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Assessment of Heavy Metal Contents and Associated Health Risks in Groundwater Samples Around Federal College of Animal Health and Production Technology, Ibadan, Nigeria Students' Residential Areas

***Alade, Adetomiwa Adebayo, Jones, Sinmi Ayodeji, Amao, Oluwatoyin Atilola and Mohammed, Liman**

Science Laboratory Technology, Federal College of Animal Health and Production Technology, Ibadan, Nigeria.

*Corresponding author's email: adetomiwa.alade@fcahptib.edu.ng Phone: +2348053519870

ABSTRACT
Groundwater is a major source of water for students at the Federal College of Animal Health and Production Technology, Ibadan students' residential areas. Hence, the quality of water of the study was determined by assessing the heavy metal contents and evaluating the associated health risks. A total of ten samples (five boreholes and five Wells) were collected from five different locations within the study area. Coordinates of the sampling points were taken with the aid of global pointing system while atomic absorption spectrometer was employed to determine the concentration of the heavy metal in the samples. Results of the heavy metal contents (mg/L) showed: Pb (BDL - 0.65), Zn (2.50 - 6.10), Mn (0.35 - 2.95), Cr (BDL - 20.43), Cd (0.18 - 0.88), Ni (1.25 - 7.80), Fe (BDL - 9.85) and Cu (0.35 - 6.40). Risk parameters such as contamination factor (CF), degree of contamination (DoC), and a Quantification of contamination index (QC) were also evaluated. DoC showed a very high indication of contamination of the groundwater samples of the study while QC indicates that most of the contamination is of anthropogenic origin. In order to assess the safety of the students' populace due to oral and dermal exposure, average daily dose (ADD), hazard quotient (HQ) and hazard Index (HI) were evaluated. The values ranged as follows: ADDoral (0.0000 - 8.00 × 10^{-5}) mg/L/day; ADDdermal (0.0000 - 9.63 × 10^{-12}) mg/L/day ; HQoral (0.0000 - 9.77× 10^{-5}) ; HQdermal (0.0000 - 9.65 × 10^{-15}) ; HIoral (1.50 × 10^{-1}) and HIdermal (0.0000 - 7.06 × 10^{-7}). All the values obtained were below the provisional tolerable daily intake. Hence, there may be no potential risks for ingestion of the groundwater samples of the study. However, the routine monitoring of the groundwater samples should be encouraged to curtail health-related risks from exposure to heavy metal toxicity.

Keywords:
Groundwater,
Heavy metal,
Health risk.

INTRODUCTION

Groundwater is one of the most significant natural water resources readily available in many countries and has considerably been utilized for drinking and irrigation purposes (Amadi *et al*., 2013; Selvakumar *et al*., 2017; Mahammad *et al*., 2022). Groundwater is known as the pure source of water due to bacteriologically free and consists of high nutrients were suitable for human health (Mohamad *et al*., 2021). Groundwater sources include water from boreholes, hand dug wells, hand pumps, and springs (Diloha and Nwankwoala, 2018). Groundwater is believed to be comparatively much clean and free from pollution than surface water (Okoro *et al*., 2012). Despite the perceived safety associated with groundwater consumption, several researches have shown that groundwater can also be susceptible to contamination. Groundwater contamination through naturally occurring potentially heavy metals has become a major concern throughout the scientific community and the world's policymakers (Bundschuh *et al*., 2017; Nwankwo *et al*., 2020; Tomašek *et al*., 2022).

Heavy metals are relatively dense, non-biodegradable, persistent, and can bio-accumulate in nature even at low concentrations (Ali *et al*., 2019). They can be absorbed into soils and water bodies and enter the human body through inhalation, ingestion or dermal absorption while indirect exposure occurs as a result of bioaccumulation and thus endanger human health (Eboagu *et al*., 2020). Heavy metals can be released into groundwater from chemical weathering of rock and minerals (Rango *et al*., 2009). Anthropogenic sources like urbanization, industrialization, solid waste dumping, agricultural activity, etc. can also release heavy metals in the shallow groundwater (Kumar *et al*., 2016; Bhattacharjee *et al*., 2019). Although some heavy metals (e.g., Cu, Mn, and Cr) are essential for humans, their presence in excess amounts may be toxic. In addition, other metals (e.g., As, Hg, Cd, and Pb) are highly toxic at very low concentrations with no known benefits for human health (Saha and Paul, 2019). Heavy metal can also cause damage to the brain, gastrointestinal abnormalities, dermatitis, and death in humans (Sankhla *et al*., 2016). As the World Health Organization (WHO, 2007) indicated, inappropriate or polluted water causes around 80% of all diseases in human beings.

The consumption of water contaminated with heavy metals may cause adverse health effects, such as hypertension, cancer, vascular disease, restrictive lung disease, bleeding from the gastrointestinal tract, neurological disorder, and effects on reproduction, if these metals are present in excessive amounts in the groundwater and ingested over time (Muhammad *et al*., 2011; Lu *et al*., 2015; Nkpaa *et al*., 2018). Health-associated risks caused by using groundwater call for a complete assessment of the effect of industrial activities on the water bodies (Aralu *et al*., 2024). Assessment of the potentially harmful metals levels in groundwater sources is necessary in order to understand the sources, fate, and potential health risks of heavy metals. Hence, the study was conducted to assess the heavy metal Contents and associated health risks in Groundwater Samples around FCAH & PT, Ibadan students' residential areas in order to ascertain the safety for the populace using such water samples.

MATERIALS AND METHODS

Study Area

The study was conducted at the residential areas of the students of Federal College of Animal Health and Production Technology (FCAH & PT), Moor Plantation, Ibadan. These areas included Adabeji, Odo Ona, Gbekuba, Main hostel and Bora hostel. Elevation and coordinate values were taken for each sample location with the aid of global positioning system (GPS) Garmin channel eTrex10 and map of the sampling points was drawn using a Geographical information system (GIS) and are presented in Figure 1.

Sample Collection

Groundwater samples were collected from borehole and hand dug well used by students of FCAH & PT, Ibadan as source for drinking, cooking and bathing purposes. A total of ten groundwater samples (five boreholes and five well) were randomly collected from the locations within the study area.

Samples from the wells were collected by lowering a clean plastic container tied to a synthetic rope down the well. Samples from borehole water were collected by first opening the tap to flow out for about two minutes, before putting the containers to collect.

Prior to sampling, the bottles were washed with detergent and rinsed with the groundwater to be sampled. Groundwater samples were then collected in 2-L polyvinyl chloride bottles to prevent unpredictable changes in characteristics. After collecting the water samples, each sampling bottle's cap was tightly screwed to prevent leakage (Odukoya and Abimbola, 2010; Ganiyu *et al.,* 2018). The collected samples were treated with few drops of nitric acid (to keep metals in solution) and kept at in an ice-crested cooler to prevent any kind of chemical or biological reaction prior to chemical analysis (Ukah *et al.,* 2019). All the water samples were well labeled and transported in black polyethylene bags to the laboratory for relevant chemical analysis within 24 hours from the time of sample collection. The quantitative chemical analysis was conducted at the Multipurpose Laboratory of Federal College of Animal Health and Production Technology, Ibadan.

Heavy metal analysis

Prior to heavy metal analysis, water samples were digested. The water samples were digested and analyzed for heavy metals. 2mL of each of the test substances was transferred to a pre-washed 100-mL beaker containing analytical grade, 25mL of aqua regia mixture (70% HNO_3 and HCl ratio: 3:1). The mixture was digested in a digestion vessel at the temperature of 80 °C until a homologous solution is obtained. Afterward, the solution was cooled, filtered through a Whatmann No.42 filter paper into a 50-mL volumetric flask, and diluted to the mark with deionized water. The filtrates were made up to the 100 mL mark with deionized water and analysed for metals of interest using A320N Biobase, Atomic Absorption Spectrophotometer using appropriate hollow cathode lamps at Multipurpose Laboratory, Federal College of Animal Health and Production Technology, Ibadan, Nigeria.

Risk Calculation of Heavy Metal Pollution in the Groundwater Samples

Several pollution indices can be employed to assess the degree to which heavy metals contaminate water resources (Devanesan *et al*., 2017; Rahman *et al*., 2020; Kumar *et al*., 2020). The risk assessment methods of heavy metal pollution degree were used to assess the heavy metal pollution in the groundwater in the study area via parameters such as contamination factor, degree of contamination and quantification of contamination.

Contamination Factor

It is used to evaluate how a single heavy metal pollutes groundwater at a sampling site and it is evaluated based on the expression given by Islam and Mostafa (2021) and Ganiyu *et al.* (2021):

$$CF = \frac{C_{metal}}{C_{standard}} \quad (1)$$

Where CF = contamination factor, C_{metal}= measured content of heavy metal in groundwater (mg/L) and $C_{standard}$ = evaluation standard of concentration of heavy metal in the groundwater (mg/L). Here, the guideline value given by WHO (2017) will be followed with the maximum permissible concentrations of Mn, Fe, Cu, Pb, Zn, Ni, Cr and Cd as 0.5, 0.3, 2.0, 0.01, 3.0, 0.07, 0.05 and 0.003 mg/L respectively.

A CF< 1 = low contamination; 1≤CF< 3 = moderate contamination; 3≤CF< 6 = considerable contamination and CF ≥ 6 = very high contamination (Ganiyu *et al*., 2021).

Degree of contamination (DoC)

It is an evaluation technique that determines the combined effects of heavy metals on the overall quality of groundwater (Boateng *et al*., 2015; Mostafa *et al*., 2017). It is therefore computed as the summation of individual CF for heavy metals in equation (3.2) given by Ganiyu (2022):

$$DoC = \sum CF = CF_{Pb} + CF_{Zn} + CF_{Cd} + CF_{Ni} + CF_{Cu} + CF_{Fe} + CF_{Mn} + CF_{Cr} \quad (2)$$

A DoC ≤ 10 = low; DoC (11 – 20) = medium and DoC> 20 = high (Ganiyu *et al*., 2021).

Quantification of contamination (QC)

It is the index of contamination and it is expressed by the equation given by Ganiyu *et al.* (2021):

$$QC\,(\%) = \left[\frac{C_{metal} - C_{standard}}{C_{metal}}\right] \times 100 \quad (3)$$

Where C_{metal}= measured content of heavy metal in groundwater (mg/L); $C_{standard}$ = background concentration of a given metal in groundwater (mg/L). A positive value QC signifies contamination is of anthropogenic origin while a negative QC value signifies contamination is of lithogenic origin (Asaah *et al.,* 2006; Ganiyu *et al*., 2021).

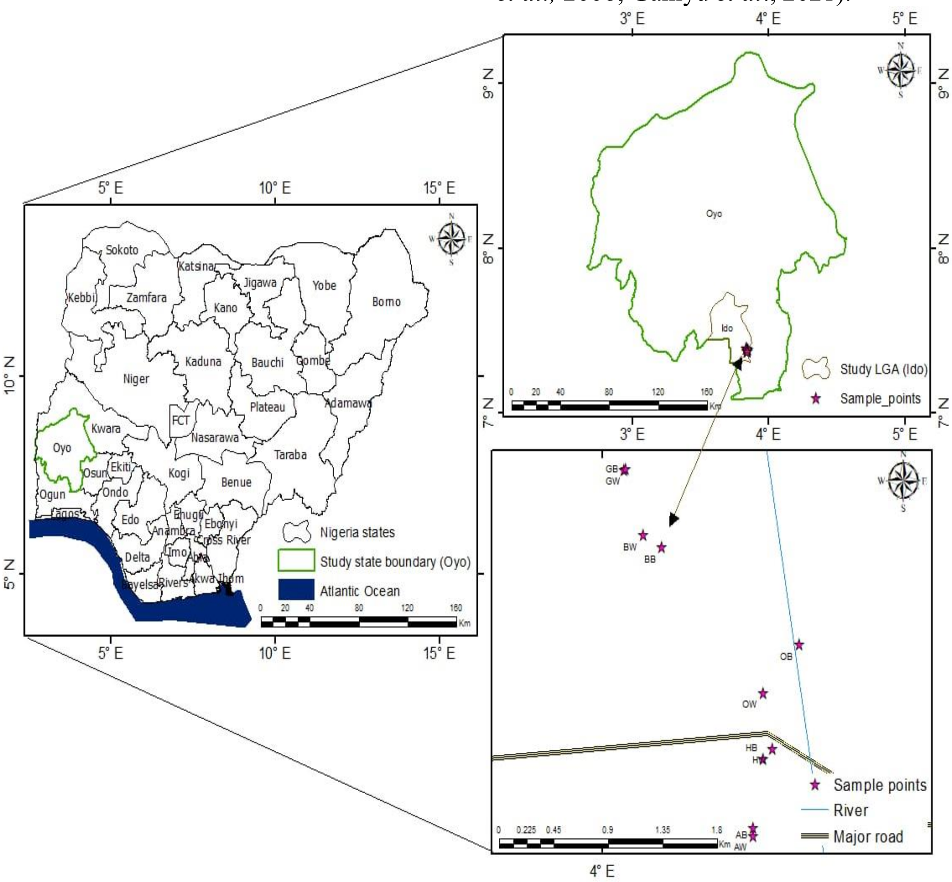

Figure 1: Map of the Study Area Showing the Sampling Points

Human Health Risk Assessment

Human exposure to heavy metals is through several pathways including oral, inhalation and dermal (Elumalai *et al*., 2017). Contamination of water gives rise to many health challenges. Risk assessment is a tool developed in order to measure and evaluate likely health risk associated with the exposure to certain elements such as heavy metals which could be injurious to the human health (Elemile *et al.,* 2021). It is used to estimate the impact of carcinogens and the future rate at which an individual is affected by carcinogenic metals (Laniyan and Adewumi, 2019). In this study, the non-carcinogenic and carcinogenic risks related to the exposure to heavy metals via oral ingestion and dermal contacts were estimated.

Average daily dose (ADD)

Average daily dose of heavy metals (mg/L/day), expressed as daily dose over body weight is a parameter used for determining the exposure dose of metals over a specific period. It is the estimations of the magnitude, frequency and duration of human exposure

in the environment (Boateng *et al*., 2019; Siriwong, 2006).
In estimating the risk related to the exposure to heavy metals in the groundwater, average daily dose via oral ingestion and dermal contact were estimated by the expression given in equations (3.4) and (3.5) respectively (USEPA, 2000; Elemile *et al*., 2021; Mawari *et al.,* 2023):

$$ADD_{oral} = \frac{C_{metal} \text{ x IR x EF x ED}}{B_w \text{ x AT}} \text{ x CF} \quad (4)$$

$$ADD_{dermal} = \frac{C_{metal} \text{ x EF x ED x ET x SA x KP}}{B_w \text{ x AT}} \text{ x CF} \quad (5)$$

Where ADD_{oral} and ADD_{dermal}= the exposure dosage (mg/L/day) by oral intake and dermal route respectively; C_{metal} = mean concentration of heavy metal (mg/L); IR = ingestion rate (L/day); EF = exposure frequency (days/year); ED = exposure duration (years), B_w= average body weight (kg), AT = average time period of exposure (days); ET = exposure time (hour/day); SA = surface area of contact (exposed skin surface) (cm^2); KP = dermal permeability coefficient (m/h) and CF = conversion factor.
The following assumptions were made to quantify exposure: people residing in the sampled location are assumed to drink 2L/day of water (Egbueri, 2020; Ramadan and Haruna, 2019; Mawari *et al.¸* 2023); EF is taken as 350 days because it was assumed that a student will leave the area for about two weeks per year (Mawari *et al.¸* 2023). For non-carcinogens, ED is taken as 1 year because there is a possibility of rent expiration for any residence and such may not renewed it; B_w is assumed to be 45 kg for the students' populace, AT is the period which exposure duration is averaged (EF x ED = 1 x 350 = 350 days); ET and SA were taken as 0.58 hour/day and 1.8 m^2respectively (USEPA, 2011; Mawari *et al.¸*2023); KP taken as 0.001, 0.001, 0.001 and 0.0006 m/hr for Cu, Fe, Mn and Zn respectively (USEPA, 2004) and CF = 1 x 10^{-3} L//m (USEPA, 2011; Mawari *et al.¸* 2023).

Hazard quotient (HQ)

To indicate the potential non-carcinogenic risk to human health posed by a hazardous material, the hazard quotient has been developed. It is the ratio of estimated heavy metals exposure of test water and oral reference dose (Mawari *et al.,* 2023; USEPA, 2011). It indicates potential hazards to human health. It is evaluated by comparing the estimated amount of pollutants from different routes of exposures (oral and dermal) with an established reference dose by the expression given by Deng *et al*. (2019) and Mawari *et al.* (2023):

$$HQ_{oral} = \frac{ADD_{oral}}{RfD} \quad (6)$$

$$HQ_{dermal} = \frac{ADD_{dermal}}{RfD} \quad (7)$$

Where HQ = hazard quotient, ADD = average daily dose and RfD = oral reference dose of a specific metal (mg/L/day). The oral reference dose of Cd, Pb Ni, Cu, Zn, Mn, Fe and Cr are 0.001, 0.0035, 0.02, 0.04, 0.3, 0.014, 0.3 and 0.003 mg/kg/day respectively while in the case of dermal reference dose of Cd, Pb Ni, Cu, Zn, Mn, Fe and Cr are 0.00001, 0.00025, 0.0054 (0.00054), 0.012, 0.06, 0.00005, 0.0045 and 1.5 mg/kg/day respectively (Duggal *et al*., 2017; Enuneku *et al*., 2018).
The HQ value less than 1 indicates no non-carcinogenic health risk while the HQ value greater than 1 indicates an unacceptable health risk (USEPA, 2011).

Hazard index (HI)

Human exposure to more than one pollutant can results in additive effects (Ametepey *et al.,* 2018). Hazard index can be used to estimates the likely impacts of these additives effects. The HI is therefore computed as the summation of individual hazard quotients for heavy metals in the equation given by Mawari *et al.* (2023):

$$HI_{oral} = \sum HQ_{oral} \quad (8)$$

$$HI_{dermal} = \sum HQ_{dermal} \quad (9)$$

$$HI = \sum HQ_{oral} + \sum HQ_{dermal} \quad (10)$$

Where HI = hazard index and HQ= hazard quotient.
For non-carcinogenic risk, H1 > 1 signifies a high potential health risk; it suggests that the non-carcinogenic risk of ingesting a specific metal surpasses the acceptable safe limit (Ukah *et al*., 2019). However, HI less than unity means that the non-carcinogenic health risk lies within theacceptances limit (Afrifa *et al*., 2013; Kladsomboon *et al*., 2019; Wu and Sun, 2016; Egbueri and Mgbenu 2020).

RESULTS AND DISCUSSION

Results of the Heavy Metal Analysis

Heavy metal analysis was carried out on ten groundwater samples around FCAH &PT, Ibadan students' residential areas using atomic absorption spectrometry. Results are presented in Table 1. All the results are compared with permissible limit recommended by World Health Organization (WHO).
Iron is an essential element for dietary requirement for most of organisms, and it is central atom in haemoglobin and helpful to transport the oxygen in to various organs through the blood (Tadiboyina and Rao, 2016). In this study, it varied from BDL – 9.85 mg/L with an average value of 3.73 mg/L. *A significant difference of* difference ($p < 0.05$) was observed among all the groundwater samples of the study. All the values obtained are above the WHO (2017) limit of 0.3 mg/L which could indicate that the groundwater sample is contaminated with iron metal. Chronic consumption *of* water with iron overload may results in fatigue, weight loss, joint pains and ultimately heart disease, liver problems and diabetes (US-CDC 2011).
Copper is a trace essential heavy metal found in environment and spread through the natural phenomenon which enters into groundwater through industrial wastes, agriculture pesticides and corrosion of copper pipes (Tadiboyina and Rao, 2016). It varied from 0.35 mg/L (Hostel well) to 6.40 mg/L (Gbekuba Borehole) with a mean concentration of 1.89 mg/L. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study. Values of Cu

obtained in the study are below the WHO (2017) limit of 2.0 mg/L except for Adabeji well, Gbekuba Borehole and Bora Hostel Borehole. Cu exposure could lead to gastrointestinal disorders and liver damage (Taylor *et al*., 2020).

Zinc is an essential trace metal that enters into water through industrial wastewaters, galvanic industries, battery production, zinc leaks from zinc pipes and rain pipes etc. (Tadiboyina and Rao, 2016). In the study, it ranged from 2.50 mg/L (Gbekuba Well) to 6.10 mg/L (Odo Ona Borehole) with an average concentration of 4.58 mg/L. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study. The values of Zn of the study are above the WHO (2017) limit of 3.0 mg/L (except at Gbekuba Well). Zinc exposure has been shown to promote apoptosis in the brain (Plum *et al.,* 2010). Long term ingestion of zinc in water has been known to cause vomiting, anaemia, and stomach cramps (Singh *et al*., 2018).

Manganese is one of the common essential trace elements that enter into atmosphere via suspended particulates resulting from industrial emissions, soil erosion, volcanic emissions and the burning human activities are also responsible for much of the manganese contamination in water in some areas (Tadiboyina and Rao, 2016). Its value ranged between 0.38 mg/L to 2.95 mg/L with the least value obtained at Bora Hostel Borehole and the highest value at Gbekuba Borehole. The average value of 0.96 mg/L was obtained in the study. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study. All the values of the study are above the safe limits of 0.5 mg/L (except in Main Hostel Borehole and Bora Hostel Borehole) set by WHO (2017).Excessive Mn intake via drinking water can lead to a neurological disorder, including a reduction in intellectual capacity and DNA damage (WHO, 2011; Annaduzzaman *et al*., 2018).

Chromium is an essential trace element for man and animals that is discharged into groundwater or surface water through metal refinery industries and alloy industries. In the study, it varied from BDL to 20.43 mg/L with an average value of 8.74 mg/L. The maximum value was obtained at Odo Ona Borehole. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study.All the values of the study are above the safe limits of 0.05 mg/L (except at Main Hostel Well and Gbekuba Well) set by WHO (2017*)*. Chromium has been linked to cancer and tumors of the respiratory system (Mawari et al., 2023). Consumption of water with a high Cr concentration may cause gastrointestinal cancer for long-term exposure (Eboagu and Ajiwe, 2022).

Nickel is one of the essential heavy metal present in the earth crust. It is found in sand stone and slate, mainly present as pentlndate, element accumulates in sediments of biological cycles (Tadiboyina and Rao, 2016). It varied between 1.25 mg/L (Main Hostel Well) and 7.80 mg/L (Adabeji Well) with a mean concentration of 4.27 mg/L. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study .All the values of the study are above the safe limits of 0.02 mg/L set by WHO (2017)*.* Ni exposure has been reported to cause cardiovascular and renal disorders, as well as lung and nasal cancer (Genchi *et al*., 2020).

Cadmium is one of the toxic heavy metals that may occur in groundwater naturally or as a contaminant from sewage sludge, fertilizers, polluted groundwater or mining and industrial effluents (Tadiboyina and Rao, 2016). It is found to vary from 0.18 mg/L (Odo Ona Well) to 0.88 mg/L (Adabeji Well) with an average concentration of 0.56 mg/L. A significant difference ($p < 0.05$) was observed among all the groundwater samples of the study. All the values of the study are above the safe limits of 0.003 mg/L set by WHO (2017). Exposure to higher concentration of Cd may cause kidney damage as well as producing acute health effects (Momodu and Anyakora 2010).

Lead is a toxic heavy metal that has no biochemical or physiological importance and was considered as toxic pollutant for living things (Lokeshappa et al., 2012). It enters into water through the corrosion of pipes (Tadiboyina and Rao, 2016). Lead is a typical cumulative poison and there is no safe level for human body. In the study, it ranged from BDL to 0.65 mg/L with an average value of 0.68 mg/L. The maximum value was obtained at Odo Ona Borehole. A significant difference ($p <0.05$) was observed among all the groundwater samples of the study.All the values of the study are below the safe limits of 0.01 mg/L set by WHO (2017) except Odo Ona Borehole and Bora Hostel Borehole. Exposure to high concentration Pb may cause high blood pressure, anaemia, kidney and brain damage especially in adults (Jaishankar et al., 2014; WHO, 2011).

Risk Calculation of Heavy Metal Pollution in the Groundwater Samples

In order to estimate the risk parameters of the metal pollution in the groundwater samples of the study, some parameters such as contamination factor, degree of contamination and quantification of contamination were evaluated and results are then presented in Tables 2 – 3 respectively.

CF is used to evaluate how a single heavy metal pollutes groundwater at a sampling site. A $CF< 1$ = low contamination; $1 \leq CF<3$ = moderate contamination; $3 \leq CF<6$ = considerable contamination and $CF \geq 6$ = very high contamination (Ganiyu *et al*., 2021).The mean CF values for Cu, Zn and Mn were found to be in the range of $1 \leq CF< 3$, an indication of moderate contamination of these metals in the groundwater samples of the study, while mean CF values for Fe, Pb, Mn, Cr and Cd were found to be in the range of $CF \geq 6$ is an indication of very high contamination of these metals in the groundwater samples of the study.

A DoC is an evaluation technique that determines the combined effects of heavy metals onthe overall quality of groundwater (Boateng *et al*., 2015; Mustafa *et al*., 2022). A DoC ≤ 10 = low contamination; DoC (11 – 20) = medium contamination and DoC> 20 = high contamination (Ganiyu *et al*., 2021). Thus, the values of DoC in the study fall within the high contamination zone (DoC> 20).

Table 3 gives the quantification of contamination values of heavy metal in groundwater samples of the study. A positive value QC signifies that contamination is of anthropogenic origin while a negative QC value signifies that contamination is of lithogenic origin (Asaah *et al.,* 2006; Ganiyu *et al*., 2021). For the study, Fe, Zn (except in Gbekuba well), Cr, Cd and Ni contamination are of anthropogenic origin while Cu (except Gbekuba borehole, Adabeji well and Bora Hostel borehole) could be of lithogenic origin.

Results of the Human Health Risk Assessment

In order to estimate the risk parameters associated with the oral and dermal exposure of heavy metals in groundwater samples of the study, the average daily dose, hazard quotient and hazard indices were evaluated and results are as presented in Tables 4 – 7 respectively.

Table 4 shows the average daily dose intake of heavy metals for the students' populace through oral exposure duration in comparison with the provisional daily intake set by WHO. The average daily dose for the heavy metals (mg/L/day) ranged as follows: Fe (0.0000 to 4.38×10^{-4}) with an average of 7.10×10^{-5} mg/L/day; Cu (3.45×10^{-10} to 4.88×10^{-5}) with an average of 2.00×10^{-5} mg/L/day; Mn (2.67×10^{-6} to 8.00×10^{-5}) with an average of 2.13×10^{-5} mg/L/day; Zn (1.30×10^{-6} to 2.10×10^{-4}) with an average of 5.50×10^{-5} mg/L/day; Cr (0.0000 to 8.00×10^{-4}) with an average of 2.00×10^{-4} mg/L/day; Ni (0.095×10^{-4} to 1.80×10^{-4}); Cd (1.37×10^{-6} to 0.36×10^{-4}) with an average of 8.00×10^{-6} mg/L/day and Pb (0.0000 and 0.05×10^{-4}) with an average of 7.78×10^{-7} mg/L/day. Values obtained were lower for various metals were within the PTDI limits set by WHO. Generally, for all the heavy metals of the study, the overall average daily dose was found to be in the following order: Cr >Fe >Ni>Zn>Mn> Cu >Cd> Cd.

Table 5 shows the average daily dose intake of heavy metals for the students' populace through dermal exposure in groundwater samples around FCAH & PT, Ibadan students' residential areas in comparison with the provisional daily intake set by WHO. The average daily dose for Fe in the groundwater samples ranged from 0.0000 mg/L/day to 7.03×10^{-13} mg/L/day; for Cu, it ranged 0.0000 to 9.28×10^{-14} mg/L/day; for Mn, it varied from 1.07×10^{-13} mg/L/day to 8.99×10^{-13} mg/L/day. Similarly for Zn, it ranged between $1.07 \times 10^{--12}$ mg/L/day to 9.63×10^{-12} mg/L/day; for Cd, it ranged between 0.0000 mg/L/day and 5.0×10^{-14} and for Pb, it ranged between 0.0000 to 4.86×10^{-14} mg/L/day. All values were lower than PTDI limits of 1.0 mg/L/day set by WHO. Generally, for all the heavy metals of the study, the overall average daily dose were found to be in order of Fe ≥ Cu ≥ Mn ≥ Zn ≥ Cr ≥ Ni ≥ Cd ≥ Pb.

Table 6 gives the hazard quotient and hazard index for oral ingestion in Groundwater collected from the Sampling point within the study area. Hazard quotient indicates the potential hazards of human health (Deng *et al*., 2019). The value ranged as follows; Fe (0.0000 - 9.71×10^{-5}), Cu (0.0000 - 6.67×10^{-5}), Mn (1.08×10^{-3} - 5.71×10^{-4}), Zn (0.0000 - 1.06×10^{-4}), Cr (0.0000 - 5.19×10^{-2}), Ni (0.0000 - 9.05×10^{-3}), Cd (0.0000 - 5.90×10^{-3}), and Pb (0.0000 - 5.99×10^{-4}). The results indicates that the values were values greater than unity (HQ>1) indicating an unacceptable health risk (USEPA, 2011).

Hazard index is the summation of individual hazard quotient heavy metals (Mawari *et al.,* 2023). From the study, it was observed that mean value could suggest that there is no - carcinogenic of exposure due to oral ingestion of any specific metal since HI > 1 (Ukah *et al*., 2019).

Table 7 gives the hazard quotient and hazard index for dermal ingestion in Groundwater collected from the Sampling point within the study area. HQ indicates the potential hazards of human health (Deng *et al*., 2019). . The values ranged as follows; Fe (0.0000 - 8.05×10^{-11}), Cu (0.0000 - 9.43×10^{-11}), Mn (0.0000 - 7.13×10^{-9}), Zn (0.0000 - 9.65×10^{-13}), Cr (0.0000 -6.58×10^{-8}) ,Ni (0.0000- 7.63×10^{-13}), Cd (0.0000 - 5.33×10^{-9}), and Pb (0.0000 - 2.7 >1) indicating unacceptable health risk (USEPA, 2011). Hazard index is the summation of individual hazard quotient heavy metals (Mawari *et al.,* 2023). From the study, it was observed that mean value could suggest that there is no - carcinogenic of exposure due to dermal ingestion of any specific metal since HI > 1 (Ukah *et al*., 2019).

Table 1: Heavy Metal of the Groundwater Samples of the Study (mg/L)

Samples	Pb	Zn	Mn	Cr	Cd	Ni	Fe	Cu
Borehole								
AB	BDL	4.65bcd	0.65d	11.35d	0.80a	4.03cd	9.85a	1.08f
HB	BDL	4.70bcd	0.40d	13.53c	0.43cde	2.85e	8.93b	1.65d
OB	0.65a	6.10a	0.65d	20.43a	0.73ab	7.60a	3.98d	0.98f
GB	BDL	5.45ab	2.95a	8.10e	0.68abc	2.38e	2.85e	6.40a
BB	0.28b	4.63bcd	0.38d	4.48f	0.78a	5.50b	2.05f	3.28b
Well								
AW	BDL	5.28abc	0.60d	0.50g	0.88a	7.80a	7.65c	2.73c
HW	BDL	3.85d	2.00b	BDL	0.50bcd	1.25f	BDL	0.35h

OW	BDL	4.48cd	0.55d	12.85cd	0.18e	3.80d	0.78h	0.58g
GW	BDL	2.50e	1.05c	BDL	0.40de	4.55c	BDL	1.43e
BW	BDL	4.18d	0.35d	16.20b	0.18e	2.90e	1.2g	0.45h
Average	**0.68**	**4.58**	**0.96**	**8.74**	**0.56**	**4.27**	**3.73**	**1.89**
PL	**0.01**	**3.00**	**0.50**	**0.05**	**0.003**	**0.07**	**0.30**	**2.00**

PL = Permissible Limits (WHO, 2017) Means with same letter (s) in a column are not significantly different at 5% level of probability by Duncan Multiple Range Test (DMRT); BDL = ≤ 0.005mg/L
Key: A = Adabeji; B= Bora Hostel; G = Gbekuba; O = Odo Ona; H= Main Hostel; Pb = Lead; Zn = Zinc; Mn = Manganese; Fe = Iron; Cu = Copper; Cr = Chromium; Cd= Cadmium; Ni = Nicke; BDL = Below Detection Limit

Table 2: Contamination Factor (CF) and Degree of Contamination (DoC) in Groundwater Samples of the Study

Samples	Fe	Pb	Cu	Zn	Mn	Cr	Cd	Ni	DoC
Borehole									
AB	32.83	0.00	0.54	1.55	1.30	227.00	266.67	201.25	731.14
HB	29.75	0.00	0.83	1.57	0.80	270.50	141.67	142.50	587.61
OB	13.25	65.00	0.49	2.03	1.30	408.50	241.67	380.00	1112.24
GB	9.50	0.00	3.20	1.82	5.90	162.00	225.00	118.75	526.17
BB	6.83	27.50	1.64	1.54	0.75	89.50	258.33	275.00	661.1
Well									
AW	25.50	0.00	1.36	1.76	1.20	10.00	291.67	390.00	721.49
HW	0.00	0.00	0.18	1.28	4.00	0.00	166.67	62.50	234.63
OW	2.58	0.00	0.26	1.49	1.10	257.00	58.33	190.00	510.77
GW	0.00	0.00	0.71	0.83	2.10	0.00	133.33	227.50	364.48
BW	4.00	0.00	0.23	1.39	0.16	324.00	60.00	145.00	534.78
Mean	13.36	10.28	1.02	1.54	2.05	158.28	198.15	220.83	605.51

Table 3: Quantification of Contamination (QC) Values of Heavy Metal

Samples	Fe	Pb	Cu	Zn	Mn	Cr	Cd	Ni
Borehole								
AB	96.95	-	-86.05	35.48	23.08	99.56	99.63	99.50
HB	96.64	-	-21.21	36.17	-25.00	99.63	99.29	99.30
OB	92.45	98.46	-105.13	50.82	23.08	99.76	99.59	99.74
GB	89.47	-	68.75	44.95	83.05	99.38	99.56	99.16
BB	85.37	96.36	38.93	35.14	-33.33	98.88	99.61	99.64
Well								
AW	96.08	-	26.61	43.13	16.67	90.00	99.66	99.74
HW	-	-	-471.43	22.08	75.00	0.00	99.40	98.40
OW	61.29	-	-280.95	32.96	9.09	99.61	98.29	99.47
GW	-	-	-40.35	-20.00	52.38	0.00	99.25	99.56
BW	75.00	-	-344.44	28.23	-42.86	99.69	98.33	99.31

Table 4: Oral Exposure Duration, for the Groundwater Samples of the Study (mg/L/day)

Sample	Fe	Cu	Mn	Zn	Cr	Ni	Cd	Pb
Borehole								
AB	$4.38x\ 10^{-4}$	$4.78\ x\ 10^{-5}$	$2.89\ x\ 10^{-5}$	$2.10\ x\ 10^{-4}$	$5.00\ x\ 10^{-4}$	$1.80\ x\ 10^{-4}$	$0.36\ x\ 10^{-4}$	0.0000
HB	$6.80x\ 10^{-5}$	$1.26\ x\ 10^{-5}$	$3.05\ x\ 10^{-6}$	$3.58\ x\ 10^{-5}$	$1.00\ x\ 10^{-4}$	$0.22\ x\ 10^{-4}$	$0.032\ x\ 10^{-4}$	0.0000
OB	$3.03x\ 10^{-5}$	$7.43\ x\ 10^{-6}$	$4.95\ x\ 10^{-6}$	$4.65\ x\ 10^{-5}$	$1.60\ x\ 10^{-4}$	$0.58\ x\ 10^{-4}$	$0.055\ x\ 10^{-4}$	$0.05x\ 10^{-4}$
GB	$2.17x\ 10^{-5}$	$4.88\ x\ 10^{-5}$	$2.25\ x\ 10^{-5}$	$4.15\ x\ 10^{-5}$	$0.62\ x\ 10^{-4}$	$0.18\ x\ 10^{-4}$	$0.051\ x\ 10^{-4}$	0.0000
BB	$1.56\ x\ 10^{-5}$	$2.50\ x\ 10^{-5}$	$2.86\ x\ 10^{-6}$	$3.52\ x\ 10^{-5}$	$0.34\ x\ 10^{-4}$	$0.42\ x\ 10^{-4}$	$0.059\ x\ 10^{-4}$	$0.02\ x\ 10^{-4}$
Well								
AW	$5.83\ x\ 10^{-5}$	$2.08\ x\ 10^{-5}$	$4.57\ x\ 10^{-6}$	$4.02\ x\ 10^{-5}$	$3.80\ x\ 10^{-6}$	$0.59\ x\ 10^{-4}$	$0.067\ x\ 10^{-4}$	0.0000
HW	0.0000	$2.67\ x\ 10^{-6}$	$1.52\ x\ 10^{-5}$	$2.93\ x\ 10^{-5}$	0.0000	$0.095\ x\ 10^{-4}$	$0.038\ x\ 10^{-4}$	0.0000
OW	$5.90\ x\ 10^{-6}$	$4.00\ x\ 10^{-6}$	$4.19\ x\ 10^{-6}$	$3.41\ x\ 10^{-5}$	$9.80\ x\ 10^{-5}$	$0.29\ x\ 10^{-4}$	$0.013\ x\ 10^{-4}$	0.0000
GW	0.0000	$1.09\ x\ 10^{-5}$	$8.00\ x\ 10^{-5}$	$1.90\ x\ 10^{-5}$	0.0000	$0.35\ x\ 10^{-4}$	$0.03\ x\ 10^{-4}$	0.0000
BW	0.0000	$3.45\ x\ 10^{-10}$	$2.67\ x\ 10^{-6}$	$1.30\ x\ 10^{-6}$	$8.00x\ 10^{-4}$	$0.76\ x\ 10^{-4}$	$1.37\ x\ 10^{-6}$	0.0000
Mean	$\mathbf{7.10\ x\ 10^{-5}}$	$\mathbf{2.00\ x\ 10^{-5}}$	$\mathbf{2.13\ x\ 10^{-5}}$	$\mathbf{5.50\ x\ 10^{-5}}$	$\mathbf{2.00\ x\ 10^{-4}}$	$\mathbf{6.45\ x\ 10^{-5}}$	$\mathbf{8.00\ x\ 10^{-6}}$	$\mathbf{7.78\ x\ 10^{-7}}$
PTDI	**0.3**	**2.0**	**0.4**	**1.00**	**0.05**	**0.02**	**0.003**	**0.01**

PTDI = Provisional tolerable daily intake (WHO, 2011)
Key: A = Adabeji; H = Main Hostel; O = Odo Ona; G = Gbekuba; B = Bora Hostel

Table 5: Dermal Exposure Duration, ADD_{dermal} for the Groundwater Samples of the Study(mg/L/day)

Sample	Fe	Cu	Mn	Zn	Cr	Ni	Cd	Pb
Borehole								
AB	1.02×10^{-11}	1.11×10^{-12}	1.16×10^{-12}	4.79×10^{-12}	4.04×10^{-11}	1.43×10^{-11}	1.42×10^{-12}	0.0000
HB	1.58×10^{-12}	2.92×10^{-13}	1.22×10^{-13}	8.31×10^{-13}	8.24×10^{-12}	1.74×10^{-12}	1.26×10^{-13}	0.0000
OB	7.03×10^{-13}	1.72×10^{-13}	1.98×10^{-13}	1.07×10^{-12}	1.24×10^{-11}	4.63×10^{-12}	2.21×10^{-13}	1.15×10^{-13}
GB	5.04×10^{-13}	1.13×10^{-12}	8.99×10^{-13}	9.63×10^{-12}	4.93×10^{-12}	1.45×10^{-12}	2.06×10^{-13}	0.0000
BB	3.62×10^{-13}	5.79×10^{-13}	1.14×10^{-13}	8.17×10^{-13}	2.72×10^{-12}	3.35×10^{-12}	2.36×10^{-13}	4.86×10^{-14}
Well								
AW	0.0000	0.0000	0.0000	9.32×10^{-13}	3.05×10^{-13}	0.0000	0.0000	0.0000
HW	0.0000	6.19×10^{-14}	6.10×10^{-13}	6.81×10^{-13}	0.0000	7.62×10^{-13}	1.53×10^{-13}	0.0000
OW	1.37×10^{-13}	9.28×10^{-14}	1.68×10^{-13}	7.91×10^{-13}	7.83×10^{-12}	2.32×10^{-12}	$5. \times 10^{-14}$	0.0000
GW	0.0000	2.52×10^{-13}	3.20×10^{-13}	4.42×10^{-13}	0.0000	2.78×10^{-12}	1.22×10^{-13}	0.0000
BW	0.0000	1.95×10^{-11}	1.07×10^{-13}	2.30×10^{-11}	9.48×10^{-14}	6.73×10^{-12}	1.37×10^{-13}	0.0000
PL	**1.0**	**5.0**	**1.0**	**5.0**	**0.1**	**0.1**	**0.1**	**0.06**

PL = Permissible Limit (USEPA, 2015)

Table 6: Hazard Quotient and Hazard Index for Oral Ingestion in Groundwater of the Study Area

Sample	Fe	Cu	Mn	Zn	Cr	Ni	Cd	Pb	HI
Borehole									
AB	$6.25 x 10^{-}$	$1.19 x 10^{-3}$	$2.06 x 10^{-3}$	$6.89 x 10^{-4}$	$1.68 x 10^{-1}$	$8.94 x 10^{-3}$	$3.55 x 10^{-2}$	0.0000	$2.20 x 10^{-1}$
HB	$9.71 x 10^{-}$	$3.14 x 10^{-4}$	$2.17 x 10^{-4}$	$1.19 x 10^{-4}$	$3.43 x 10^{-2}$	$1.08 x 10^{-3}$	$3.23 x 10^{-3}$	0.0000	$4.00 x 10^{-2}$
OB	$4.33x 10^{-5}$	$1.85 x 10^{-4}$	$3.53 x 10^{-4}$	$1.55 x 10^{-4}$	$5.19 x 10^{-2}$	$2.89x 10^{-3}$	$5.52 x 10^{-3}$	$1.41x 10^{-3}$	$6.24 x 10^{-2}$
GB	$3.00x 10^{-1}$	$1.21 x 10^{-3}$	$1.80 x 10^{-8}$	$1.38 x 10^{-4}$	$2.06 x 10^{-2}$	$9.05 x 10^{-3}$	$5.14 x 10^{-3}$	0.0000	$3.61 x 10^{-2}$
BB	$2.33 x 10^{-}$	$6.23 x 10^{-4}$	$2.04 x 10^{-4}$	$1.17 x 10^{-4}$	$1.13 x 10^{-2}$	$2.09 x 10^{-3}$	$5.90 x 10^{-3}$	$5.99 x 10^{-4}$	$2.10 x 10^{-2}$
Well									
AW	0.0000	0.0000	$3.27 x 10^{-4}$	0.0000	0.0000	0.0000	0.0000	0.0000	$3.27 x 10^{-4}$
HW	0.0000	$6.67 x 10^{-5}$	$1.08 x 10^{-3}$	$9.77 x 10^{-5}$	0.0000	$4.76 x 10^{-4}$	$3.81 x 10^{-3}$	0.0000	$6.00 x 10^{-3}$
OW	$8.44 x 10^{-}$	$1.00 x 10^{-4}$	$2.99 x 10^{-4}$	$1.14 x 10^{-4}$	$3.26 x 10^{-2}$	$1.45x 10^{-4}$	$1.33 x 10^{-3}$	0.0000	$3.50 x 10^{-2}$
GW	0.0000	$2.71x 10^{-4}$	$5.71x 10^{-4}$	$6.35 x 10^{-5}$	0.0000	$1.37 x 10^{-3}$	$3.05 x 10^{-3}$	0.0000	$5.32 x 10^{-3}$
BW	0.0000	$1.51 x 10^{-5}$	$1.37 x 10^{-3}$	$1.06 x 10^{-4}$	$1.43 x 10^{-1}$	$1.11 x 10^{-3}$	$1.40 x 10^{-3}$	0.0000	$1.50 x 10^{-1}$
Mean	**9.00×10^{-5}**	**4.42×10^{-4}**	**7.20×10^{-4}**	**$1.50 x 10^{-4}$**	**$5.13 x 10^{-1}$**	**$3.01 x 10^{-3}$**	**$7.21 x 10^{-3}$**	**$2.23 x 10^{-4}$**	**$6.40 x 10^{-2}$**

Table 7: Hazard Quotient and Hazard Index for Dermal Ingestion in Groundwater of the Study Area

Sample	Fe	Cu	Mn	Zn	Cr	Ni	Cd	Pb	HI
Borehole									
AB	$2.26x 10^{-9}$	$9.37 x 10^{-11}$	$2.31 x 10^{-8}$	$7.99 x 10^{-11}$	$5.38 x 10^{-7}$	$1.43 x 10^{-11}$	$1.42 x 10^{-7}$	0.0000	$7.06 x 10^{-7}$
HB	$3.51x 10^{-10}$	$2.43 x 10^{-11}$	$2.44 x 10^{-9}$	$8.31 x 10^{-13}$	$1.01 x 10^{-7}$	$1.74 x 10^{-12}$	$1.26x 10^{-8}$	0.0000	$1.20 x 10^{-7}$
OB	$1.56 x 10^{-10}$	$1.44 x 10^{-11}$	$3.35 x 10^{-9}$	$1.08 x 10^{-12}$	$1.66 x 10^{-7}$	$4.63 x 10^{-12}$	$2.21 x 10^{-8}$	$2.74x 10^{-10}$	$2.00 x 10^{-7}$
GB	$1.12x 10^{-10}$	$9.43x 10^{-11}$	$1.80 x 10^{-8}$	$9.65 x 10^{-13}$	$6.58 x 10^{-8}$	$1.45 x 10^{-12}$	$2.01 x 10^{-8}$	$1.16x 10^{-10}$	$1.04 x 10^{-7}$
BB	$8.05 x 10^{-11}$	$4.82 x 10^{-11}$	$2.29 x 10^{-9}$	$8.18 x 10^{-13}$	$3.64 x 10^{-8}$	$3.35 x 10^{-12}$	$2.36 x 10^{-8}$	0.0000	$6.24 x 10^{-7}$
Well									
AW	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.0000	0.0000
HW	0.0000	$5.15 x 10^{-12}$	$1.22 x 10^{-8}$	$6.80 x 10^{-13}$	0.0000	$7.63 x 10^{-13}$	$1.53 x 10^{-8}$	0.0000	$3.00 x 10^{-7}$
OW	$3.04 x 10^{-11}$	$7.73 x 10^{-12}$	$3.35 x 10^{-4}$	$7.91 x 10^{-13}$	$1.04. x 10^{-7}$	$2.32 x 10^{-12}$	$5.33 x 10^{-9}$	0.0000	$3.40 x 10^{-4}$
GW	0.0000	$2.10 x 10^{-11}$	$6.40x 10^{-1}$	$4.42 x 10^{-13}$	0.0000	$2.78x 10^{-12}$	$1.22 x 10^{-8}$	0.0000	$6.40 x 10^{-1}$
BW	0.0000	$5.52 x 10^{-3}$	$7.13 x 10^{-9}$	$1.23 x 10^{-11}$	$6.60 x 10^{-8}$	$3.37 x 10^{-7}$	$4.49 x 10^{-9}$	0.0000	$5.52 x 10^{-3}$
Mean	**2.98×10^{-10}**	**5.52×10^{-4}**	**0.06×10^{-0}**	**7.99×10^{-10}**	**1.08×10^{-7}**	**3.37×10^{-8}**	**2.57×10^{-8}**	**3.9×10^{-11}**	**$7.20 x 10^{-2}$**

Key
A = Adabeji; H = Main Hostel; O = Odo Ona; G = Gbekuba; B = Bora Hostel; Pb = Lead; Zn = Zinc; Mn = Manganese; Cr = Chromium; Cd = Cadmium; Ni = Nickel; Fe = Iron; Cu = Copper

CONCLUSION

This study assessed the heavy metal contents and associated health risks in groundwater samples obtained around Federal College of Animal Health and Production Technology, Ibadan Students' residential areas. The study revealed that the water samples contained mean concentrations of Pb, Cd, Fe, Zn, Cr, Mn and Ni above the WHO limits except for Cu, with contamination factor values indicating moderate contamination for Cu, Zn and Mn, and very high contamination for Fe, Pb, Mn, Cr, Ni and Cd; quantification of contamination showed that most of the heavy metals, except Cu in certain locations, were of anthropogenic origin; although average daily dose, hazard quotients, and hazard index values for both oral and dermal exposures were below the provisional tolerable daily intake limit – indicating negligible immediate health risks. However, routine monitoring of the groundwater water samples of the study area should be encouraged, to curtail health-related risks from exposure to heavy metal toxicity.

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