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TOXIC IMPLICATIONS OF HEAVY METALS IN DRINKING WATER SOURCES OF LOKO AND MARARRABA IN NASARAWA STATE, NIGERIA

[*1]Rilwan, U., [2]Bello, A. A. and [3]Ubaidullah, A.

[1]Department of Physics, Nigerian Army University, PMB 1500 Biu, Borno State, Nigeria.
[2]Department of Physics, Federal University, Lafia, Nasarawa State, Nigeria.
[3]Federal University Dutsin-ma, P.M.B 5001 Dutsin-ma, Katsina State, Nigeria.

[*]Corresponding Author email: rilwanusman@naub.edu.ng

ABSTRACT
Metals are substances with high electrical conductivity, malleability, and luster, which voluntarily lose their electrons to form cations. This study aimed at assessing the Toxic implications of Heavy Metals in Drinking Water Sources of Loko and Mararraba in Nasarawa using Micro Plasma Atomic Emission Spectroscopy (MP-AES). The results showed that, seven heavy metals along with their respective concentrations for both Loko and Mararraba in mg/L (Zn (0.19 and 0.23), Cd (0.00 and 0.00), Fe (0.05 and 0.04), Cu (0.01 and 0.01), Pd (0.01 and 0.01), Ni (0.003 and 0.002) and Mn (0.092 and 0.027)) respectively were present in the water samples. The Hazard Quotient (HQ) was all recorded to be lower than unity. The Hazard Index (HI) was also recorded to be $4.6x10^{-4}$ and $5.7 x 10^{-4}$ for both Loko and Mararraba respectively, value less than unity. This makes non-carcinogenic effects negligible. The total excess life cancer risk was found to be $36.1.4x10^{-13}$ and $41.46x10^{-13}$ for both Loko and Mararraba respectively, value less than that of U.S ($1.0x10^{-4}$ to $1.0x10^{-6}$) and South Africa ($5.0x10^{-6}$). This makes carcinogenic effects negligible. Regular monitoring and evaluation of the water at the sample locations is recommended.

Keywords: Heavy metals; cancer risk; total risk; hazard quotient; hazard index; micro plasma atomic emission spectroscopy.

INTRODUCTION

The inability to access potable water supply in developing countries according to WHO (2005) and Rilwan *et al.,* (2020) is a global issue that needs urgent attention. About 884 million people in the world, mostly in developing countries do not have access to drinking water sources that conform to the permissible limit specification of WHO. More so, in developing countries of the world, about 780 million people lack access to potable water as result of pollution, which has been attributed to contamination with microorganisms and chemicals as pointed out by Cervantes *et al* (2001) and Usman *et al*. (2020). These chemical contaminations involve mainly pollution of water bodies with heavy metals through anthropogenic activities. The principal sources of surface and groundwater pollution by heavy metals according to Gupta *et al.* (2013) and Rodriguez *et al.* (2007) are natural processes and anthropogenic activities. The rise in concentration of heavy metal in water irrespective of the origin as pointed out by Zayed & Terry (2003) and Rodriguez et al. (2007) is posing a serious health threats to human and aquatic ecosystems. Arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn) as reported by WHO (2005) and Jarup (2003) are the most familiar heavy metals of health concern to human. When the concentrations of heavy metal in water surpass the environmental acceptable border, the use of such water for agricultural purposes might be detrimental to the aquatic ecosystem and human through the food chain as pointed out by Wright and Nagajyoti (2010). For instance, several kinds of diseases besides organ dysfunction had correlation with raised levels of heavy metal concentrations in drinking water sources above the permissible limit specified by regulatory bodies reported by Morais (2012) and Gurkan *et al*. (2012). Additionally, heavy metal contamination of drinking water sources has been linked with deficiencies of some essential nutrients, which culminates in compromised immunological defenses, disabilities associated with malnutrition, intrauterine growth retardation, impaired psychosocial faculties, and increased prevalence of upper gastrointestinal cancers as in Lambert et al. (2000) and Ghani (2011). Although few of these heavy metals like Cu, Iron (Fe), Ni and Zn are essential nutrients required in trace amount for animals and plants; they are harmful at high levels. However, some heavy metals like Cd, Cr, Pb and cobalt (Co) have no known physiological functions and are deleterious at certain levels according to Flora et al. (2008), Khlifi & Hamza-Chaffai (2010) and Jaishankar et al. (2014). This study is therefore aimed at determining and comparing the levels of some heavy metals (Pb, Cd, Fe, Ni, Mn, Cu and Zn) in the drinking water sources from Loko and Mararraba community in Nasarawa Local Government Area using Micro Plasma Atomic Emission Spectrometer (MP-AES). It also seeks to assess the trace metal indices in comparison with the observed concentration of water quality permissible limit specified by WHO (2005), even though similar work has been reported but different location by the same author.

MATERIALS AND METHOD

Materials

The instruments/materials that were used for the assessment of heavy metals concentration in portable drinking water across

Loko and Mararraba of Nasarawa Local Government Area in Nasarawa State are shown in Table 1

Table 1: Materials, Specifications and Uses

Materials	Quantity	Specifications	Uses
500ml bottles	1	Plastic Type	Used for collection of water samples.
Funnel	1	Plastic Type	Used for easy passage of water samples into the sample bottles.
Cup	1	Plastic Type	Used for easy transfer of water sample through the funnel to bottles.
Hand Glove	5 sets	Polythene	Used to protect the hand from direct contact to the chemicals.
pH Metre	1	Hanna Plastic type, Range 0-14, Resolution 0.1, Accuracy ±0.1, Consort C937.	Used for measuring the acidity and basicity of the water samples.
Concentrated Nitric Acid	500 ml	Liquid Type	Used for rinsing the sample bottles before (HNO_3) sample collection.
Drawer	1	Rubber Type	Used for drawing water from the well.
Masking Adhesive Tapes	1	Paper Type	Used for labeling the water samples as well as sealing the mouth of the bottles.
Global Positioning System	1	URIC Type	Used for taking the coordinates of each sample points.
Sack	1	Leather Type	Used for packaging of collected water samples for easy transportation.
Macro Plasma Atomic Emission Spectrometer.		MP-AES-MY17380004	Used for analyzing the water samples in the laboratory.

Method

On the basis of geologic and tectonic setting, two towns having 3 each were selected for water sampling. The representative water samples (1 L each) were therefore, collected from Borehole (1 sample), well (1 sample) and stream (1 sample). The pH was measured on the spot, using a pH meter (Hanna instrument). From each sampling point, the water samples were collected in cleaned plastic bottles pre-washed with 20% dilute nitric acid (HNO_3) and double distilled water. The water samples were filtered and a few drops of $HNO_3$was then added before transporting the sample to the laboratory for analysis.

Study Area

This research work centered on Loko and Mararraba of Nasarawa Local Government, in Nasarawa State. The sample points are abbreviated as L1, L2 and L3, for Loko Borehole, Loko Well and Loko Stream respectively, while, M1, M2 and M3 for Mararraba Borehole, Mararraba Well and Mararraba Stream respectively. These points are located at $8^0 00'13.40''N$ and $7^0 50'17.58''E$, $8^0 59'45.25''N$ and $7^0 50'30.54''E$, $8^0 00'06.25''N$ and $7^0 36'36.55''E$, for Loko, while, $8^0 31'59.12''N$ and $7^0 43'31.61''E$, $8^0 18'35.26''N$ and $7^0 48'13.22''E$, $8^0 18'25.30''N$ and $7^0 48'28.12''E$, for Mararraba.

Method of Sample Collection

Six (6) water samples were randomly collected from different points in different district across Loko and Mararraba in Nasarawa Local Government Area. The sampling was carried out in a season. Two (2) drops of nitric acid (HNO_3) was added to each water sample before analyzed to maintain the constant pH and minimize loss of sample because of variation in pH, evaporation, precipitation and other relevant physical and chemical properties. Samples were collected from different water sources such as streams, wells and boreholes located at Loko and Mararraba. The samples were collected randomly using acidified plastic bottles and mixed. The bottles were filled and then sealed tightly to avoid head space that might cause loss of samples because of oxidation.

Method of Sample Preparation

The samples for analysis were digested by measuring 250ml of the water sample in a conical flask and 5ml of concentrated nitric acid was added to the measured sample and then heated on microwave machine until the total volume was reduced to about one third of the initial volume to break the complex bond and release the sample into solution. The solution was then filtered using a filter paper into another beaker, made up of 50ml with distilled water and mixed thoroughly. The sample was packaged into samples bottles before taking to MP-AES machine for analysis.

Method of Sample Analysis

All filtered and acidified water samples were analyzed for all the heavy metals by using Micro Plasma Atomic Emission Spectrometer under standard operating conditions. In view of data quality assurance, each sample is analyzed in triplicate and after every samples two standards (one blank and another of 2.5 mg/L) of respective metal was analyzed on atomic emission. The reproducibility was found to be at 95%confidence level. Therefore, the average value of each water sample was used for further interpretation. Standard solutions of all elements was prepared by dilution of 1000 mg/L certified standard solutions of corresponding metal ions with double distilled water. All the acids and reagents used were of analytical grade. All these analyses were performed in the Micro Plasma Atomic Emission Spectrometer (MP AES), at Bayaro University Kano, Kano State, Nigeria.

Method of Data Analysis

In other to compute the analyzed result for the carcinogenic and non-carcinogenic health risk assessment (that is ingestion of heavy metals through soil, inhalation of heavy metals through water and dermal contact of heavy metals with soil), the following methods and formulas were used as pointed out by EPA (2005):

$$MDI_{ing} = \frac{C_s * IR * EF * ED * CF}{BW * AT} \quad (1)$$

$$MDI_{inh} = \frac{C_s * IR_{air} * EF * ED}{BW * AT * PEF} \quad (2)$$

$$MDI_{derm} = \frac{C_s * SA * FE * AF * ABS * EF * ED * CF}{BW * AT} \quad (3)$$

$$RiskPathway = \sum_{k=1}^{n} MDI_K CSK_K \quad (4)$$

$$Risk_{(total)} = Risk_{(inj)} + Risk_{(inh)} + Risk_{(derm)} \quad (5)$$

$$HQ = \frac{MDI}{RfD} \quad (6)$$

$$HI = \sum_{k=1}^{n} HQ_k = \sum_{k=1}^{n} \frac{MDI_k}{RfD_k} \quad (7)$$

Where MDI_{ing}, MDI_{inh}, and MDI_{derm} are the Mean Daily Intake for the Exposure Dose via ingestion, inhalation and dermal contact in mg/kg/day respectively. HQ, HI, RfD and CSK are the hazard quotients, hazard index, reference dose and cancer slope factor respectively. C_s is the concentration of heavy metal in water in mg/L. The abbreviated parameters in equation (1), (2) and (3) are explain in Table 2. Also, the values for the conversion factors in equation (4), (5), (6) and (7) are presented in Table 3. Equation (4) and (5) are the equations for the carcinogenic risk assessments while (6) and (7) are the non-carcinogenic risk assessments.

Table 2: Exposure Parameters Used for the Health Risk Assessment.

Parameter	Unit	Children	Adults	References
Body Weight (BW)	Kg	15	70	(EPA, 2005)
Exposure Frequency (EF)	Days	350	350	(EPA, 2005)
Exposure Duration (ED)	Years	6	30	(EPA, 2005)
Ingestion Rate (IR)	mg/day	200	100	(EPA, 2005)
Inhalation Rate (IR air)	m^3/day	10	20	(EPA, 2005)
Skin Surface Area (SA)	cm^2	2100	5800	
Soil Adherence Factor (AF)	mg/cm^2	0.2	0.07	(EPA, 2005)
Dermal Absorption Factor (ABS)	None	0.1	0.1	(EPA, 2005)
Dermal Exposure Ratio (FE)	None	0.61	0.61	(EPA, 2005)
Particulate Emission Factor (PEF)	m^3/kg	1.3×10^9	1.3×10^9	(EPA, 2005)
Conversion Factor (CF)	mg/kg	10^{-6}	10^{-6}	(EPA, 2005)
Average Time (AT)				(EPA, 2005)
For Carcinogens	Days	365 x 70	365 x 70	
For Non- Carcinogens	Days	365 x ED	365 x ED	

Table 3: Reference Doses (RfD) and Cancer Slope Factors (CSF) for different Heavy Metals.

Heavy Metal	Oral RfD	Dermal RfD	Inhalation RfD	Oral CSF	Dermal CSF	Inhalation CSF	References
As	3.0×10^{-4}	3.0×10^{-4}	3.0×10^{-4}	0.15 x 10	1.5 x 10	1.5 x 10	(WHO, 2005)
Hg	3.0×10^{-4}	3.0×10^{-4}	8.6×10^{-5}	NA	NA	NA	(WHO, 2005)
Cd	5.0×10^{-4}	5.0×10^{-4}	5.7×10^{-5}	NA	NA	6.3 x 10	(WHO, 2005)
Cr (VI)	3.0×10^{-3}	NA	3.0×10^{-5}	5.0×10^{-1}	NA	4.1 x 10	(WHO, 2005)
Ni	2.0×10^{-2}	5.6×10^{-3}	NA	NA	NA	NA	(WHO, 2005)
Cu	3.7×10^{-2}	2.4×10^{-2}	NA	NA	NA	NA	(WHO, 2005)
Zn	3.0×10^{-1}	7.5×10^{-2}	NA	NA	NA	NA	(WHO, 2005)

NA = Not Available

If the (HI) value is less than one (<1), the exposed population is unlikely to experience adverse health effects. However, if the (HI) value exceeds one (>1), then there may be concern for potential non-carcinogenic effects.

RESULTS AND DISCUSSION

Results

The data collected from Loko and Mararraba of Nasarawa L.G.A was analyzed using Micro Plasma Atomic Emission Spectrometer (MP-AES). The results of the analysis were obtained and presented in Table 2, which are the Concentration Level of Heavy Metals such as Manganese (Mn), Nickel (Ni), Copper (Cu), Zinc (Zn), and Lead (Pb).

Table 4: Heavy Metals Concentration (mg/L)

Villages	Sample Points	pH	Zn	Fe	Cu	Pb	Ni	Mn
Loko	L1	0.5	0.22	0.060	0.01	0.01	0.0050	0.0140
	L2	0.4	0.16	0.020	0.01	0.01	0.0010	0.1230
	L3	0.8	0.18	0.060	0.01	0.02	0.0030	0.1390
Mean			**0.19**	**0.050**	**0.01**	**0.01**	**0.0030**	**0.0920**
Mararraba	M1	0.5	0.12	0.060	0.01	0.01	0.0010	0.0130
	M2	3.9	0.19	0.060	0.01	0.01	0.0020	0.0140
	M3	1.5	0.38	0.070	0.01	0.01	0.0030	0.0550
Mean			**0.23**	**0.040**	**0.01**	**0.01**	**0.0020**	**0.0270**
WHO (2005)			**3.00**	**0.300**	**2.00**	**0.01**	**0.1000**	**0.5000**
Mean (Loko & Mararraba)			**0.21**	**0.045**	**0.01**	**0.01**	**0.0025**	**0.0595**

1 = Borehole 2 = Well 2 = Stream L = Loko M = Mararraba

Table 5: Carcinogenic Mean Daily Intake Values in (mg/L/day)

Sample Points	Rec.	Pathway	Zn	Fe	Cu	Pb	Ni	Mn	Total
Loko	Ing.	Child x 10^{-10}	22.8	6.00	1.200	1.200	0.3000	12.0	43.500
	Ing.	Adult x 10^{-10}	10.5	2.80	0.600	0.600	0.2000	5.50	20.200
	Inh.	Child x 10^{-13}	8.00	2.10	0.400	0.400	0.1000	4.20	14.200
	Inh.	Adult x 10^{-13}	17.1	4.50	0.900	0.900	0.3000	9.00	32.700
	Der.	Child x 10^{-9}	26.6	7.00	1.400	1.400	0.4000	14.0	50.800
	Der.	Adult x 10^{-9}	28.5	7.50	1.500	1.500	0.5000	15.0	54.500
	Mean x 10^{-8}		**0.97**	**0.26**	**0.051**	**0.051**	**0.0160**	**0.51**	**1.9000**
	EPA (2005)x10^{-8}		**330**	**9.50**	**66.00**	**3.100**	**3.1000**	**15.0**	**427.03**
Mararraba	Ing.	Child x 10^{-10}	27.6	4.80	1.200	1.200	0.2000	3.70	38.700
	Ing.	Adult x 10^{-10}	12.7	2.20	0.600	0.600	0.1000	1.70	17.900
	Inh.	Child x 10^{-13}	9.70	1.70	0.400	0.400	0.1000	1.30	13.600
	Inh.	Adult x 10^{-13}	20.7	3.60	0.900	0.900	0.2000	2.80	28.900
	Der.	Child x 10^{-9}	32.2	5.60	1.400	1.400	0.3000	4.30	45.200
	Der.	Adult x 10^{-9}	34.5	6.00	1.500	1.500	0.3000	4.70	48.500
	Mean x 10^{-8}		**1.20**	**0.21**	**0.051**	**0.051**	**0.0110**	**0.16**	**1.7000**
	EPA (2005)x10^{-8}		**3.30**	**9.50**	**66.00**	**3.100**	**3.1000**	**15.0**	**427.03**

Table 6: Non-Carcinogenic Mean Daily Intake Values in (mg/L/day)

Sample Point	Rec.	Pathway	Zn	Fe	Cu	Pb	Ni	Mn	Total
Loko	Ing.	Child x 10^{-10}	120.0	32.0	6.4	6.40	0.13	64.0	228.9
	Ing.	Adult x 10^{-10}	51.00	14.0	2.7	2.70	0.50	27.0	98.90
	Inh.	Child x 10^{-13}	93.00	25.0	4.9	4.90	0.98	49.0	177.8
	Inh.	Adult x 10^{-13}	40.00	11.0	2.1	2.10	0.42	21.0	72.62
	Der.	Child x 10^{-7}	9.500	25.0	5.0	5.00	0.10	14.0	58.50
	Der.	Adult x 10^{-6}	25.00	5.50	1.1	1.10	0.22	11.0	43.92
	Mean x 10^{-5}		**0.430**	**0.096**	**0.037**	**0.037**	**0.038**	**0.37**	**0.830**
	EPA (2005)x10^{-5}		**2.700**	**2.30**	**0.53**	**1.20**	**1.20**	**8.00**	**15.93**
Mararraba	Ing.	Child x 10^{-10}	150.0	26.0	6.40	6.40	0.13	13.0	201.9
	Ing.	Adult x 10^{-10}	62.00	11.0	2.70	2.70	0.50	5.00	83.90
	Inh.	Child x 10^{-13}	110.0	20.0	4.90	4.90	0.98	9.80	150.6
	Inh.	Adult x 10^{-13}	48.00	8.40	2.10	2.10	0.42	4.20	65.22
	Der.	Child x 10^{-7}	12.00	2.00	1.40	1.40	0.10	1.00	17.90
	Der.	Adult x 10^{-6}	25.00	4.40	1.10	1.10	0.22	2.20	34.02
	Mean x 10^{-5}		**0.440**	**0.077**	**0.037**	**0.037**	**0.038**	**0.038**	**0.600**
	EPA (2005)x10^{-5}		**2.700**	**2.30**	**0.53**	**1.20**	**1.20**	**8.00**	**15.93**

Table 7: Carcinogenic Risk Assessments

VILAGES	Rec.	CANCER RISK x 10^{-13}	TOTAL RISKx10^{-13}
Loko	Ing.	21.1	
	Inh.	0.06	
	Der.	20.3	41.46
Mararraba	Ing.	19.8	
	Inh.	0.06	
	Der.	16.2	36.1

Table 8: Non-Carcinogenic Risk Assessments

VILLAGES	Rec.	HAZARD QUOTIENT (HQ)x10^{-4}	HAZARD INDEX (HI) x10^{-4}
Loko	Ing.	0.0018	
	Inh.	NA	
	Der.	5.7000	5.7
Mararraba	Ing.	0.0035	
	Inh.	NA	
	Der.	4.6000	4.6

RESULT ANALYSIS

In order to analyze the results obtained and presented in the above Tables, charts were plotted and comparison was made with Environmental Protection Agency for all the Carcinogenic and Non-Carcinogenic Risk Assessment.

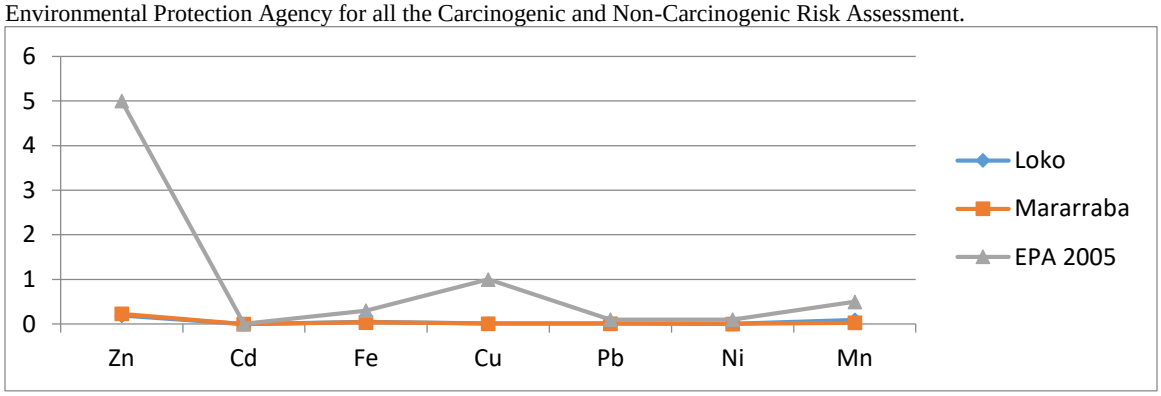

Fig. 1: Comparison of Heavy Metals Concentration with World Health Organization guide line

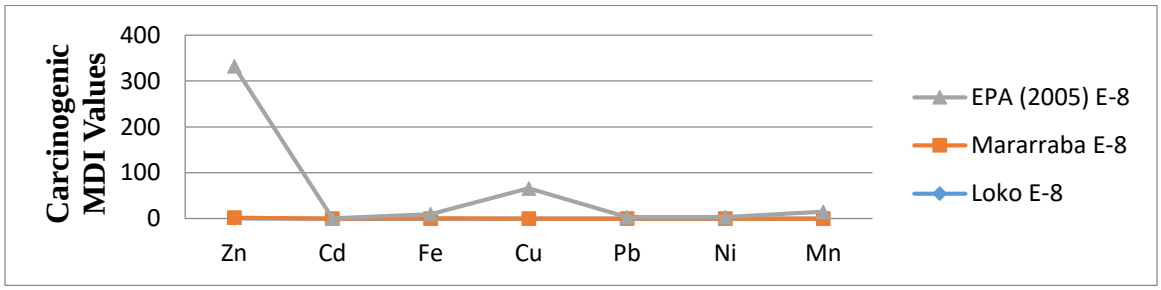

Fig. 2: Comparison of Carcinogenic Mean Daily Intake with World Health Organization guide line

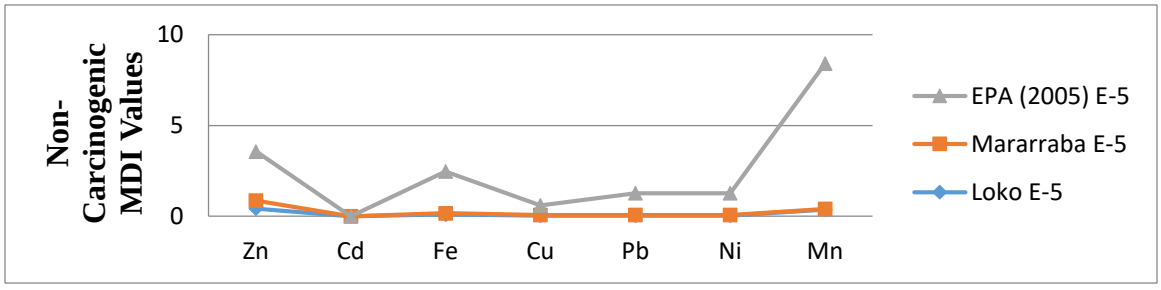

Fig. 3: Comparison of Non-Carcinogenic Mean Daily Intake with World Health Organization guide line

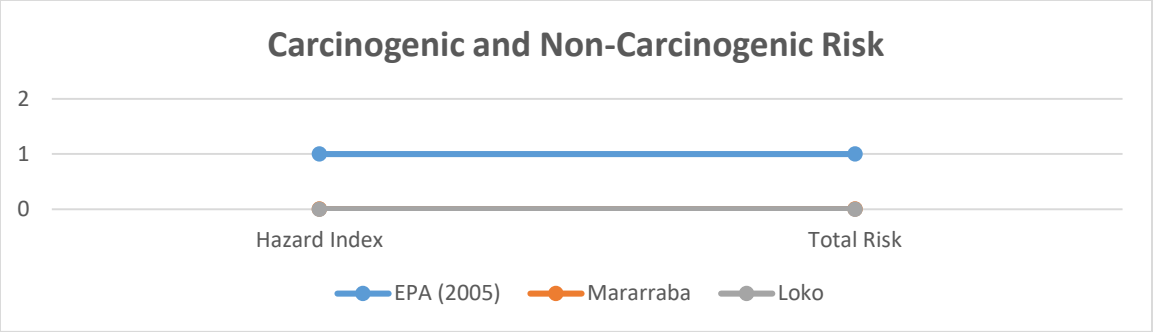

Fig. 4: Comparison of Carcinogenic and Non-Carcinogenic Risk with World Health Organization guide line

DISCUSSION

Concentration level (Table 4 and Fig. 1)

The results of the Radiometric Evaluation of Heavy Metals in Loko and Mararraba Water Sources of Nasararawa Local Government Area in Nasarawa State, Nigeria using Micro Plasma Atomic Emission Spectrometer have been presented. The mean concentration of various heavy metals found in the water samples are presented in Table 4. Seven heavy metals along with their respective concentrations for Loko and Mararraba in mg/L (Zn (0.19 and 0.23), Fe (0.05 and 0.04), Cu (0.01 and 0.01), Pd (0.01 and 0.01), Ni (0.003 and 0.002) and Mn (0.092 and 0.027)) respectively were found in the water samples.

Finding of this study have revealed that the mean Concentration of the analyzed heavy metals in the all water samples for both villages arranged in decreasing order is Zn > Mn > Fe > Pb; Cu > Ni > Cd for Loko, while Zn > Fe > Mn > Pb;Cu > Ni for Mararraba.

These values were found to be lower than the safe limit recommended by EPA for all heavy metals. This implies that the mean concentration level of heavy metals in those areas is not significant and may not cause immediate radiological hazard to the populace of the study area.

Mean daily intake (Tables 5, 6 and Figs. 2, 3)

The results of mean daily intake of Heavy Metal for both carcinogenic and non-carcinogenic risk in Portable Drinking Water Source of the study area have been presented in Tables 5 and 6.

Finding of this study revealed that both carcinogenic and non-carcinogenic mean daily intake values were found to be lower than the safe limit recommended by EPA for all heavy metals. This implies that the carcinogenic and non-carcinogenic mean daily intake of heavy metals in those areas is not significant and may not cause immediate radiological hazard to the populace of the study area.

Risk Assessments (Table 7, 8 and Fig. 4)

It was observed from Table 7, 8 and Fig. 4 that, the cancer risk and Hazard Quotient (HQ) for the area under investigation were less than unity, indicating that both cancer risk and Hazard Quotient (HQ) are negligible according to EPA.

CONCLUSION

This work shows the preliminary net that is chosen to analyze Loko and Mararraba, and it is possible to verify that seven heavy metals along with their respective concentrations for both Loko and Mararraba in mg/L (Zn (0.19 and 0.23), Fe (0.05 and 0.04), Cu (0.01 and 0.01), Pd (0.01 and 0.01), Ni (0.003 and 0.002) and Mn (0.092 and 0.027)) respectively were found in the water samples. From the findings presented, it can be concluded that the mean concentration level of heavy metals in those areas in all locations is not significant and may not cause radiological hazard to the populace unless when accumulated over a long period of time. The cancer risk and Hazard Quotient (HQ) for the area under investigation were less than unity, indicating that both cancer risk and Hazard Quotient (HQ) are negligible. Since concentration levels found and the risk assessments show that the study site can be considered as a free area. It is therefore an indication that the water in the area may be considered as a good water, even though, on accumulation, it may appear to have much impact on the radiation burden of the populace, hence, gross alpha and beta as well as carcinogenic and non-carcinogenic risk assessment of water in the area will compliment this work. It is therefore recommended that proper monitoring exercise should be conducted on the water in the study area from time to time in order to safeguard the population from high concentration of these heavy metals as they elevate with time and cause various forms of cancer to the populace of the study areas.

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