through consumption and dermal exposure and thus endanger human health [13]. Heavy metals such as Pb, As and Cr are very toxic when their threshold values are exceeded, and can potentially lead to cancer in the human body [14]. Heavy metal can cause damage to the brain, gastrointestinal abnormalities, dermatitis, and death in humans [15–17]. Heavy metal contamination of underground water and the potential risks associated with the pollution of such waters have been investigated by Akoto et al. [14]. Health-associated risks caused by using borehole water call for a complete assessment of the effect of industrial activities on the water bodies [18]. To the best of our knowledge, no significant health risk assessments have been reported around the Nnewi industrial location of Anambra State, Nigeria. Children and adults in the community have often been reported to be sick with typhoid, diarrhea, cough, chest pains, itchy skin, and tuberculosis. This is also the case with heavy metal contamination, which means that their various risks are lacking. Cancer and non–cancer health risk assessments were estimated in the study through dermal and ingestion routes. Given the foregoing, it is vital to evaluate the levels of heavy metal pollution and their effect on human health-related risks for adults and children in the Nnewi urban area. It is for this reason that the impact of industrial activities on heavy metal contamination of borehole water quality and their health risk was studied within the Nnewi industrial area in this research. The findings of this work will help to mitigate the risks posed by exposure to heavy metals and help government institutions to determine better ways of improving waste disposal in the environment.

# 2. Materials and Methods

### 2.1. Study Area

Nnewi is one of the cities in Anambra State, Nigeria, with Nnewi North comprised of four autonomous communities, which are Umudim, Nnewichi, Uruagu and Otolo. According to the census 2006, it has a population of about 391,227 [19]. Nnewi urban area lies between latitudes of 6° 01' and 6° 57' N and longitudes of 6° 45' and 6° 55' E. The annual rainfall in the area is about 2000 mm [20]. The famous Nkwo market sited at Uruagu is known for the diversity of goods and services it offers. The Nnamdi Azikiwe University Teaching Hospital is located at Nnewi Ichi. Most of the major industries are located in Umudim and Otolo Nnewi.

The city is well known for its high industrialization, manufacture of automobiles and fabrication of spare parts. It is also home to some food processing industries, that produce vegetable oil, engine oil, plastic tanks, jerry cans, soaps etc. The wastewater from this industry is channelled through a drainage system that empties into the stream. The areas of study involved borehole water sites around eight industries in Nnewi urban area.

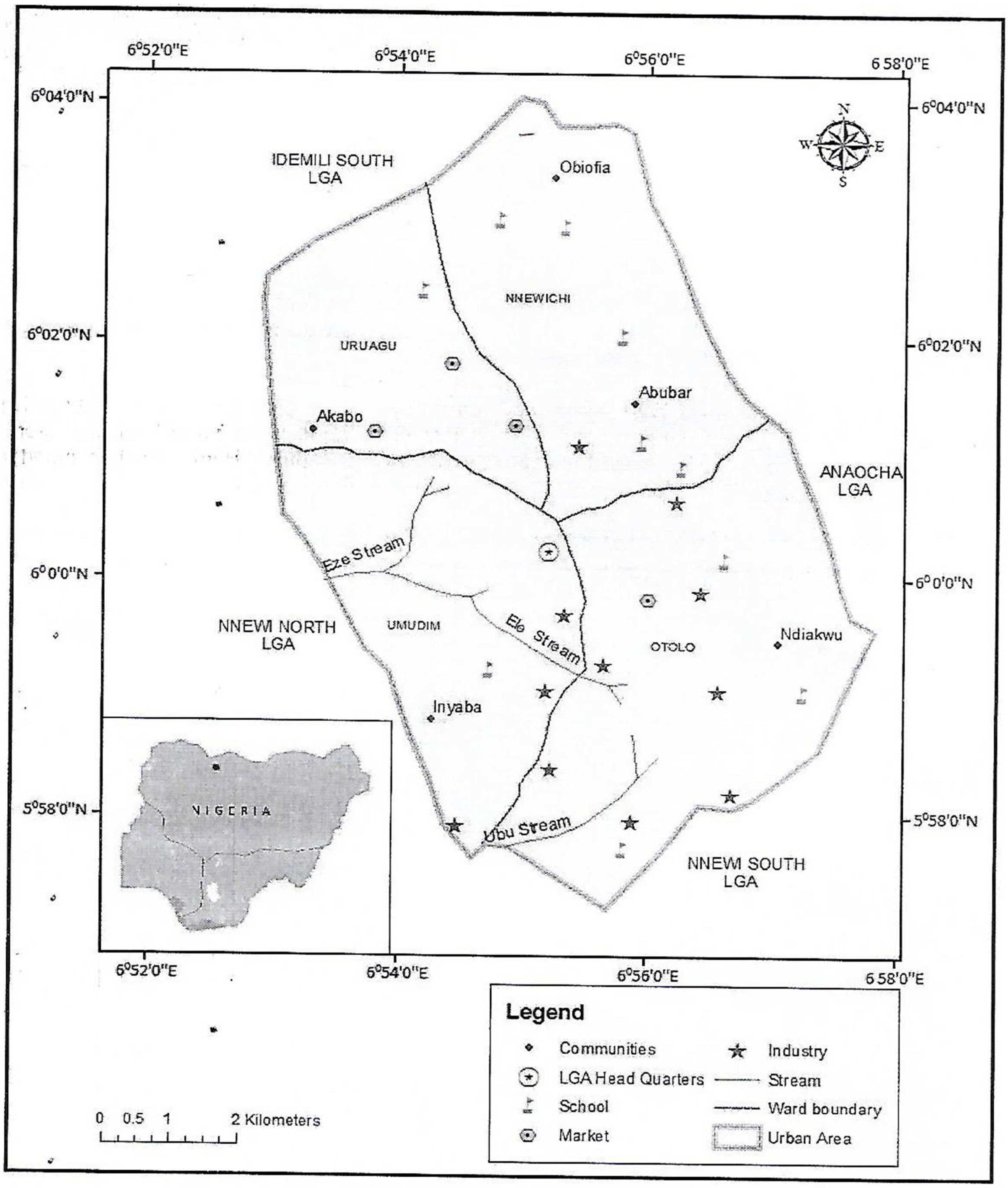
### 2.2. Sampling of Borehole Water

The various industries were located on the map of the Nnewi North Local Government Area (Figure 1). Water samples were collected from 16 different borehole sampling points around eight industries (two borehole water samples around each industry) in Nnewi urban area. The sampling descriptions adopt a code for each borehole waters sampling location of the borehole (Table 1). The water samples were collected at one-month intervals for twelve consecutive months, both in the rainy and dry seasons. Sampling was done between 8 am – 10 am each day. A two-litre container (plastic) with a screw cap was used to collect water samples from each sampling point. The container was washed thoroughly with a little detergent, rinsed with HCl and finally rinsed three times with distilled water. At the point of sample collection, the tap was allowed to run for 1 minute. The plastic containers were rinsed several times with the target samples before filling them with water samples. Thereafter, the containers were properly labelled. Samples collected were placed inside an ice chest and then transported to the research laboratory for further analysis. All the samples for heavy metal analysis were stabilized with 1ml concentrated HCl in each container to avoid micro-organisms affecting their concentrations and then stored in the laboratory. Distilled water and high pure (analytical reagent grade) chemicals were used to prepare the solution for heavy metal analysis. Borehole sampling sites were selected based on their closeness to the industries. The descriptions of sampling locations are presented in Table 1.

***Table 1.*** *Descriptions of sampling locations.*

| Sample Codes | Identification of groundwater | Sampling locations |
|---|---|---|
| 1 | Borehole | A – Z petroleum product limited Umudim Nnewi |
| 2 | Borehole | A – Z petroleum product limited Umudim Nnewi |
| 3 | Borehole | RIMCO Nigeria limited Umudim Nnewi |
| 4 | Borehole | RIMCO Nigeria limited Umudim Nnewi |
| 5 | Borehole | Tummy-Tummy foods Ind. Ltd Umudim Nnewi |

| Sample Codes | Identification of groundwater | Sampling locations |
|---|---|---|
| 6 | Borehole | Tummy-Tummy foods Ind. Ltd Umudim Nnewi |
| 7 | Borehole | C. O. Prince Aluminum Nnewi-Ichi |
| 8 | Borehole | C. O. Prince Aluminum Nnewi-Ichi |
| 9 | Borehole | Innoson Vehicle Manufacturing Co. Ltd Umudim Nnewi |
| 10 | Borehole | Innoson Vehicle Manufacturing Co. Ltd Umudim Nnewi |
| 11 | Borehole | Ibeto Petrochemical Industries Ltd Otolo Nnewi |
| 12 | Borehole | Ibeto Petrochemical Industries Ltd Otolo Nnewi |
| 13 | Borehole | Jimex Industries Nigeria Ltd Otolo |
| 14 | Borehole | Jimex Industries Nigeria Ltd Otolo |
| 15 | Borehole | Cutix Company Otolo Nnewi |
| 16 | Borehole | Cutix Company Otolo Nnewi |




Source: Ministry of Commerce and Industry Anambra State, Nigeria (2013).

***Figure 1.*** *Map of Nnewi North LGA Showing Location of Industries.*

### 2.3. Samples Preparation and Heavy Metal Analyses

Samples were digested with concentrated $HNO_3$ before analysis using AAS (Model WFX 210). The borehole water sample was properly shaken and 100mL of each sample was transferred into a 250mL Pyrex beaker. 10 ml concentrated $HNO_3$ was added. The solution was heated gently and then evaporated on a hot plate to the lowest possible volume (about 20mL). Then, another 5mL of concentrated $HNO_3$ was added followed by the addition of 5mL $H_2O_2$. The beaker was covered with a watch glass immediately. The mixture was heated continuously until white fumes evolved and a clear solution was obtained. The beaker with its content was allowed to cool at room temperature. The reason for the digestion before analysis was to destroy organic matter, removes interfering ions and brings metallic compounds in suspension to the solution [21]. After digestion, some quantity of distilled water was added. After cooling, the solution was then filtered through Whatman paper No 42. The filtrates were transferred into a 100ml volumetric flask and made up to the mark with distilled water and then mixed well. The solution was then transferred into a polypropylene bottle, ready for AAS analysis.

Atomic absorption spectrophotometer (AAS) was used to determine heavy metals from the digested water samples. For individual metal concentration determinations, the respective hollow cathode lamp was applied accordingly. An incision width of 0.4 nm was used with corresponding wavelengths of elements of 324.8, 283.3, 248.3, 213.8, 253.7, and 193.7 nm for Cu, Pb, Fe, Zn, Cr, and As, respectively. All the chemicals and reagents used were of certified analytical grade and procured from Sigma-Aldrich.

A 1000 mg/L stock solution of 2% $HNO_3$ was used to prepare a standard solution and calibration standards for the experiment. For each heavy metal, two standard solutions were prepared from the stock solution.

The quality of the analytical data was guaranteed by implementing standard quality assurance procedures. Each sample was analysed in triplicates. After every 10 samples, a certified standard and a blank solution were run to check for contamination and drift.

Cu, Pb, Fe, Zn, Cr and As determination and their instrumentation protocols were applied as per standard guidelines [22]. Every batch of samples was prepared similarly to the reagent blanks. Analysis of a mixture of metal standards (Cu, Pb, Fe, Zn, Cr and As) prepared from their stock solutions was also carried out as part of the analytical data quality assurance. Evaluation of the precision and accuracy of the analytical instrument was performed by triplicate standard analysis. The analysis of each heavy metal was done in triplicate and mean values were recorded.

### 2.4. Statistical Analyses

Data were analysed using a statistical package (SPSS 21.0). A Pearson correlation matrix was used to measure the strength of the linear association relationship between variables in water. Microsoft Office Excel 2007 was used for the computation of the pollution indices.

### 2.5. Health Risk Assessment of Borehole Water Samples

Interviews were conducted with some households leaving around Nnewi industrial area. Information concerning their ages, sources of water, how they dispose of their waste, treatment and protect their water and other health-related issues. Most of the people involved in the interview use borehole water for drinking, bathing, cooking and washing.

Health risk indicators such as hazard index (HI), hazard quotient (HQ) and chronic daily intake (CDI) were calculated based on equations (1 – 5) respectively as shown below, [3, 23–26].

The health risk assessment caused by the ingestion and dermal exposure of metal-contaminated water from the borehole water samples was assessed using equations (1) and (2) [25, 26].

$$\mathrm{CDI_{ing}} = \frac{\mathrm{C \times IR \times ED \times EF}}{\mathrm{BW \times AT}} \times \mathrm{CF} \tag{1}$$

$$\mathrm{CDI_{derm}} = \frac{\mathrm{C \times SA \times SAF \times DAF \times ED \times EF}}{\mathrm{BW \times AT}} \times \mathrm{CF} \tag{2}$$

Where $\mathrm{CDI_{derm}}$ and $\mathrm{CDI_{ing}}$ represent chronic daily intake of dermal and ingestion contact of the heavy metals of the borehole water [27–29]. The exposure parameters used to estimate the risks are shown in Table 2.

C means the concentration of each metal in the borehole water (mg/L), ED means exposure duration (years), IR means ingestion rate (L/day), and AT means the average time of life expectancy (days). EF means exposure frequency (day/year). BW means body weight (Kg). 0.78L for child and 2.5L for adult (L/day) was the standard amount of water intake used [30]. EF of 350 days per year was also used [25]. 15 kg for child and 80 kg for adult was the average body weight used.

#### 2.5.1. Non-Carcinogenic Risk Assessment

The non-carcinogenic risk was estimated using the HQ [25]. For non-carcinogenic risks, the HQ was evaluated using Equations (3) and (4) [31]. HI was evaluated using Equation (5). If the HQ or HI < 1, the exposed population is not at risk. The HQ or HI ≥ 1, the exposed population is at risk [25].

$$\mathrm{HQ} = \frac{\mathrm{CDI_{ing}}}{\mathrm{RfD}} \tag{3}$$

$$\mathrm{HQ} = \frac{\mathrm{CDI_{derm}}}{\mathrm{RfD}} \tag{4}$$

$$\mathrm{HI} = \sum \mathrm{HQs} \tag{5}$$

Where, $\mathrm{CDI_{derm}}$ and $\mathrm{CDI_{ing}}$ represent chronic daily intake of dermal and ingestion contact of the heavy metals of the borehole water sample. RfD stands for the reference dose of each heavy metal as listed in Table 3.

#### 2.5.2. Carcinogenic Risk (CR) Assessment

The heavy metal concentration of the water samples was used to examine the rate at which cancer developed in each individual over their lifetime [25, 26, 28]. The cancer risks (CR) and HI in the borehole water samples were evaluated using Equations (6 and 7) [25, 26, 32].

$$CR = CDI_{ing} \times SF \quad (6)$$

$$CR = CDI_{derm} \times SF \quad (7)$$

$$HI = \sum CDIs \quad (8)$$

Where CR means cancer risk, CDI means chronic daily intake and SF means cancer slope factor as listed in Table 3. USEPA [25] recommends that a CR value less than $1 \times 10^{-6}$ is regarded as negligible whereas a CR that exceeds $1 \times 10^{-4}$ is likely to be harmful to human health.

***Table 2.*** *Health risk assessment of heavy metal parameters used for different exposure pathways of borehole water samples.*

| Parameters | Unit | Adult | Child | References |
|---|---|---|---|---|
| Concentration of metal (C) | mg/L | - | - | - |
| Ingestion rate (IR) | L/day | 2.5 | 0.78 | [25, 26] |
| Body weight (BW) | Kg | 80 | 15 | [25, 29] |
| Exposure frequency (EF) | days/year | 350 | 350 | [25, 26] |
| Average time (AT) non-cancer | days | 7300 | 2190 | [25, 26] |
| Average time (AT) cancer | days | 25550 | 25550 | [25, 26] |
| Surface area (SA) | $cm^2$ | 6032 | 2373 | [25, 26] |
| Dermal absorption factor (DAF) | - | 0.001 | 0.001 | [25, 26] |
| Skin adherence factor (SAF) | $mg/cm^2$ | 0.07 | 0.2 | [25, 26] |
| Exposure duration (ED) | Years | 20 | 6 | [25, 26] |
| Conversion factor (CF) | | 1E-06 | 1E-06 | [25, 26] |

***Table 3.*** *Reference dose (RfD) and Cancer Slope Factor (CSF) for non-carcinogenic and carcinogenic risks of some heavy metals.*

| Heavy metal | Reference doses (RfD) | | Slope factors (SF) | | References |
|---|---|---|---|---|---|
| | Dermal | Ingestion | Dermal | Ingestion | |
| Cu (mg/L) | 0.012 | 0.04 | – | – | [25, 26] |
| Pb (mg/L) | 0.000524 | 0.0014 | – | 0.0085 | [25, 26] |
| Fe (mg/L) | 0.7 | 0.7 | – | – | [25, 26] |
| Zn (mg/L) | 0.06 | 0.3 | – | – | [25, 26] |
| Cr (mg/L) | 0.003 | 0.003 | 2 | 0.5 | [25, 26] |
| As (mg/L) | 0.000123 | 0.0003 | 3.66 | 1.5 | [25, 26] |

### *2.6. Pollution Index (PI)*

PI is the ratio of the concentration of each parameter against the standard given by the World Health Organization. It provides information on the relative pollution contributed by each sample. When the critical value is greater than 1.0, it shows a significant degree of pollution whereas a value less than 1.0 indicates no pollution [33]. PI was calculated using equation (9):

$$PI = \frac{\text{Concentration}}{\text{Standard}} \quad (9)$$

### *2.7. Correlation Analysis*

Pearson's correlation analysis was used at 0.01 or 0.05 levels to evaluate heavy metal results obtained from the borehole water samples. A negative correlation was an indication of an inverse relationship between variables whereas a positive correlation was an indication of a direct relationship between variables [34].

## 3. Results and Discussion

### *3.1. Concentration of Heavy Metals*

Statistical analyses of heavy metal concentrations of sampled borehole water are presented in Tables 4 and 5.

From Table 4, the arsenic concentration of sampled borehole water during the rainy season varied from 0.01 – 0.02mg/L with the mean value of 0.013 ± 0.001mg/L. As values obtained were above the WHO recommended limit of 0.01mg/L. Similar high values of arsenic were reported by Longe and Enekwechi; Ali and Ahmad [35, 36]. The high values of As might be associated with heavy rainfall during the rainy season which encouraged the leaching of pollutants into the groundwater [21, 37]. The iron (Fe) values of borehole water samples varied from 0.00 – 0.35mg/L with the mean value of 0.124± 0.086 mg/L. Fe values were below the WHO [38] permissible limit. Zn values in sampled borehole water range from 0.51 – 1.48mg/L with the mean value of 0.697± 0.234 mg/L. Zn values were below the WHO [38] permissible limit of 3mg/L. The values of Cr in borehole water samples varied from 0.00 – 0.09mg/L with the mean value of 0.057± 0.008 mg/L. Most of the values of Cr were above the WHO recommended limit of 0.05mg/L. Long-time exposure to chromium can cause liver, kidney and nerve tissue damage [39].

The comparative data analyses of sampled borehole water showed that Pb, Cr, and As had a high mean concentration in the rainy season in respective order of Cr > Pb >As; with Cr being 0.057±0.008 mg/L, Pb being 0.015 ± 0.018mg/L and As being 0.013 ± 0.001 mg/L which had a coefficient variation of 13.65%, 121.21% and 10.65% respectively. Then Cu, Fe and Zn had a low mean concentration in the rainy season in respective order of Zn >Cu > Fe; with Zn being 0.697±0.234 mg/L, Cu being 0.281±0.157 mg/L and Fe being 0.124±0.086 mg/L which had a coefficient variation of 33.54%, 55.90% and 69.02% respectively. The increase in values of coefficient variation and mean concentration of sampled borehole water during the rainy season is a response to various factors like physiological factors, depth and age [40]. High concentrations of these metals show that sampled borehole waters were contaminated in the rainy season. Pollution of this borehole water might be due to the heavy discharge of effluent from the industries which entered the underground via leaching [41].

***Table 4.*** *Statistical analysis of heavy metal concentrations of sampled borehole water of the rainy season.*

| Parameter (mg/L) | Mean | Standard Deviation | Variance | Coefficient Variation (%) | Range | WHO standard [38] |
|---|---|---|---|---|---|---|
| Cu (mg/L) | 0.281 | 0.157 | 0.025 | 55.90 | 0.11 – 0.81 | 2 |
| Pb (mg/L) | 0.015 | 0.018 | 0.00034 | 121.21 | 0.00 – 0.09 | 0.01 |
| Fe (mg/L) | 0.124 | 0.086 | 0.007 | 69.02 | 0.00 – 0.35 | 0.3 |
| Zn (mg/L) | 0.697 | 0.234 | 0.055 | 33.54 | 0.51 – 1.48 | 3 |
| Cr (mg/L) | 0.057 | 0.008 | 0.00006 | 13.65 | 0.00 – 0.09 | 0.05 |
| As (mg/L) | 0.013 | 0.001 | 0.000002 | 10.65 | 0.01 – 0.02 | 0.01 |

***Table 5.*** *Statistical analyses of heavy metal concentrations of sampled borehole water of the dry season.*

| Parameter (mg/L) | Mean | Standard Deviation | Variance | Coefficient Variation (%) | Range | WHO Standard [38] |
|---|---|---|---|---|---|---|
| Cu (mg/L) | 0.255 | 0.110 | 0.012 | 43.33 | 0.04 – 0.58 | 2 |
| Pb (mg/L) | 0.013 | 0.002 | 0.000 | 18.68 | 0.01 – 0.02 | 0.01 |
| Fe (mg/L) | 0.114 | 0.168 | 0.028 | 146.61 | 0.00 – 0.83 | 0.3 |
| Zn (mg/L) | 0.448 | 0.108 | 0.012 | 24.18 | 0.26 – 0.76 | 3 |
| Cr (mg/L) | 0.042 | 0.006 | 0.000 | 14.46 | 0.01 – 0.05 | 0.05 |
| As (mg/L) | 0.012 | 0.001 | 0.000 | 6.18 | 0.01– 0.013 | 0.01 |

In the dry season, the mean concentration of the heavy metals analyzed followed the descending order: Zn > Cu > Fe > Cr > Pb > As, with the mean values of 0.448 (mg/L) > 0.255 (mg/L) > 0.114 (mg/L) > 0.042 (mg/L) > 0.013 (mg/L) > 0.012 (mg/L) respectively (Table 5). The mean value of Cu, Fe, Zn and Cr were within the WHO [38] recommended limit. Moreover, the mean value of As (0.012mg/L) and Pb (0.013mg/L) were above the WHO [38] recommended limit. Values of heavy metals above the recommended safe limit can cause serious health risks like cancer and liver problem [42, 43].

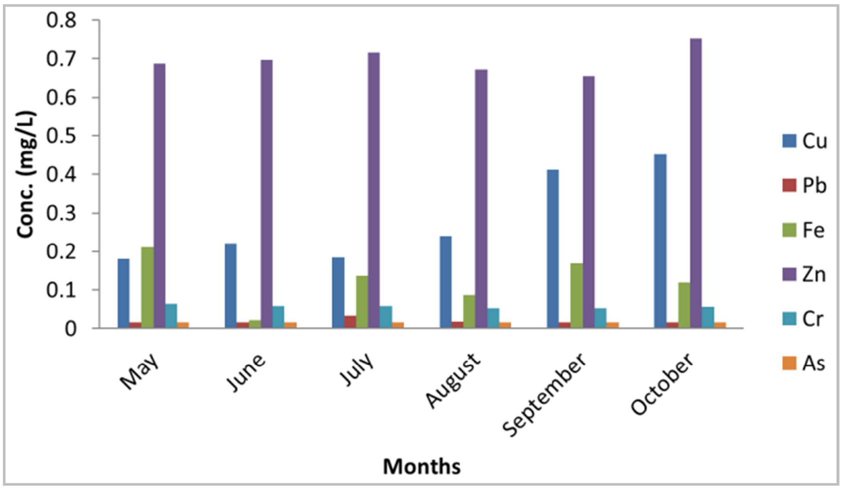



***Figure 2.*** *Monthly mean distribution of heavy metal concentration of sampled borehole water of the rainy season.*

The least concentration of 0.052 mg/L for chromium was observed in August whereas the highest concentration of 0.064 mg/L was observed in May (Figure 2). Chromium had an average value of 0.058 mg/L in the rainy season which was slightly above WHO [38] recommended limit of 0.05mg/L. High values of Cr in these sampled borehole water might be an indication of high infiltration of leachates and water from dumpsites and landfill as a result of heavy rainfall [18]. Moreover, high values of Cr in the sampled borehole water might also be a result of the heavy disposal of metal products around the industrial area [1]. Consumption of water with a high Cr concentration above 0.05mg/L may cause gastrointestinal cancer for long-term exposure [12].

Iron had the least concentration of 0.022 mg/L which was observed in June whereas the highest concentration of 0.211 mg/L was observed in May (Table 7). In the rainy season, Fe had an average value of 0.124 mg/L which was within the WHO [38] acceptable limit of 0.3mg/L.

The monthly mean values of Cu in all the sampled borehole water of the rainy season ranged from 0.181 – 0.452 mg/L. The Cu values were within the WHO-recommended limits of 0 – 2 mg/L [38]. Consumption of water below 1.0mg/L concentration of Cu will cause no adverse health effects [44].

Pb had the least value of 0.008 mg/L in May whereas the highest value of 0.034 mg/L was observed in July. Pb had an average value of 0.015mg/L. Most of the mean values of Pb obtained were above the WHO [38] standard of 0.01mg/L. The high values of Pb might be a result of a large volume of industrial wastes generated from the industries, which entered the underground via leaching [1]. A similar high value of Pb was reported by Ali and Ahmad [36]. Exposure to high concentration Pb may cause high blood pressure, anaemia, kidney and brain damage especially in adults [42, 45].

Zinc (Zn) had the least value of 0.654 mg/L in September whereas the highest value of 0.752 mg/L was observed in October with an average value of 0.697mg/L. All the boreholes water samples for Zn complied with the recommended limit of 3mg/L and 5mg/L respectively set by the WHO; NIS [38, 46]. There is no health effect for the consumption of water with low Zn concentration because zinc has antioxidant properties that protect human beings against accelerated ageing of skin and muscles [47].

Arsenic (As) had the least value of 0.013mg/L in June, July and August while the highest value of 0.014mg/L in May, September and October. The average value of As was 0.013mg/L. As values were above the WHO [38] recommended limit of 0.01mg/L. Similar high values of As were also reported by Longe and Enekwechi; Ali and Ahmad [35, 36]. The high values of As obtained might be a result of heavy rainfall in the rainy season which encouraged the leaching of the pollutants in the groundwater and seepage from dumpsites [21].

Borehole water samples were slightly contaminated with heavy metals such as; As, Cr and Pb during the rainy season with values that exceeded the recommended limits of the WHO; NIS [38, 46]. Therefore, sampled borehole waters in the rainy season are not potable.

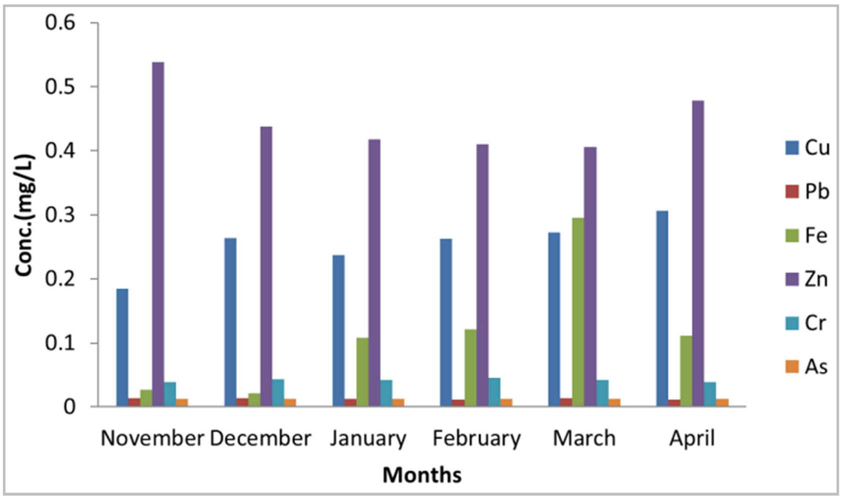



***Figure 3.*** *Monthly mean distribution of heavy metal concentration of sampled borehole water of the dry season.*

From Figure 3, the minimum concentration of Pb in the dry season was 0.011mg/L which was observed in February and April whereas maximum concentrations of 0.014mg/L were observed in November and December, respectively. Pb values of all the sampled borehole water were above the WHO; NIS [38, 46] acceptable limit of 0.01 mg/L. The values of Pb obtained were similar to that of Faisal et al.[48]. Environmental Protection Agency recommended level of Pb is zero due to its toxic nature [49]. High values of Pb in all the sampled borehole water at different locations might be due to the heavy discharge of lead-rich wastewater from the nearby paint industry. The wastewater deposited into the soil surface found its way into the underground via leaching [50]. The high concentration of Pb in water above the WHO recommended limit might cause hypertension, and tissue and organ damage in humans [30, 51]. Chromium concentrations had an average value of 0.042 mg/L (Figure 3). The Cr values were within the WHO permissible limit of 0.05 mg/L and above the NIS permissible limit of 0.01 mg/L. Cr values obtained were similar to Buridi and Gedala [52]. The health implication of excessive exposure to chromium causes lung cancer, kidney damage and high blood pressure. Arsenic concentrations had an average value of 0.012 mg/L in the dry season. The values of As were above WHO [38] acceptable limit of 0.01mg/L. In the dry season, the mean values of the heavy metals analyzed in sampled borehole water followed the descending order; Zn > Cu > Fe > Cr > Pb > As. Most of the sampled borehole waters were contaminated with heavy metals like; Pb and As which were above the WHO [38] permissible limit. The study revealed that borehole water samples were more contaminated in the rainy season than in the dry season. These might be a result of the high infiltration of water from landfill via leaching due to heavy rainfall. Therefore, the waters from these boreholes are not potable.

### *3.2. Metal Pollution Index*

***Table 6.*** *Computation of pollution index of sampled borehole waters in rainy and dry seasons.*

| Parameters (mg/L) | Mean Rainy season | Mean Dry season | Allowable limit (mg/L) WHO [38] | PI (Rainy season) | PI (Dry season) |
|---|---|---|---|---|---|
| Cu (mg/L) | 0.281 | 0.255 | 2 | 0.141 | 0.128 |
| Pb (mg/L) | 0.015 | 0.013 | 0.01 | 1.500 | 1.300 |
| Fe (mg/L) | 0.124 | 0.114 | 0.3 | 0.413 | 0.380 |
| Zn (mg/L) | 0.697 | 0.448 | 3 | 0.232 | 0.149 |
| Cr (mg/L) | 0.057 | 0.042 | 0.05 | 1.140 | 0.840 |
| As (mg/L) | 0.013 | 0.012 | 0.01 | 1.300 | 1.200 |
| ∑ PI | | | | 4.726 | 3.997 |

In the rainy season, the parameters such as Pb, As and Cr had high pollution indexes of 1.500, 1.300 and 1.140 whereas in the dry season, As and Pb had high pollution indexes of 1.300 and 1.200 respectively (Table 6). Pb, As and Cr values were greater than 1.0 which showed a significant degree of pollution whereas the pollution index of the other parameters was less than 1.0 which indicated that sampled borehole water was not polluted. Since the value of PI of Pb, As and Cr were above 1.0 (PI> 1.0), it suggested that borehole water consumption may cause serious health risks because the higher the values of the pollution index, the higher the rate of the hazard risk on the human body [53]. The pollution index of borehole water samples in rainy and dry seasons were 4.726 and 3.997 respectively. This shows that the rainy season value of the pollution index was greater than the dry season value. These might be due to the leaching of groundwater by waste through rainfall, which polluted the borehole water.

### *3.3. Non-Carcinogenic Risk Via Water Ingestion*

***Table 7.*** *Hazard index and hazard quotient results of heavy metals through ingestion of water from the borehole.*

| Parameters | Adult | | Child | |
|---|---|---|---|---|
| | Rainy season | Dry season | Rainy season | Dry season |
| Cu (mg/L) | 2.11E-07 | 1.91E-07 | 3.5E-07 | 3.18E-07 |
| Pb (mg/L) | 3.21E-07 | 2.78E-07 | 5.34E-07 | 4.63E-07 |
| Fe (mg/L) | 5.31E-09 | 4.88E-09 | 8.83E-09 | 8.12E-09 |
| Zn (mg/L) | 6.96E-08 | 4.47E-08 | 1.16E-07 | 7.45E-08 |
| Cr (mg/L) | 5.69E-07 | 4.2E-07 | 9.47E-07 | 6.98E-07 |
| As (mg/L) | 1.3E-06 | 1.2E-06 | 2.16E-06 | 1.99E-06 |
| HI = ∑ HQs | 2.47E-06 | 2.14E-06 | 4.12E-06 | 3.56E-06 |

Table 7, showed the HQ and HI values of non-carcinogenic risk via water ingestion. The HQ and HI values of borehole water samples for both age categories for both seasons were below the recommended value of 1, suggesting that there is no risk of non-carcinogenic diseases [54, 55]. This shows that there are no adverse health risks to be caused by all these heavy metals when the borehole waters were used by all ages. A similar trend in results was observed in a previous study by Adimalla [55].

### *3.4. Non-Carcinogenic Risk Via Dermal Pathway*

***Table 8.*** *Hazard index and hazard quotient results of heavy metals through the dermal pathway of borehole water.*

| Parameters | Adult | | Child | |
|---|---|---|---|---|
| | Rainy season | Dry season | Rainy season | Dry season |
| Cu (mg/L) | 1.19E-07 | 1.08E-07 | 7.1E-07 | 6.45E-07 |
| Pb (mg/L) | 1.45E-07 | 1.26E-07 | 8.69E-07 | 7.53E-07 |
| Fe (mg/L) | 8.97E-10 | 8.24E-10 | 5.37E-09 | 4.94E-09 |
| Zn (mg/L) | 5.88E-08 | 3.78E-08 | 3.52E-07 | 2.27E-07 |
| Cr (mg/L) | 9.62E-08 | 7.09E-08 | 5.76E-07 | 4.25E-07 |
| As (mg/L) | 5.35E-07 | 4.94E-07 | 3.21E-06 | 2.96E-06 |
| HI = ∑ HQs | 9.54E-07 | 8.36E-07 | 5.72E-06 | 5.01E-06 |

The hazard quotient and hazard index values of the sampled borehole water around the Nnewi industrial area are presented in Table 8. HI or HQ < 1 showed that non-carcinogenic risk was not significant, whereas when the value is greater than 1 (HI or HQ > 1) the effect will be substantial [27, 54, 56]. The rainy season HI values were greater than the dry season values of HI for both age categories. This might be due to the heavy discharge of effluent from the industries which is transported into the underground via leaching during the rainy season [1, 41]. The HI values via dermal contact were below the safe limit of one (HI < 1) for all the sampling locations, which showed no adverse health effect of the non-carcinogenic disease of these heavy metals in the study area for both age categories [55].

### *3.5. Carcinogenic Risk Via Ingestion Pathway*

***Table 9.*** *Carcinogenic risk induced by heavy metals via ingestion of water for sampled borehole water*

| Parameters | Adult | | Child | |
|---|---|---|---|---|
| | Rainy season | Dry season | Rainy season | Dry season |
| Pb (mg/L) | 1.09E-06 | 9.46E-07 | 5.45E-07 | 4.72E-07 |
| Cr (mg/L) | 0.000244 | 0.00018 | 0.000122 | 8.98E-05 |
| As (mg/L) | 0.000167 | 0.000154 | 8.33E-05 | 7.69E-05 |
| HI | 4.12E-04 | 3.35E-04 | 2.06E-04 | 1.67E-04 |

Table 9 showed the cancer risk and hazard index values through the ingestion pathway for the borehole water samples around Nnewi industrial area. The carcinogenic risk values of Pb for both age categories were within the acceptable safe limit of $1.0 \times 10^{-6}$. The values of carcinogenic risk of Cr and As for adults and children were higher than the recommended safe limit of $1.0 \times 10^{-6}$, which implies that adults and children were facing high health risks in the study area. The hazard index values for adults and children in both seasons were above the recommended safe limit of 1.0E−06 which may be tolerable but not recommendable [54]. The HI values of the child were at a higher risk than that of adults. The HI values for the rainy season were greater than the HI values for the dry season for both age categories. The ingestion route seems to contribute high to cancer risk. It is, therefore, inferred that the borehole waters around Nnewi industrial areas are unfit for drinking for both age categories because there are chances of exposure to cancer risk.

### *3.6. Carcinogenic Risk Via Dermal Pathway*

***Table 10.*** *Carcinogenic risk induced by heavy metals via dermal pathway for sampled borehole water.*

| Parameters | Adult | | Child | |
|---|---|---|---|---|
| | Rainy season | Dry season | Rainy season | Dry season |
| Cr (mg/L) | 0.000165 | 0.000121 | 0.000296 | 0.000218 |
| As (mg/L) | 6.88E-05 | 6.35E-05 | 0.000124 | 0.000114 |
| HI | 2.34E-04 | 1.85E-04 | 4.20E-04 | 3.33E-04 |

Table 10 showed the cancer risk via dermal exposure for the borehole water samples. The cancer risk of one in a million populations (1.0E−06) is recommendable by USEPA. Values above 1.0E−05 but below 1.0E−04 can be tolerable but not recommendable whereas values up to 1.0E−04 or above cause serious cancer risk in humans [54, 57]. Cancer risks via dermal contact with the highest value were observed for a child with a value of $4.20\times 10^{-4}$ recorded in the rainy season. The values of HI were higher than the recommended safe limit of $1.0 \times 10^{-6}$ in both age categories for both seasons [54]. The Cr values were above the recommended safe limit of $1.0 \times 10^{-6}$ [26]. This shows that Cr poses higher health risks of carcinogenic effects to children than the adults in the study area [54]. The risk indices for the two age categories showed that the child risk index was predominantly higher than the adult risk index for both seasons [57]. This showed that the chances of a child's exposure to carcinogenic risk are greater than that of an adult [58]. It is, therefore, inferred that the borehole waters around Nnewi industrial areas are unfit for bathing and showering for adults and children because there are chances of exposure to cancer risks.

### *3.7. Correlation Analyses of the Heavy Metal Parameters*

***Table 11.*** *Correlations matrices for the heavy metal concentration of sampled borehole water for the rainy season.*

| | Cu | Pb | Fe | Zn | Cr | As |
|---|---|---|---|---|---|---|
| Cu (mg/L) | 1 | | | | | |
| Pb (mg/L) | -0.168 | 1 | | | | |
| Fe (mg/L) | 0.136 | -0.028 | 1 | | | |
| Zn (mg/L) | 0.100 | -0.106 | 0.099 | 1 | | |
| Cr (mg/L) | -0.142 | 0.058 | 0.212* | 0.078 | 1 | |
| As (mg/L) | 0.254* | -0.276** | 0.041 | -0.068 | -0.162 | 1 |

The results showed a significant direct correlation between Cu and As ($r = 0.254$, $P < 0.05$), Fe – Cr ($r = 0.212$ at $P < 0.05$) and a negative correlation between Pb – As ($r = -0.276$, $P < 0.01$) for borehole water samples during the rainy season (Table 11). This means that an increase in Pb leads to a decrease in the other parameters and since the value is less than 0.01 the relationship between the two is weak. Then, the correlation between Cu and As is 0.254 which implied that an increase in Cu leads to an increase in As and since the value is greater than 0.05, the relationship between the two is strong. The correlation values of heavy metal concentration of the sampled borehole waters indicated a moderate positive correlation between the samples during the rainy season.

***Table 12.*** *Correlations matrices for the heavy metal concentration of sampled borehole waters for the dry season.*

| | Cu | Pb | Fe | Zn | Cr | As |
|---|---|---|---|---|---|---|
| Cu (mg/L) | 1 | | | | | |
| Pb (mg/L) | 0.009 | 1 | | | | |
| Fe (mg/L) | -0.087 | -0.147 | 1 | | | |
| Zn (mg/L) | -0.160 | 0.221* | -0.216* | 1 | | |
| Cr (mg/L) | -0.031 | -0.035 | -0.021 | -0.131 | 1 | |
| As (mg/L) | -0.079 | -0.230* | 0.077 | 0.022 | 0.011 | 1 |

*. Correlation is significant at the 0.05 level (2-tailed).

The result showed a significant direct correlation between Pb – Zn (r = 0.221, P < 0.05) and a negative correlation between Pb – As (r = – 0.230, P < 0.05), Fe – Zn (r = – 0.216, P < 0.05) for borehole water during the dry season (Table 12). The correlation values of the heavy metal concentration of the borehole water samples indicated a moderate positive correlation between the samples. The correlation between these metal pairs might be a result of the existence of some of the heavy metals in similar oxidation states, reacting and relating in the same manner [59]. Metals correlation in borehole water reflected contribution from both anthropogenic sources and lithological origin since researchers reported that correlation between metal pairs gets separated or diminished with anthropogenic influence [60].

# 4. Conclusions

The results reveal that borehole water in the area studied is significantly affected by industrial discharges and flooding, as shown by the pollution index values of some heavy metals monitored. All the heavy metal concentrations examined were below the WHO permissible limits except As, Cr and Pb. The high values of As, Cr and Pb indicated that borehole water is not suitable for drinking. The PI values of As, Cr and Pb in both seasons confirm the presence of high inorganic and organic materials in the borehole waters which could pose health risks to humans. The results reveal that the values of Cr, As and Pb are above the WHO-acceptable limits for safe drinking water. The results also suggest that the presence of excessive heavy metals (Pb, As and Cr) could be detrimental to human health, which implies that industrial and domestic effluents, decomposing refuse dumps and flooding have negative impacts on the studied boreholes' water.

Pearson's correlation reveals that heavy metal concentrations of water are moderately correlated with one another at either P < 0.05 or < 0.01. It is observed from the correlation analysis that Pb, As, Zn and Cu were derived from anthropogenic activities (mineral exploitation and industrial wastewater) while Fe and Cr might be associated to release from natural sources. The HI values of adults and children via ingestion and dermal contact with sampled borehole waters were less than the recommended safe limit of 1 (HI < 1). These indicate that the non-carcinogenic effect of these metals had no significant health risk, for both age categories in this study. The values of carcinogenic risk of adults and children are above the recommended safe limit of $1.0 \times 10^{-6}$, which implies that children and adults face higher health risks. For the carcinogenic effect, the ingestion pathway contributes very highly to the cancer risk than the dermal pathway. This quantitative evidence demonstrates the critical need for environmental regulations to protect people leaving around the study area from heavy metal contamination in the environment. It is, therefore, anticipated that the results obtained from this study will help to initiate water management policies to reduce water contamination in Nnewi urban area.

It is concluded that borehole water in the study area is not suitable for drinking and therefore should be used for other domestic purposes. Consequently, all borehole waters in the study area should be properly treated to meet the various WHO standards for potable water before releasing it to the public for consumption. Routine monitoring of the borehole water within the industrial area should be encouraged, to curtail health-related risks from exposure to heavy metal toxicity.

# Conflicts of Interest

The authors declare that they have no conflict of interest.

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