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Assessment of Heavy Metals, Water Quality and Health Risk of Surface Water in Some Towns and Villages Along Hawul River Basin

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ABSTRACT

For lives to be sustain adequate, safe and accessible water must be available for all and sundry. In fact, due to the importance of access to water, the United Nations made it a priority in sustainable development goal (SDGs 6) and history have it that access to water is a major factor in the settlements of most communities. Human activities have introduced so many chemical and biological contaminants in to the water bodies with devastating ecological and adverse health effect. Water quality index, Heavy metal pollution index, heavy metal evaluation index, environmental water quality index, Hazard quotient, Hazard index and incremental lifetime cancer risks were computed and the relevant findings presented as table and figures. The result of this study indicates poor water indices for all the sampling locations. HQoral values for heavy metals are less 1.0 which is the threshold for non-carcinogenic health hazard, thus, all the metals are within the acceptable limits of noncarcinogenic health risk hazard from all sampling sites. Hazard Index (HI) which is the summation of total potential non-carcinogenic health ranges between (5.8717 $X 10^{-5} - 2.0947 \times 10^{-4}$) for dermal route with while (1.6643 x $10^{-5} - 3.3138 \times 10^{-4}$) for oral route. Maximum Cancer risk contribution due to oral route are in order of As $(5.3165 \times 10^{-7}) > Cr(3.1779 \times 10^{-7}) > Cd(2.2293 \times 10^{-7}) > Pb(6.1260 \times 10^{-9}), while$ that of dermal contribution are in the order Cr $(9.5000 \times 10^{-5}) > Cd (2.0289 \times 10^{-5}) >$ As (2.4192×10^{-6}) > Pb (8.813×10^{-9}) . The incremental cancer risk (ILCR) ranges between 2.9250 X 10^{-5} – 1.04 X 10^{-4} implying that about 29 to 104 out of a million people of the population in the study areas may suffer cancer in their lifetime as a result of the exposure from heavy metals.

KEYWORDS Heavy Metals, Water Quality, Health Risk

Introduction

The world population is increasing at an alarming rate which in turn leads to demand for more food and good drinking water. According to WHO (2011), for lives to be sustain adequate, safe and accessible water must be available for all and sundry. In fact, due to the importance of access to water, the United Nations made it a priority in sustainable development goal (SDGs 6) and history have it that access to water is a major factor in the settlements of most communities (Akoteyon, 2019, Omorova et al 2019).

Among the various source of water, surface waters such as rivers, lakes, springs and streams are the most common and accessible (Ishaku et al., 2011). Over the years human activities such as mining, smelting, agriculture (pesticides and phosphate fertilizers) industrial emission and some natural disaster such as weathering, volcanic eruption, land slide, flood etc. have introduced so many chemical and biological contaminants in to the water bodies with devastating ecological and adverse health effect (Masindi and Muedi, 2018; Ali et al., 2019).

Globally and locally, so many investigations have reported the contamination and pollution of many surface waters from difference point source and non-point source. Among the various environmental contaminants, the accumulation of heavy metals in soils and water resources has received a lot of attention as a potential toxicity to both terrestrial and aquatic lives and may have grave poisoning consequences on humans through the food chain (Shirisha et al., 2014; Uzairu et al., 2014). The most common heavy metals contaminants reported in literature are Arsenic (As), Cadmium (Cd), Chromium (Cr), Lead (Pb) and Mercury (Hg). These metals pose a serious threat to the environment due to their persistence, bioaccumation and magnification in food chain (Sharma and Agrawal, 2013). As, Cd, Cr, Pb and Hg in drinking water has been recognized as a major public health problem in several regions of the world (Mazumder, 2015). Major countries affected are Bangladesh, India,

Taiwan, China, Mexico, Argentina, Chile and the USA (Chatterjee et al., 2017).

Uzairu et al (2014) have reported the contamination of river Challawa with heavy metals from the industrial effluents. Onyel and Anyanwu (2018) reported metal contamination of geogenic origin in water samples fom lyinna spring of Umuariaga Community, Southeast Nigeria. Pobi et al (2019) also reported that concentrations of Pb, Hg and Fe in the natural stream water of Durgapur industrial zone the international standard exceed recommendations. Similarly, Obasi Akudinobi (2020) water sources around active mines of lead-zinc mining communities of Abakaliki are polluted with heavy metals.

Both Poonam et al (2013) and Ghaderpoori et al (2018) posited that regular water quality monitoring of the water resources are absolutely necessary to assess the quality of water for ecosystem health and hygiene, industrial use, agricultural use and domestic use.

It is against this backdrop that this research was conceived to study the levels of some heavy metals in water and establish the health hazard implications that may arise from the use of this waters by the inhabitants of this communities.

Materials and methods

The Study area lies between longitudes 11.00°N and 10.00°N and Latitude 12.00°E to 13.00° E as shown in the map below. The sample collection locations were Kopri (10° 28'2"N, 12°50'49"E) Ndabna (10° 23'2"N, 12°49'27"E) in Hong L.G.A, Garkida WB (10° 24'52"N, 12°33'58"E) Garkida (10° 24'52"N, 12°33'58"E) in Gombi L.G.A, Kiri (9° 35'41" N, 12°00'05" E) and Daba (9° 40'0"N, 12°10′59"E) in Shelleng L.G.A. The sampling locations are steep part of the basin which receive their waters from the flood plains of the Hawul basin and keeps them throughout the year. The important human activities around the sampling areas are irrigation farming, fishing, washing, swimming during the day and some pockets of illegal mining.

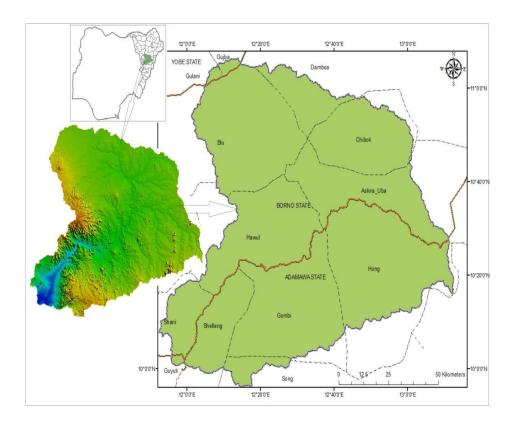


Figure -- Map of the study area sourced from Mayomi et al., 2018.

Sample collection

The study area was be divided in to six sampling sites along the Adamawa part of Hawul River Basin in which samples of water, sediments and fish was collected. Each sample was taken in triplicate from which a representative sample was drawn from. A total volume of 1 L water sample was collected as reported by Olawale et al (2016) from each site in polyethylene bottles (twice rinsed with deionized water) and acidified with 3% HNO₃ then stored in an ice box and transported to the laboratory for further analysis. Each sample was taken in triplicate from which a representative sample was drawn from.

Sample analysis

Digestion of water samples was carried out using mixed acids as reported by Olawale et al., (2016) and Cobbina et al., (2015).

One hundred millilitres of the filtered water sample was mixed with 5 mL concentrated nitric acid (HNO_3) and 5 mL concentrated sulphuric acid (H_2SO_4). To allow the acids to

become concentrated, the mixture was then heated until the volume was reduced to about 15 to 20 mL. The digested sample was allowed to cool to room temperature. It was then filtered through Whatman's 0.45 μ m filter paper. The final volume was adjusted to 100 mL with distilled water and stored for analysis.

Determination of Metal Concentrations

AAS Buck 205 was used for the determination of all heavy metals as reported by Oyedotun (2018).

Method validation of the procedure for metal determination and efficiency of AAS was conducted via standard addition methods by spiking a sample with multi-element standard solution containing of all metals analysed. All samples were run in triplicates.

Water quality index (WQI)

The method reported by Tyagi et al., (2013) in calculating the WQI for assessing the suitability of water sources for drinking purposes was

adopted in this work. The index values were computed by the following:

$$Qi = \frac{((Vactual - Videal)x \ 100)}{(Vstandard - Videal)}$$
(1)

Quality rating scale (Qi) for each selected parameter was computed by the following expression:

Where,

V_{actual} is the calculated value of ith heavy metal in the analysed water sample;

 V_{ideal} is the ideal value of this heavy metal in pure water. The ideal value is assumed zero for all heavy metal and

V_{standard} is the standard value of ith heavy metal for the drinking water.

The unit weight (Wi) for each heavy metal was determined using the following formula:

$$W_i = K V standard - - - - - - - (2)$$

Where,

K is the proportionality constant which is calculated using the following equation:

$$K=1 \sum (1/V standard)$$
 (3)

Step-IV: Finally, WQI was calculated using the following formula.

$$WQI = \frac{\sum Qi \times Wi}{\sum Wi} - \dots$$
 (4)

The water quality ratings as proposed by Tyagi et al., (2013): 0-25 (Excellent, Grade-A); > 25-50 (Good, Grade-B); > 50-75 (Poor, Grade-C); > 75-100 (Very poor, Grade-D) and > 100 (Unsuitable, Grade-E).

Heavy metal pollution index (HMPI)

The HMPI was calculated as reported by Zakir et al., (2020) based on weighted arithmetic quality mean method using the following two steps- (i) establish a rating scale (Qi) for each heavy metal following the equation mentioned

in step-II of WQI, and (ii) calculate the unit weightage (Wi) as a value inversely proportional to the standard of the corresponding heavy metal following the formula mentioned in step-III of WQI. Finally, HMPI was calculated using the following expression-

$$H M P I = \frac{\sum Qi \times Wi}{\sum Wi} - \dots$$
 (5)

To assess the level of contamination, the HMPI values are categorized into 3 groups- (i) Low (HMPI value < 15); (ii) Medium (HMPI value = 15-30) and (iii) High (HMPI value > 30).

Heavy metal evaluation index (HMEI)

Both the HMPI and HMEI provides information about overall water quality as regards to heavy metals. The HMEI was calculated using the following equation-

$$H M E I = \sum \left(\frac{\text{HMconc}}{\text{HMmpc}}\right)$$
 -----(6)

Where HM_{Conc} = the monitored concentration of a particular heavy metal and HM_{MPC} = the maximum permissible concentration of the same heavy metal.

To assess heavy metal contamination level in surface and groundwater, the threshold value was set at 1.0, which means HMEI value < 1.0 is rated as "Fit" and the value > 1.0 is considered as "Unfit" for domestic usage (Singh et al., 2017).

3.7.4 Environmental water quality index (EWQI)

The assessment of EWQI is a new index proposed by Ali et al. (2017). In the estimation of EWQI, first, the heavy metal toxicity index (HMTI) was calculated as follows by multiplying the contents of each heavy metal measured in this study with the corresponding total score as assigned by the Toxicological Profiles of the Priority List of Hazardous Substances prepared by the Agency for Toxic Substances and Disease Registry (ATSDR, 2019).

$$H M T I = \sum C_{HM} X T S_{HM} H M T I = \sum C HM x T SHM$$
 -----(7)

Where, C $_{\text{HM}}$ is the concentration of each heavy metal; and TS $_{\text{HM}}$ is the total score of the same heavy metal as mentioned by ATSDR (As = 1676; Cu = 805; Zn = 913; Cr = 893; Pb = 1531 and Cd = 1318; Hg = 1458). The content of Fe was excluded from the calculation of HMTI due to lack of its total score value. Finally, the EWQI was calculated by dividing the WQI value with the HMTI value as follows-

$$EWQI = WQI / HMTI EWQI = \frac{WQI}{HMTI} - ... (8)$$

Assessment of human health risk

Non-carcinogenic health risk

Non-carcinogenic health risk and Carcinogenic health risk were studied by evaluating the Chronic Daily Intake (*CDI*) of heavy metal through ingestion and dermal adsorption of waters to the people of the study area. This was calculated using the following Eqs. (9) and (10), respectively as outlined by the US

Environmental Protection Agency (USEPA, 2004). Hazard Quotients (*HQ*), Hazard Index (*HI*) and Incremental lifetime cancer risk (*ILCR*) were measured in this study, were adult peoples of the country were considered as the target group.

$$CDIoral(mgKg^{-1}day^{-1}) = \frac{Chm \times DI \times ABS \times EF \times ED}{BW \times AT} - \dots$$
 (9)

$$CDIdermal(mgKg^{-1}day^{-1}) = \frac{Chm \times SA \times Kp \times ABS \times ET \times EF \times ED \times CF}{BW \times AT} - \dots (10)$$

The HQ is the ratio between the calculated mean chronic daily in- takes (CDI) of heavy metal to the oral reference dose (RfD) for the same heavy metal. The HQ of heavy metal through ingestion and dermal adsorption of waters to the people of the area was calculated using the following Eqs. (11) and (12), respectively-

$$\begin{split} HQoral &= CDIoral/RFDoral ------ (11) \\ HQdermal &= CDIdermal / RFDdermal ----- (12) \end{split}$$

The HI is the total potential non-carcinogenic health risks caused by different heavy metals present in waters. It was also calculated according to the USEPA guideline for ingestion and dermal adsorption of waters to the people of the study area using the following Eqs. (5) and (6), respectively

$$HIoral = \sum_{k=0}^{n} HQoral = HQcu + HQfe + HQAs + HQzn + HQcr + HQpb + HQcd - (13)$$

$$HIdermal = \sum_{k=0}^{n} HQdermal = HQcu + HQfe + HQAs + HQzn + HQcr + HQpb + HQcd - (14)$$

To assess potential non-carcinogenic health risks caused by different heavy metals present in waters, the threshold value was set at 1.0, which means HI value < 1.0 means the exposed populations are unexpected to experience

hazardous health impacts. On the other hand, the HI value > 1.0 means the possibilities of non-carcinogenic health risks may occur to the local people of the study area (Mohammadi et al., 2019).

Carcinogenic health risk index

The equation used to calculate the ILCR for each carcinogen was as follows-

$$ILCR = CDI \times CSF -----(15)$$

According to USEPA, the acceptable range for $\Sigma ILCR$ is 1.0×10^{-6} to 1.0×10^{-4} for a single carcinogenic element and/or multi-element carcinogens.

Table 1: parameters for computing health risk

Parameters	Unit	Ingestion	Dermal	References
Heavy metal concentration (C hm)	mg/l	-	-	-
Daily average intake (DI)	L/day	2.2	-	USEPA, 2004
Skin surface area (SA)	cm ²	-	18,000	USEPA, 2004
Permeability coefficient (K p)	cm/hr	-	Cd, Cr, Fe & Cu = 0.001; Pb = 0.0001 and Zn = 0.0006	USEPA, 2004

Exposure time (ET)	Hour/eve nt	-	0.58	USEPA, 2004
Exposure frequency (EF)	Days/year	365	350	USEPA, 2004
Exposure duration (ED)	year	70	30	USEPA, 2004
Conversion factor (CF)	L/cm ³	-	0.001	USEPA, 2004
Average body weight (BW)	Kg	60	60	-
Absorption factor (ABS)	-	-	0.001	USEPA, 2004
Average time (AT)	Day	25,550	10,800	-

Results

Table 2: Mean of total metal concentrations in Water (mgL⁻¹)

	KOPRI	Ndabna	Garkida(WB)	Garkida	Daba	kiri
As	ND	ND	ND	ND	0.0019	0.0029
Cd	0.008	0.0014	ND	ND	0.002	0.0024
Cr	0.0129	0.0105	0.0052	0.0065	0.0144	0.0171
Hg	ND	ND	ND	ND	ND	ND
Pb	0.0104	0.0127	0.0209	0.0237	0.0261	0.0278
Cu	0.0062	0.0029	0.0018	0.0039	0.0386	0.0154
Fe	0.0113	0.0155	0.0033	0.0084	0.0294	0.0626
Zn	0.0052	0.0044	0.0012	0.002	0.0058	0.0081

ND = Not detected

Table 3: Water quality index (WQI)

Metals	Kopri	Ndabna	GarkidaWB	Garkida	Daba	Kiri
As	NA	NA	NA	NA	19	29
Cd	26.67	46.67	NA	NA	66.67	80
Cr	25.8	21	10.4	13	28.8	34.2
Hg	NA	NA	NA	NA	NA	NA
Pb	104	127	209	237	267	278
Cu	0.62	0.29	0.18	0.39	3.86	1.54
Fe	3.77	5.17	1.1	2.8	9.8	20.9
Zn	0.173	0.147	0.04	0.066	0.19	0.27

Total	160.86	200.13	220.68	253.19	395.13	443.64	
Grade	Е	Е	Е	Е	Е	Е	
Description	Unsuitable	Unsuitable	Unsuitable	Unsuitable	Unsuitable	Unsuitable	

Table 4: Heavy metal pollution index (HMPI)

Metals	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
As	NA	NA	NA	NA	19	29
Cd	26.67	46.67	NA	NA	66.67	80
Cr	25.8	21	10.4	13	28.8	34.2
Hg	NA	NA	NA	NA	NA	NA
Pb	104	127	209	237	267	278
Cu	0.62	0.29	0.18	0.39	3.86	1.54
Fe	3.77	5.17	1.1	2.8	9.8	20.9
Zn	0.173	0.147	0.04	0.066	0.19	0.27
Total	160.86	200.13	220.68	253.19	395.13	443.64
Description	High	High	High	High	High	High
Mean: 278.93	min:	max:				
	160.86	443.64				

Table 5: Heavy metal evaluation index (HMEI)

Metals	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
As	NA	NA	NA	NA	0.19	0.29
Cd	2.67	0.47	NA	NA	0.67	0.8
Cr	0.258	0.21	0.104	0.13	0.288	0.342
Hg	NA	NA	NA	NA	NA	NA
Pb	1.04	1.27	2.09	2.39	2.61	2.78
Cu	0.0062	0.0029	0.0018	0.0039	0.0386	0.0154
Fe	0.037	0.052	0.011	0.028	0.098	0.208
Zn	0.0017	0.00146	0.004	0.0016	0.0019	0.0027
Σ HM _{Conc} /	4.0129	2.0064	2.2108	2.5535	3.8965	4.4381
HM _{MPC}	Cit	unfit	C '.1	C :1	Ct	C '1
·	Description unfit		unfit	unfit	unfit	unfit
Mean = 3.1864	min =	max =				
	2.0064	4.4381				

Table 6: Environmental water quality index (EWQI)

Metals	Kopri	Ndabna	Garkida WB	Garkida	Daba	Kiri
As	NA	NA	NA	NA	5.9666	5.9666
Cd	2.5294	25.2927	NA	NA	25.2921	25.2908
Cr	1.7406	1.7406	1.7406	1.7406	1.7406	1.7406
Hg	NA	NA	NA	NA	NA	NA
Pb	6.5316	6.5316	6.5316	6.5316	6.7613	6.5316
Cu	0.1122	0.1119	0.1119	0.1119	0.1119	0.1119
Fe	NA	NA	NA	NA	NA	NA
Zn	0.0364	0.0366	0.0209	0.0361	0.0359	0.0365

Table 7: Calculated average chronic daily intake (CDI) due to ingestion and dermal exposure

Metals	Kopri Ndabna Garkida WB Gark	da Daba	Kiri Kop	ri Ndabna	Garkida WB Garkida	Daba	Kiri
	<u>INGESTION</u>				<u>DERMAL</u>		
As	NA NA NA NA	6.97E-8	1.06E-7	NA NA	NA NA	3.17E-10	4.84E-10
Cd	2.9E-7 5.13E-8 NA NA	7.33E-8	8.80E-8	1.33E-9 2	.34E-10 NA NA	3.34E-	10 4.00E-10
Cr	4.73E-7 3.85E-7 1.91E-7 2.38E-	7 5.28E-7	6.27E-7	2.15E-9	1.75E-9 8.68E-10 1.	08E-9 2.40	DE-9 2.85E-9
Pb	3.81E-7 4.66E-7 7.66E-7 8.69E	-7 9.57E-7	10.19E-7	1.74E-10	2.12E-10 3.49E-10 3	.95E-10 4.3	6E-10 4.64E-10
Cu	2.27E-7 1.06E-7 6.60E-8 1.43E-	7 1.42E-6	5.65E-7	1.03E-9	4.84E-10 3.00E-10 6.	51E-10 6.4	4E-9 2.57E-9
Fe	4.88E-7 5.68E-7 1.21E-7 3.08E-	7 1.08E-7	2.30E-6	2.22E-9	2.58E-9 5.51E-10 1	.40E-9 4.9	1E-9 1.04E-8
Zn	1.91E-7 1.61E-7 4.40E-8 7.33E-8	3 2.13E-7	2.97E-7	5.21E-10	4.41E-10 1.20E-10 2.	00E-10 5.83	1E-10 8.11E-10

Table 8: Health Hazard Quotient (HQDERMAL)

Location	AS	Cd	Cr	Cu	Pb	Fe	Zn	HI(∑HQ)
Kopri	ND	5.3392E-3	1.4349E-4	8.6208E-8	4.1413E-7	7.3967E-9	8.6762E-9	1.9739E-4
Ndabna	ND	9.3436E-6	1.1679E-4	4.0322E-8	3.045E-7	8.6207E-9	7.3413E-9	1.2649E-4
Garkida WB	ND	ND	5.784E-5	2.5028E-8	8.3026E-7	1.8353E-8	2.0022E-9	5.8717E-5
Garkida	ND	ND	7.2300E-5	5.4223E-8	9.4150E-7	1.3383E-9	3.3370E-9	7.3300E-5
Daba	1.0567 E-6	1.3384E-5	1.6017E-4	5.367E-7	1.0369E-6	1.6351E-8	9.6772E-9	1.7621E-4
Kiri	1.6128E-6	1.6018E-5	1.900E-4	2.1413E-7	1.6044E-6	3.4817E-9	1.3515E-8	2.0947E-4

Table 9: Health Hazard Quotient (HQ_{INGESTION})

Location	As	Cd	Cr	Cu	Pb	Fe	Zn	HI(∑HQ)
Kopri	ND	5.8667E-7	1.5767E-7	5.6832E-9	2.7234E-7	6.9667E-5	6.3557E-10	7.0689E-5
Ndabna	ND	1.0267E-7	1.2833E-7	2.6583E-9	3.3262E-7	8.1190E-5	5.3777E-10	8.1757E-5
Garkida WB	ND	ND	6.3557E-7	1.6500E-9	5.4738E-7	1.7286E-5	1.4667E-10	1.8471E-5
Garkida	ND	ND	7.9443E-8	3.5700E-9	6.2071E-7	4.4000E-5	2.4444E-10	4.4704E-5
Daba	2.3223E-7	1.4667E-7	1.7600E-7	3.5383E-8	6.8357E-7	1.5400E-5	7.0890E-10	1.6643E-5
Kiri	3.5443E-7	1.7660E-7	2.0900E-7	1.4117E-8	7.2071E-7	3.2990E-4	9.9000E-10	3.3138E-4

Figure 1: Percentage contribution of Hms to Hazard Quotients (Dermal) Figure 2: Percentage contribution of HMs to Hazard Quotients (Ingestion)

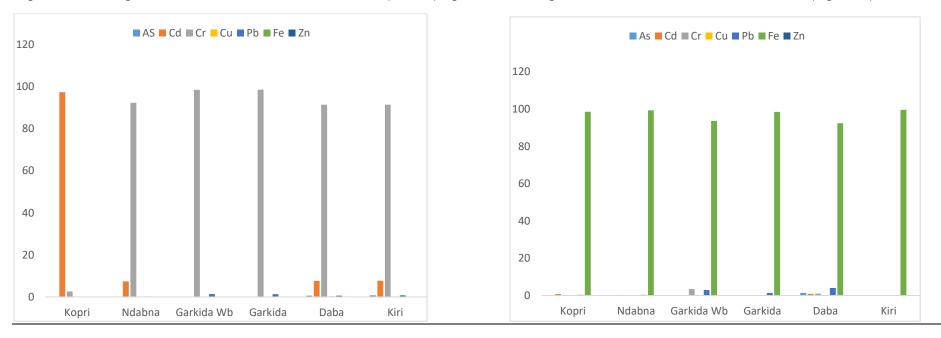


Table 10: Carcinogenic health risk (incremental life time cancer risk)

Location		As		Cd		Cr		Pb	∑ILCR
	Ingestion	Dermal	Ingestion	Dermal	Ingestion	Dermal	Ingestion	Dermal	
Kopri	NA	NA	2.2293E-7	2.0289E-5	7.8350E-8	7.1745E-5	2.3234E-9	3.5201E-9	9.2341E-5
Ndabna	NA	NA	3.9015E-8	3.5506E-6	6.4165E-8	5.8395E-5	2.8273E-9	2.5883E-9	6.2054E-5
Garkida WB	NA	NA	NA	NA	3.1779E-7	2.8921E-5	4.6527E-9	7.0572E-9	2.9250E-5
Garkida	NA	NA	NA	NA	3.9722E-8	3.6150E-5	5.1230E-9	8.0028E-9	3.6202E-5
Daba	3.4835E-7	1.5851E-6	5.5735E-8	5.0859E-6	8.8000E-8	8.0085E-5	5.8103E-9	8.8137E-9	8.7300E-5
Kiri	5.3165E-7	2.4192E-6	6.7108E-8	6.0868E-6	1.045E-7	9.5000E-5	6.1260E-9	1.3637E-9	1.0400E-4
Mean	4.4 E-7	2.0 E-6	9.6197 E-8	8.7531E-6	11.5421E-8	6.1716E-5	4.477E- 9	5.2243E-9	6.8525E-5
Min	3.4835E-7	1.5851E-6	3.9015E-8	3.5506E-6	3.9722E-8	2.8921E-5	2.3234E-9	1.3637E-9	2.9250E-5
Max	5.3165E-7	2.4192E-6	2.2293E-7	2.0289E-5	3.1779E-7	9.5000E-5	6.1260E-9	8.8137E-9	1.0400E-4

Discussions Water quality index (WQI) with respect to heavy metals

The water quality index is an important tool use to assess the suitability or otherwise of surface or ground water for domestic or industrial usage by comparing the different physicochemical parameters with their respective permissible limits set by regulatory bodies (Adelagun et al., 2021). Water Quality summarises the entire different parameters into a single number which expresses the water quality of certain location. In this study the water quality index with respect to heavy metal are computed based on method outlined by Tyagi et al., (2013) as reported by zakir et al., (2020). The computed WQI with respect to heavy metal are presented in table 2. The computed WQI for the study area at the sampling locations and their description ranges from 160.86 to 443.64 with lowest at Kopri while the highest is at Kiri. This implies that all samples from the study areas are "unsuitable" since they all fall within the grade "E" of the description. This unsuitable quality can be attributed the high values of As in Daba and Kiri, Cd in all sampling sites except Garkida WB and Garkida, and Cr and Pb in all the sampling sites.

1. Heavy metal pollution index (HMPI)

Heavy metal pollution index is another parameter used in the assessment of water quality for the purpose of consumption or industrial usage. This index is employed in the identification and quantification of heavy metals distribution and movements in water bodies for the purpose of assessing overall water quality for drinking with regards heavy metals (Ghaderpoori et al., 2018). The calculated HMPI from all sampling site are presented in table 3. The HMPI ranges from 160.86 to 443.64, with the minimum at Kopri and maximum at Kiri, and a mean value of 278.93. All the sampling sites have fallen within the "High" polluted water for domestic consumption based on the classification proposed by Edet and Offiong, 2002. This also aligns with the WQI value which described the waters from all sampling sites as "unsuitable" for domestic consumption.

2. Heavy metal evaluation index (HMEI)

Another important model used in the assessment of the water quality in terms of heavy metal content is the HMEI which is the ration between the heavy metal content (HM_{Conc}) and maximum permissible concentration (HM_{MPC}). The computed HMEIfor all sampling sites are presented in table 4. The values of the HMEI ranges between 2.0064 and 4.4381 with a mean value of 3.1864. The computed HMEI shows that all the sampling sites are above the threshold value of 1 according to Singh et al., (2017) and are considered "unfit" for domestic consumption. HMEI value also strongly agrees with the two earlier models of WQI and HMPI description of the sampling sites.

3. Environmental water quality index

Environmental water quality index was computed for all sampling sites using heavy metal toxicity index (HMTI), which is the product of the concentration of heavy metals in the sample and its total score on the priority list of hazardous substances prepared by the Agency for Toxic Substances and Disease Registry (ATSDR, 2019). The HMTI showed heavy metal contribution in the order of Pb (15.9-42.5) > Cu (1.60-34.4) > Cr (5.97-19.6) >Cd (1.84-10.54) > Zn (1.82-7.39) > As (3.18-4.86). The HMTI of iron notably absent due to the lack of total score for iron on the priority list of ATSDR. Although the EWQI model has no known threshold but higher value means it characterizes the lower quality of water. The EWQI in this study have shown higher values associated with Cd (2.52- 25.29), Pb (6.53-6.6) and As (5.96) which are known to be very toxic. The EWQI have followed similar trends as WQI, HMPI and HMEI in giving the water from all sampling sites a poor rating with regards to human consumption.

4. Health Risk Assessments

Assessing the human health risk of heavy metals means the computation of how and to what extend the adverse effect of the heavy metals due to exposure through different media. In this study the ingestion and dermal exposure route are considered. The carcinogenic and non-carcinogenic risks were

estimated using hazard quotients and cancer risks by adopting the United States environmental protection agency's (2004) protocol.

5. Non-carcinogenic health risk hazards

The non-carcinogenic health risk hazards were measured by computing the chronic daily intake (CDI) due to ingestion and dermal exposure which in turn were used to calculate the Hazard quotient (HQ) and Hazard index (HI). The CDI_{oral} values ranges between 0.00 - 1.06 X 10^{-6} , $0.00 - 2.9 \times 10^{-7}$, $2.38 \times 10^{-7} - 6.27 - 10^{-7}$ 7 , 3.81 X 10^{-7} – 9.57 X 10^{-7} , 2.27 X 10^{-7} – 1.42 X 10^{-6} , $1.08 \times 10^{-7} - 2.30 \times 10^{-6}$, and $7.33 \times 10^{-8} 2.97 \times 10^{-7} \text{ mg kg}^{-1} \text{ day}^{-1} \text{ for As, Cd, Cr, Pb, Cu,}$ Fe and Zn respectively. From table 9, it can be seen that all the HQingestion values for heavy metals are less 1.0 which is the threshold for non-carcinogenic health hazard, thus, all the metals are within the acceptable limits of noncarcinogenic health risk hazard from all sampling sites.

The CDI_{dermal} values also ranges between 0.00 – 4.84 X 10^{-10} , 0.00 - 1.33 X 10^{-9} , 8.68 X 10^{-10} – 2.89 X 10^{-9} ,1.74 X 10^{-10} – 4.64 X 10^{-10} , 6.51 X 10^{-10} - 6.44 X 10^{-9} , 1.40 X 10^{-9} – 1.04 X 10^{-8} and 1.20 X 10^{-10} - 8.11 X 10^{-10} for As, Cd, Cr, Pb, Cu, Fe and Zn respectively. Just like in the case of the oral route, the HQ_{dermal} values are also less than 1.0, consequently, all the heavy metals are within the acceptable threshold for non-carcinogenic health risk from all the sampling sites.

Hazard Index (HI) which is the summation of total potential non-carcinogenic health ranges between (5.8717 X 10⁻⁵ - 2.0947 X 10⁻⁴) for dermal route with while (1.6643 x 10⁻⁵ - 3.3138 X 10⁻⁴) for oral route. From table 8 and 9 the computed Hazard index shows Kiri having highest value for both dermal and oral route and this may be due to the fact that Kiri is located downstream of the study area. Generally, risks caused by different heavy metals present in waters from all sampling sites are less than 1.0, therefore, the probability of potential non-carcinogenic harmful health risks to the populations of the study area are expected to be very low.

6. Carcinogenic health risk

In this study, the Carcinogenic health risk is considered for As, Cd, Cr and Pb. the computed cancer risks posed by these toxic metals through ingestion and dermal exposure to the residents of the study area are presented in table 4.11. Maximum Cancer risk contribution due to oral route are in order of As (5.3165 X 10^{-7}) > Cr (3.1779 X 10^{-7}) > Cd (2.2293 X 10^{-7}) > Pb $(6.1260 \text{ X } 10^{-9})$, while that of dermal contribution are in the order Cr (9.5000 X 10⁻⁵) $> Cd (2.0289 \times 10^{-5}) > As (2.4192 \times 10^{-6}) > Pb$ (8.813 Χ 10⁻⁹). Base on recommendations, cancer risk that are below about 1 chance in 1.00×10^{-6} are negligible, hence, the risk of developing cancer due to Pb is negligible. Similarly, the risk of developing cancer due to ingestion of both As and Cd is also negligible. On the average there are possibilities of 2, 9 and 61 people out of a million people developing cancer via the dermal route due to As, Cd and Cr respectively. The incremental cancer risk (ILCR) ranges between $2.9250 \times 10^{-5} - 1.04 \times 10^{-4}$ implying that about 29 to 104 out of a million people of the population in the study areas may suffer cancer in their lifetime as a result of the exposure from heavy metals.

Conclusions

From the results obtained, the various indices employed for the water quality evaluation shows that surface water from all the sampling locations are no fit for consumption and may pose threat to the well-being of the populace around these locations. The elevated concentration of Pb which is a carcinogen if not contained and dealt with May also pose a cancer risk in humans living around the sampling locations.

Conflict of interest

The authors declare no conflict of interest.

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