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Research Article

Assessing the Life Average Daily Dose (Ladd) due to Heavy Metal Contents in Water Samples from Covenant University, Canaanland, Ota, South West Nigeria

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Abstract. The consumption of water with elevated concentration of lead (Pb) can prevent Hemoglobin Synthesis (Anemia) and results in Kidney diseases. A cross sectional study was conducted in to estimate the risk of exposure to lead via groundwater and bottled water ingestion pathway for the population of Covenant University, Canaanland, Ota, Ogun Sate using Perkin Elmer Optima 8000 ICP-OES. The concentration of Pb, Cr, Cd and As varies from water sample to another with the highest value of .7.07 μgL^{-1} was noted in borehole water sample (BH1) behind John Hall. Comparing the value with the International recommended level by USEPA and WHO respectively, $7.07 gL^{-1}$is less than $15 \mu gL^{-1}$ and 10 μgL^{-1}. The Life Average Daily Dose (LADD) estimated in this present study reported higher in BH1 for lead (Pb) and could pose health hazard if accumulated for a long time. This work suggest measures to employ quality water treatment plant to reduce the level of heavy metals in the selected water samples and also more research on radioisotopes in the same water samples.

Keywords. Groundwater; Bottled water; Heavy metals ICP-OES; Chronic daily intake and hazard

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1. Introduction

The presence of heavy metals such as lead in drinking water resources can be dangerous for human because of toxicity and biological accumulation. The consumption of water or food which contains lead in high concentration can lead to prevent from Hemoglobin Synthesis (Anemia) and Kidney diseases. The heavy metals are the elements with a special weight 4-5 times as much as water (Duruibe et al. [14]; Raikwar et al. [42]). These elements have biological accumulation, toxicity, and environmental sustainability properties (Pekey et al. [41]). In recent years, the presence of these metals such as Arsenic (As), Cadmium (Cd), Mercury (Hg), lead (Pb), Nickel (Ni), and Chromium (Cr) in drinking water have become an international environmental and health concern (Dogaru et al. [13]; Wang et al. [53]; Ghaderpouri et al. [18]). The entry of the heavy metals in water resources can be due to the natural processes such as wastewater municipal, industrial, and agricultural sewage (Demirak et al. [12]).

Assessing the exposure and health consequences of chemicals in drinking water is a challenge: exposures are typically at low concentrations, measurements in water are frequently insufficient, chemicals are present in mixtures, exposure periods are usually long, multiple exposure routes may be involved, and valid biomarkers reflecting the relevant exposure period are scarce. In addition, the magnitude of the relative risks tends to be small (Villanueva et al. [52]). Many studies have measured the heavy metals concentration in drinking water and compared it with standard value (Arab et al. [3]; Shotyk et al. [47]; Dabeka et al. [10]; Ikem et al. [24]). Also, in some studies, carcinogenic (R) and non-carcinogenic risk (HQ) of the heavy metals which are due to drinking water consumption, have been assessed (Wang at al. [53]; Jakus et al. [26]; Muhammad et al. [35]). Metals could exert effects that are beneficial or harmful to our human body (Caussy et al. [11]). Heavy metals are especially renowned for their toxicity effects towards human beings, aquatic life and the environment. Lead is one of the heavy metals which have no known physiologically relevant role in the body (White et al. [54]). Lead from environmental pollution is not carcinogenic, but even low dose lead exposure has been shown to have detrimental and long-lasting effects on the renal, hemopoietic and nervous system (Fertmann et al. [17]).

The main target for lead toxicity is the nervous system, both in adults and children (ATSDR [4]). It can create irreversible intellectual impairment in infants and young children, even at blood lead levels below10 mg/dL (Lanphear et al. [30]; Gump et al. [20]; Jusko et al. [28]). The continuous in exposure results with the effect progresses with insomnia, confusion, impaired concentration, and memory problems (Robson [43]). In addition to exposure to lead in the air, ingestion of lead in drinking water has become one of the major sources of human exposures to lead (Matte et al. [33]). The presence of lead in drinking water is a public health problem due to their absorption and possible accumulation in organisms (Chiron et al. [8]).

Studies to assess the LADD exposure of Pb, Cr. Cd and As contaminants in both groundwater and bottled water samples collected from Covenant University, Ota, Ogun State is needed for its potential health risks for age groups of adult men, adult women and children and to compare with the standard value because of sanitary importance of lead in drinking water.

2. Geology and Geographical Location of the Study Area

Covenant University is in Ogun State, which falls within the Eastern Dahomey (Benin) Basin of south-western Nigerian that stretches along the continental margin of the Gulf of Guinea.Rocks in the Dahomey basin are Late Cretaceous to Early Tertiary in age (Jones et al. [27]; Omatsola et al. [39]; Bilman [5]; Olabode [38]). The stratigraphy of the basin has been classified into Abeokuta Group, Imo Group, Oshoshun, Ilaro and Benin Formations. The Cretaceous Abeokuta Group consists of Ise, Afowo and Araromi Formations consisting of poorly sorted ferruginized grit, siltstone and mudstone with shale-clay layers.

3. Sampling and Sample Preparation

Five different water samples (3 groundwater and 2 bottled water) used for consumption and domestic purposes in both Covenant University and Canaan Land were collected for this assessments. The pH was measured on the spot, by using a CONSORT C931 instrument. From each sampling point, the water samples were collected in cleaned plastic bottles pre-washed with 20% nitric acid (HNO_3) and double distilled water. The water samples were filtered and a few drops of HNO_3 were then added before sample transport to the laboratory. For ICP-AEO analysis, all the samples were stored in a refrigerator at 4-6°C in order to measure the heavy metals concentrations (Eaton et al. [15]).

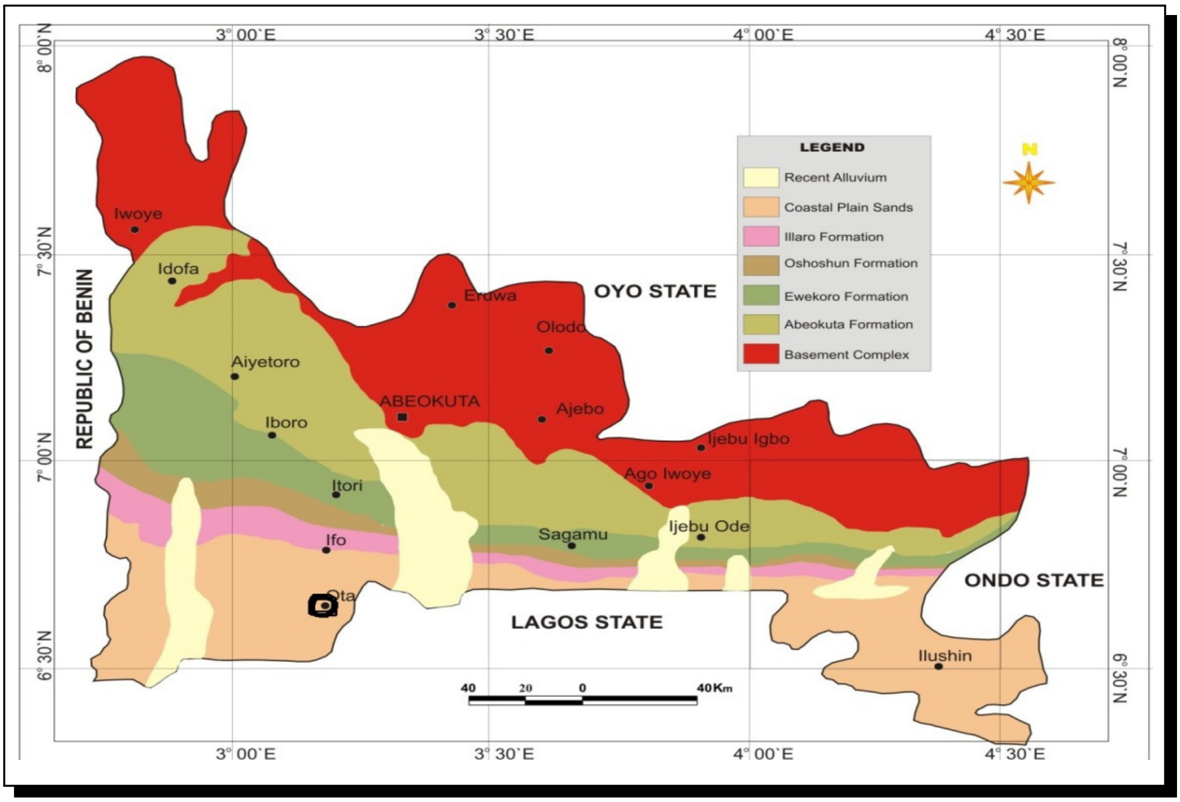

Figure 1. Geologic map of Ogun state showing the location of the study area (circled in black) (Source: Nigerian Geological Survey Agency (2006))

3.1 Chemical Analysis for Heavy Metals

All filtered and acidified water samples were analyzed for heavy metals by using ICP-AEO Under standard operating conditions. In view of data quality assurance, each sample was analyzed in triplicate and after every 10 samples two standard; one blank and another of 2.5 μg/L of respective metal were analyzed on atomic adsorption. The reproducibility was found to be at 95% confidence level. Therefore, the average value of each water samples was used for further interpretations. Standard solutions of all eight elements were prepared by dilution of 1000 mg/L certified standard solutions from the manufacturer for corresponding metal ions with double distilled water. All the acids and reagents used were of analytical grade. All these analyses were performed in the international institute for Tropical agriculture Laboratory, Ibadan, Nigeria

Chemicals that display environmental and biological persistence, bioaccumulation, toxicity and long-range transport have been previously assessed quantitatively by national and international health agencies (Szabo et al. [46]). Among the databases that offer information on the toxicity of the compounds that can be found in water, two of the most widely used are the Risk Assessment Information System reference to the WHO guidelines (WHO [56]). RAIS uses the Reference Dose (RfD), expressed as an oral dose per kilogram of body weight (given in units of mg Kg^{-1} day^{-1}), as an estimate of the lowest daily human exposure that is likely to occur without appreciable risk of deleterious, non-cancerous effects during a lifetime. WHO proposes a very similar reference value called the Tolerable

Where Di represents the dose of contaminant by water ingestion (mgKg^{-1} day^{-1}), Cw is the annual average concentration of the contaminant in water (mg L^{-1}), EF is the exposure frequency to the contaminated media (day $year^{-1}$), ED is the exposure duration (year), IRw is the rate of water intake (L day^{-1}), BW is the body weight of the receptor (Kg), and AT is the average lifetime of a person(year).

Table 1 shows the exposure values for the pathway of oral ingestion of water accordingly to RAIS and WHO for the calculation of doses. For systemic risk Di is calculated by using $AT = ED$. Then three different indexes (systemic and carcinogenic for RAIS and an index for WHO) were calculated:

3.2 Chemical Toxicity Risk of Heavy Metals

The chemical toxicity was to determine the effect of the carcinogenic risks associated with chemical toxicity of Pb, Cr, Cd and As in the water sample selected for this study. The chemical toxicity risk was evaluated using the lifetime average daily dose of Pb, Cr, Cd and As through drinking water intake, and compared it with the reference dose (RFD) of 0.6μg kg^{-1} day^{-1} (USEPA [50]) used as a standard criteria for Pb, Cr, Cd and As in several foreign organizations and thereby produce the lifetime average daily dose (LADD) (Equation (3))

$$\text{Ingestion LADD of drinking water} = \frac{EPC \times IR \times EF \times ED}{AT \times BW}, \tag{3.1}$$

where

$LADD$ = lifetime average daily dose (μg kg^{-1} day^{-1}),
EPC = the exposure point concentration (μg L^{-1}),
IR = the water ingestion rate (L day^{-1}); EF = the exposure frequency (days year^{-1}),
ED = the total exposure duration (years), AT = the average time (days), and
BW = the body weight (kg).

Using therefore, $IR = 2$ L day^{-1}, $EF = 350$ days, $ED = 45.5$ y, $AT = 16,607.5$(obtained from 45.5×365) and $BW = 70$ kg (for a standard man).

4. Results and Discussion

4.1 Concentration of Lead (Pb) in Water Samples from the Study Area

Table 1 presents the concentrations of Pb in different water samples. The concentrations of leading water samples varies from 2.84 to 7.07μgL^{-1}. The highest concentration of Pb was noted at BH2 water sample with a value of 7.07μgL^{-1} whereas the lowest value of 2.84 μgL^{-1} reported in BK water sample. This higher concentration value found in BH2 water sample could be attributed to infiltration of surface sediments contaminants through the borehole due to the rainy Season. It could report when the subsurface formation is highly saturated within the study area. In all the water samples, the concentrations vary between 2.84 to 7.07μgL^{-1}respectively. Comparing the highest value of 7.07 μgL^{-1} obtained from this present study with the International Reference Standard according to WHO [56] and USEPA [51] of 15 μgL^{-1}, it can be observed that the value is far below by a factor of 2.15. More so, comparing with the National Drinking Water Quality Standard (NDWQS) for lead (Pb) concentration in water is given as 10 μgL^{-1}, of which the values for this present study in all the water samples did not exceeded the acceptable values.

Table 1. Concentrations of Lead (Pb) in Groundwater and Bottled Water Samples in the Study Area, USEPA, WHO [56] and National Drinking Water Quality Standard (NDWQS)

Sample ID	Sample Location	Concentration of Lead Lead (Pb) (μgL^{-1})	USEPA, WHO, (μgL^{-1})	NDWQS (μgL^{-1})
BH1	John Hall	7.07	15	10
BH2	New Estate	7.51	15	10
BH3	Canaan Land	6.47	15	10
HB	Hebron Water	4.42	15	10
BK	Baker Water	2.84	15	10

4.2 Concentration of Cadmium in the Selected Water Samples from the Study Area

Cadmium in selected water samples were measured to ascertain the level of exposure to the dwellers that rely on the water samples. The concentration varies from 0.117 to 0.145 g/L. The highest value reported in BK water sample with a value of 0.145 μg/L whereas the lowest value of 0.117 μg/L noted in BH1 water samples. There are variations in concentration levels in the study area but noted that borehole samples were having less concentrations of cadmium. Comparing these values with the international reference values, it can be observed that the present study is lower as shown in Table 2.

Table 2. The Concentrations of Cadmium (Cd) in all the Selected Water Samples

Sample ID	Concentration (Cd) (μgL^{-1})	USEPA,WHO, (μgL^{-1})	NDWQS (μgL^{-1})
BH1	0.117	15	10
BH2	0.114	15	10
BH3	0.131	15	10
HB	0.141	15	10
BK	0.145	15	10

4.3 Concentrations of Arsenic (As) in the Water Samples from the Study Area

From the table below, the concentration of As varies from 0.14 to 0.18 μgL^{-1} with the highest value of 0.18 μgL^{-1} noted in BH1 borehole where a lower value of 0.14 gL^{-1} reported in BK bottled water sample. Chronic As exposure may also cause reproductive, neurological, cardiovascular, respiratory, hepatic, hematological, and diabetic effects in humans (WHO [55]). Intake of inorganic As was recognized as a cause of skin, bladder, and lung cancer (WHO [55]; IARC [23]). A number of articles have been published on chronic As exposure and its associated health effects. Herein, the adverse health effects of As are reviewed. Engel and Smith [45] reported the relationship between cardiovascular mortality and As exposure in 30 US counties where the average As concentration in drinking water was > 5 μgL^{-1}. Comparing this present study with other studies according to the relationship between exposure and internal cancer risks in Finland with concentration of <0.1 μgL^{-1}, with risk of bladder cancer, in Chile with concentrations varying from 0-10 μgL^{-1} (Ferreccio et al. [16]) with the risk of lung cancer; in Nijata, Japan, the concentration of 0.5 μgL^{-1}As was noted in drinking water, varying from 0.05 μgL^{-1}-0.99 μgL^{-1} with risk exposure of bladder cancer, the present study with concentration of 0.18 μgL^{-1} and varying from 0.14-0.18 μgL^{-1} is within range of bladder cancer exposure to the consumers. The results of the concentrations are presented in Table 3.

Table 3. Comparing the Arsenic Concentrations in Groundwater and Bottled Water Samples in the Study Area, USEPA, WHO [56] and National Drinking Water Quality Standard (NDWQS)

Sample ID	Concentration of Arsenic (As) (μgL^{-1})	USEPA, WHO (μgL^{-1})	NDWQS (μgL^{-1})
BH1	0.18	15	10
BH2	0.15	15	10
BH3	0.16	15	10
HB	0.16	15	10
BK	0.14	15	10

4.4 Concentration of Chromium (Cr) in Water Samples from the Study Area

Table 4 presents the concentration of chromium in some selected water samples in Covenant University and environs. The concentration of chromium values in the water samples selected ranged between 0.03 μgL^{-1} and 0.25 μgL^{-1} with highest concentration value of Cr of 0.25 μgL^{-1} observed in BH1 and lowest value of 0.03 μgL^{-1} in BH3. This higher concentration value observed in BH1 water sample could be related to infiltration of surface sediments contaminants such as chromium solders, brass fittings, fountains, and taps through the borehole as a result of rainy season by transporting these anthropogenic materials into the samples. It could report when the subsurface formation is highly saturated within the study area. In the entire water sample selected, the concentration varies from 0.03 μgL^{-1} to 0.25 μgL^{-1}. Comparing the highest value of 0.25 μgL^{-}obtained from this present study with the International Reference Standard according to WHO [55], WHO [56] of 50 μgL^{-1} and National Drinking Water Quality Standard (NDWQS [36]) of value of 50 μgL^{-1} respectively with this study, it was observed that the concentration of chromium level in the selected samples is within the permissible value.

Table 4. Concentrations of Chromium (Cr) in Groundwater and Bottled Water Samples in the Study Area, WHO [55], USEPA, WHO [56] and National Drinking Water Quality Standard (NDWQS [36])

Sample ID	**Concentration of Chromium (Cr) (μgL^{-1})**	**WHO** [55] **Standard**	**WHO** [56] **Standard**	**USEPA** [49] **Standard**	**NDWQS** [36]
BH1	0.25	50	50	50	50
BH2	0.19	50	50	50	50
BH3	0.03	50	50	50	50
HB	0.20	50	50	50	50
BK	0.14	50	50	50	50

4.5 Chemical Toxicity Risk of Pb, Cr, Cd and As in Water Samples from the Study Area

The chemical toxicity risk was to determine the effect of the carcinogenic risks associated with chemical toxicity of Pb in the water sample selected for this study. The chemical toxicity risk was evaluated using the lifetime average daily dose of Pb through drinking water intake, and compared it with the reference dose (RFD) of 0.6 $\mu g\ kg^{-1}\ day^{-1}$ (Ye-Sin et al. [57]; USEPA [50]) used as a standard criteria for Pb in several foreign organizations and thereby produce the lifetime average daily dose (LADD) (Equation (4.1))

$$\text{Ingestion } LADD \text{ of drinking water} = \frac{EPC \times IR \times EF \times ED}{AT \times BW} \tag{4.1}$$

Where, $LADD$ is lifetime average daily dose ($\mu g\ kg^{-1}\ day^{-1}$), EPC is the exposure point concentration ($\mu g\ L^{-1}$), IR is the water ingestion rate ($L\ day^{-1}$); EF is the exposure frequency ($days\ year^{-1}$), ED is the total exposure duration (years), AT is the average time (days) and BW is the body weight (kg). Using therefore, IR= 2 L day^{-1}, EF = 350 days, ED = 45.5 y,AT = 16,607.5 (obtained from 45.5 × 365) and BW = 76 kg (for a standard man). The chemical toxicity risk for Pb over lifetime consumption was estimated and presented in Table 5.

In Table 8, the exposure dose of Pb in all the water samples ranged from 0.10 to 0.26μg kg^{-1} day^{-1}for men whereas value of 0.09 to 0.24 μg kg^{-1} day^{-1}were found in the same BH2 water sample. The highest values of LADDs of 0.26 and 0.24 μg kg^{-1} day^{-1}reported in BH2 for both adult men and women respectively. These values that were distinctly higher in this same borehole water sample for all the assessments could be due to the upward migration of ultrabasic minerals derived from magmatic and metamorphic processes of intrusive materials in groundwater bearing formation. Comparing the LADD obtained in this study and the RFD (0.6 μg kg^{-1}day^{-1}) that is an acceptable level, the chemical toxicity risk due to Pb in the water samples were all below the RFD. It indicates that there may not be health risks associated with Pb in the water samples which are mainly due to the chemical toxicity risk of Pb.

Table 5. The lifetime average daily dose (LADD) of Lead (Pb) in the water samples

Sample ID	***LADD*** **(μg kg^{-1} day^{-1}) for lead**	**Reference Dose Level (μg kg^{-1} day^{-1}) (Ye-Shin et al. [57])**
BH1	0.24	0.6
BH2	0.26	0.6
BH3	0.22	0.6
HB	0.15	0.6
BK	0.10	0.6

4.6 Chemical Toxicity Risk of Chromium (Cr) in Water Samples from the Study Area

The chemical toxicity risk was to determine the effect of the carcinogenic risks associated with chemical toxicity of Cr in the water sample selected for this study. The chemical toxicity risk was evaluated using the lifetime average daily dose of Cr through drinking water intake, and compared it with the reference dose (RFD) of 0.6 μg kg^{-1} day^{-1} (Ye-Sin et al. [57]; USEPA [50]) using Equation (4.1).

In Table 7, the exposure dose of Cr in all the water samples ranged from 0.00075to 0.0063μg kg^{-1} day^{-1}with the highest value found in BH1 water sample. Comparing the LADD obtained in this study and the RFD (0.6 μg kg^{-1}day^{-1}) that is an acceptable level, the chemical toxicity risk due to Cr in the water samples distinctly lower than the RFD. It indicates that there may not be health risks associated with Cr in the water samples which are mainly due to the chemical toxicity risk of Cr. The results are presented in Table 6.

Table 6. The lifetime average daily dose (LADD) of chromium in the water samples

Sample ID	***LADD*** **(μg kg^{-1} day^{-1}) for chromium**	**Reference Dose Level (μg kg^{-1} day^{-1}) (Ye-shin et al. [57])**
BH1	0.0063	0.6
BH2	0.0047	0.6
BH3	0.00075	0.6
HB	0.00504	0.6
BK	0.0035	0.6

4.7 Chemical Toxicity Risk of Arsenic (As)in Water Samples from the Study Area

In Table 7, the exposure dose of As in all the water samples ranged from 0.00403to 0.0045μg kg^{-1} day^{-1}with the highest value found in BH1 water sample. Comparing the LADD obtained in this study and the RFD (0.6 μg kg^{-1}day^{-1}) that is an acceptable level, the chemical toxicity risk due to As in the water samples is below the RFD. It indicates that there may not be health risks associated with As in the water samples which are mainly due to the chemical toxicity risk of As.

Table 7. The lifetime average daily dose (LADD) of Arsenic(As) in the water samples

Sample ID	*LADD* (μg kg^{-1} day^{-1}) for Arsenic	Reference Dose Level(μg kg^{-1} day^{-1}) (Ye-Shin et al. [57])
BH1	0.0045	0.6
BH2	0.0037	0.6
BH3	0.00403	0.6
HB	0.00403	0.6
BK	0.0035	0.6

4.8 Chemical Toxicity Risk of Cadmium (Cd)in Water Samples from the Study Area

In Table 8, the exposure dose of Cd in all the water samples ranged from 0.0028to 0.0036μg kg^{-1} day^{-1}with the highest value found in BK water sample. Comparing the LADD obtained in this study and the RFD (0.6 μg kg^{-1}day^{-1}) that is an acceptable level, the chemical toxicity risk due to Cd in the water samples was far below the RFD. It indicates that there may not be health risks associated with Cd in the water samples which are mainly due to the chemical toxicity risk of Cd.

Table 8. The lifetime average daily dose (LADD) of Cadmium (Cd) in the water samples

Sample ID	*LADD* (μg kg^{-1} day^{-1}) for Cadmium	Reference Dose Level (μg kg^{-1} day^{-1}) (Ye-Shin et al. [57])
BH1	0.0029	0.6
BH2	0.0028	0.6
BH3	0.0033	0.6
HB	0.0035	0.6
BK	0.0036	0.6

In Figure 2, it presents the life average daily dose obtained from the borehole water sample one (BH1) and sample two (BH2) collected from john hall and new estate as well as water sample three (BH3) from Canaanland. Two bottled water samples labeled HB from canaanland and BK from Bake water were compared too as well as the borehole water samples. It can be noted that the highest value of LADD for lead reported higher in BH1 than other heavy metals analyzed for this study as presented in Figure 2. It can be observed that all the values in Figure 2 are less than 0.6 μg kg^{-1} day^{-1}recommended as the safe level by USEPA [49].

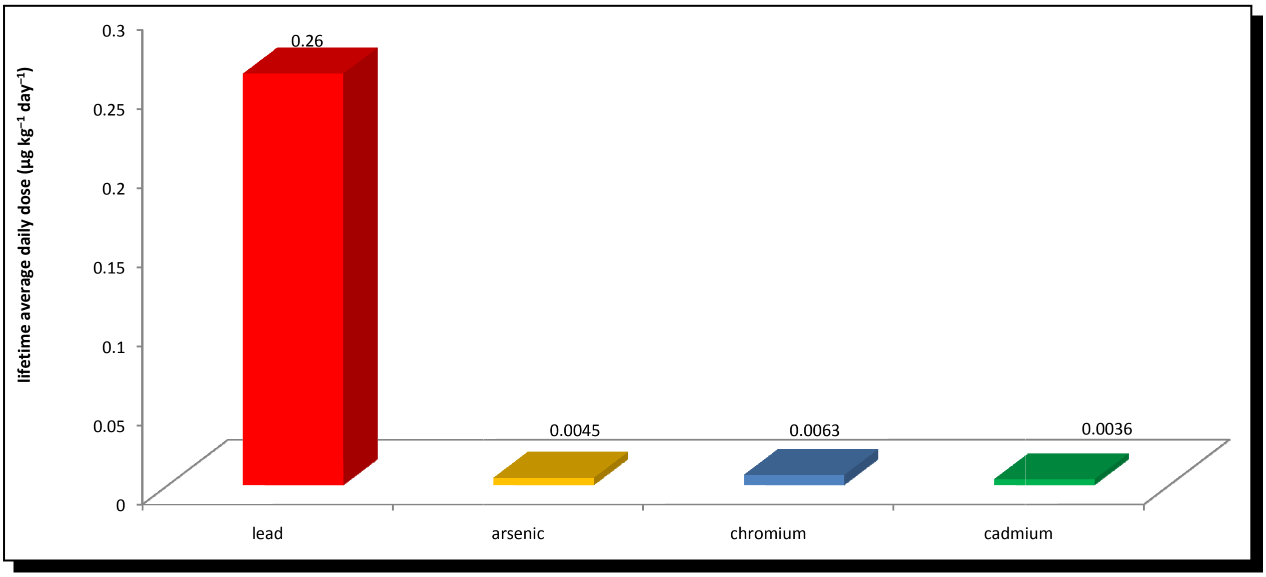

Figure 2. Plot of life average daily dose (μg kg^{-1} day^{-1}) against lead, arsenic, cadmium and chromium in the Water Samples

5. Conclusion

The concentrations of Pb, Cr, Cd and As in selected groundwater and bottled water samples in the study area are less than the standard reported values by WHO [56] and USEPA [49] of 15 μgL^{-1} as well as 10 μgL^{-1}when compared with the National Drinking Water Quality Standard (NDWQS). The LADD revealed that Lead in BH1 could pose health risk considering long term accumulation; though lower than the Reference Dose Level. This research calls for further impact assessment of risk due to radioisotopes in water samples to justify the effect of human health risk either from heavy metals or radioisotopes on the inhabitants of the study area.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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