

Studies Evaluating the Health Risks Associated with Heavy Metals and their Contamination on Ilahun River.

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Abstract: This investigation was conducted on Ilahun River in Osun State, Nigeria to ascertain the heavy metals present in the river due to mining activities carried out on the river and the health risk associated with the metals. The physico-chemical and heavy metal parameters were analyzed. Twelve samples were collected between April and July 2024 and evaluated using standard processes. Concentrations of heavy metals were verified utilizing Inductively Coupled Plasma-Optical Emission Spectroscopy. The values of pH, temperature, electrical conductivity, total Alkalinity, Chloride, turbidity, total dissolved solids, dissolved oxygen and hardness during the sampling period ranged between 6.3-7.6, 28-32°C, 70.3-628.3 µ/cm, 37.2-82.7 mg/L, 0.83-66 mg/L, 1.06-7.25 NTU, 176.3-308.6 ppm, 4.0-9.76 mg/L and 77.6-128.5 mg/L respectively. The parameters were within the standard limits of World Health Organization and the National Environmental Standards and Regulations Enforcement Agency set. The highest heavy metal contaminations were recorded in May and the trend observed in the metals are As > Ag > Al > Zn > Mn > V > B > Cd > Co > Cu > Pb > Th > U > Ni > Cr > Se, the range of the essential metal are Ca > Na > Mg > K > Fe. Values of the listed metals exceed the standard limit. The health risk assessment of the metals conducted showed a high possibility of both cancer-inducing and non-cancer-inducing effect of heavy metals via the oral and dermal contact route in both adults and children, having more effect on children than adults.

1. INTRODUCTION

In the twenty-first century, one of the most important facets of environmental research is the study of water quality. This is because water is utilized for manufacturing purposes, agriculture, building, consumption, and other domestic applications, and it must meet certain quality standards to ensure it is suitable for its intended use (Ewuzie *et al.*, 2021). Water bodies in the human environment are continually facing numerous threats (Adebanjo *et al.*, 2019). More people continue to use water from unimproved sources, making sustainable access to safe drinking water a global concern (Samuel *et al.*, 2019).

Several anthropogenic activities have an impact on water bodies and one of those activities includes mining operations (Ayiwouo *et al.*, 2022). In Sub-Saharan Africa, the mining of precious mineral deposits, especially gold, is an indispensable economic activity for millions of people and a key influence on the region's economies (Obodai *et al.*, 2023). The many chemicals and processes used in mining operations have the potential to seriously contaminate water bodies near mines. Mining and mineral processing are two of the main anthropogenic activities that release the metals in an unnaturally high concentration into the environment (Adewumi *et al.*, 2019). After prolonged exposure to some heavy metal, toxicity may be acute and may be chronic. These exposures can cause diseases in the body and harm many organs, including the kidney, liver, brain, and lungs (Engwa *et al.*, 2019).

2. MATERIALS AND METHODS

The water sample was collected from three sampling sites on the river namely: Upper stream (US), Middle stream (MS) and Lower stream (LS) for four consecutive months to determine the physicochemical parameters and heavy metals concentrations.

The water samples were put into different containers, which were firstly sterilized with 10% dilute HCL and thoroughly washed with distilled water before collection and taken to the laboratory for analysis while the temperature and pH was determined at the point of collection.



Figure1. Artisanal miners digging river banks, extracting gold using the sluicing technique

2.1. Determination of the Physicochemical Parameters

The value of the pH and temperature was taken onsite using mercury glass thermometer. Electrical Conductivity and Total Dissolved Solids was measured using Calibrated conductivity meter (Palintest-Micro800). The turbidity was checked using turbidity meter (Palintest-PTH092). Dissolved Oxygen is measured using DO meter (Meter-IC-HI98193). Chloride, Total Alkalinity and Total Hardness was evaluated using titrimetric method in the laboratory at Nigerian Stored Product Research Institute, Ilorin, Kwara State, Nigeria, using the APHA Standard method 23rd Edition.

2.2. Heavy Metals Evaluation

The samples were digested with Nitric Acid (HNO₃) using the APHA standard method for digestion and the metals were analyzed using ICP-OES.

2.3. Health Risk Assessment

The United States Environmental Protection Agency risk models were adopted to assess cancer-inducing and non-cancer-inducing health risks linked to heavy metals present in the samples collected from the river. The risk was estimated by computing the metal values.

The Chronic daily intake (CDI) is used to assess the cancer risk and the non-cancer risk of the Heavy metals analyzed with the ICP-OES, using the equation documented by Adewoye *et al.* 2020. Equation 1 was utilized to determine the CDI of the heavy metals (HMs) through oral intake, while the CDI for dermal absorption was calculated using Equation 2. Table 1 contains a summary of the assessment's parameters.

$$CDI_{ing} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$$CDI_{derm} = \frac{C \times SA \times AF \times ABF \times EF \times ED}{BW \times AT} \quad (2)$$

Where: CDI is the chronic daily intake, C is the concentration of the contaminant in water sample; IR is the ingestion rate, ED is the exposure duration, EF is the exposure frequency, BW is body weight, AT is the average exposure time (Emmanuel *et al.*, 2022). SA is the skin surface area, ABF is the dermal absorption factor and AF stands for water adherence factor (Adewoye *et al.*, 2020).

2.3.1 Non-Cancer-Inducing Health Risk

The non-cancer-inducing health risk of the heavy metals is determined using the equation 4 and 5.

$$HQ = \frac{CDI}{RfD} \tag{4}$$

$$HI = \sum HQ \tag{5}$$

HQ stands for the Hazard Quotient and HI is the hazard index of all metals present in the sample. The Reference Dose (RfD) of each metal for the Oral and Dermal route of contact, the Slope Factor (SF) for evaluating human risk assessment, are listed in Table 2 (Miletić *et al.*, 2023).

A value of HQ or HI less than 1 is the acceptable limit which implies no significant non-cancer-inducing risks; value ≥ 1 implies potential to cause non-cancer-inducing risks, the possibility rises as the value of HQ or HI rises (Jonah and Mendie, 2024).

Table1. Parameters used in the Assessment of Heavy Metal Health Risk

Parameters (Unit)	Values
Concentration (mg/L/)	Heavy Metals
Ingestion Rate (L/day) Adult	2.2
Ingestion Rate (L/day) Children	1
Exposure Frequency (Days/year)	365
Exposure Duration (Years) Adult	30
Exposure Duration (Years)Children	6
Body Weight (kg) Adult	70
Body Weight (kg) Children	15
Average Time (days)Adult	10950
Average Time (days) Children	2190
Surface Area (cm ²) Adult	17500
Surface Area (cm ²) Children	2800
Adherence Factor (mg/cm ²) Adult	0.07
Adherence Factor (mg/cm ²) Children	0.2
Absorbance Factor	0.001

2.3.2 Cancer Risk

The risk of cancer is the result of an average lifespan contact with 1 mg/kg body weight/day of a pollutant. The cancer slope factor (CSF), measured in mg/kg/day, and CDI (mg/kg/day) were multiplied to determine the cancer risk, as represented in equation 6.

$$CRI = CDI \times SF \tag{6}$$

According to regulatory criteria, the lowest or tolerable cancer risk falls between 1×10^{-6} to 1×10^{-4} by USEPA (Osae *et al.*,2023). CRI was only calculated for Pb, Cd, Cr and As.

Table2. The Reference Dose and Slope Factor of Heavy Metals

Heavy Metals	RfD _{ing}	RfD _{derm}	SF _{ing}	SF _{derm}
Pb	3.5×10^{-3}	5.25×10^{-4}	0.0085	1.5
Cd	1×10^{-3}	1×10^{-5}	6.1	6.1
Cr	3×10^{-3}	6×10^{-5}	0.5	20
As	3×10^{-4}	1.23×10^{-4}	1.5	3.66
Cu	4×10^{-2}	1.2×10^{-2}	-	-
Zn	3×10^{-1}	6×10^{-2}	-	-
Fe	7×10^{-1}	-	-	-
Ni	2×10^{-2}	5.4×10^{-3}	-	-
Mn	1.4×10^{-1}	1.84×10^{-3}	-	-
Co	2×10^{-2}	2.1×10^{-5}	-	-

3. RESULTS

3.1. Physical and Chemical Properties.

The tables (3, 4, 5 and 6) showed the values analyzed for the samples throughout the months of collection.

3.1.1. pH Value

The pH values of the collected samples from the three points of collection were seen to be within the permissible limit of WHO and NESREA. The pH of sample LS in April and that of US in May were below the permissible limit set by NESREA. The pH of the samples were lower in values (6.3 and 6.8) except of MS in May, MS and LS in June, US and MS in July which were neutral in values of 7.1, 7.1, 7.4, 7.5 and 7.6 respectively. °c

3.1.2. Temperature

The temperature observed in April and July was within the permissible limit set by WHO and NESREA with its values between 28⁰c and 30⁰c, but that of the month of May (LS) and June (US and MS) were greater than the acceptable threshold with values of 32⁰c, 32⁰c and 32⁰c respectively.

3.1.3. Electrical Conductivity

The values of conductivity obtained throughout all the months of collection were observed to be below the standard set by NESREA which is 1000µ/cm. The highest value obtained was 628.3µ/cm in the month of July (LS) and the lowest value obtained was 70.3µ/cm in May (LS).

3.1.4. Total Alkalinity

The values obtained for the Total Alkalinity in all the months of collection were observed to be below the standard limit set by NESREA. The values gotten ranged from 37.2mg/L to 82.7mg/L.

3.1.5. Chloride

The chloride result shows that the values were lower when compared to the standard limit set by WHO and NESREA, the highest value recorded was 12.3mg/L with the lowest value of 0.83mg/L.

3.1.6. Turbidity

The Standard limit set by WHO for turbidity was set at 5NTU while that of NESREA was set at 10NTU. The lowest value recorded was 1.06 NTU in the month of May (MS), while the highest value was 7.25 NTU in the month of April (LS).

3.1.7. Total Dissolved Solids

TDS values recorded showed variations in the months of collection at different points of collection. The recorded values were below the WHO standard limit of 600ppm and NESREA standard of 500ppm. The obtained values were between 176.3ppm and 308.6ppm in all samples collected across the months of collection. The month of July (LS) had the most prevalent value, while the month of May (US) had the lowest.

3.1.8. Dissolved Oxygen

The values of Dissolved Oxygen recorded were observed to be above the standard limit set by NESREA, except July (US) with the value of 3.66mg/L and July (MS) with the value 4.00mg/L, which is within the standard limit. The value recorded for the rest of the month ranges from 4.70mg/L to 9.76mg/L.

3.1.9. Total Hardness (TH)

The values of Total Hardness recorded were observed to be within the standard limit set by NESREA which is 150mg/L and below the standard limit set by WHO which is 500mg/L. The minimal value was recorded in May (MS) as 77.61mg/L and the highest value recorded was 128.56mg/L in the month of April (LS).

3.2. Heavy Metals in Surface Water

The heavy metal analysis of surface water collected from various locations using ICP-OES indicates the presence of several metals at concentrations exceeding the permissible limits established by WHO and NSDWG.

In the month of April, the concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, V, and Zn were above the WHO and NESREA standard limit, with the exception of Cu, Na, Ni, and Ba as shown in Figure 1

In May, the concentrations of Ag, Cd, Ba, Ca, Mg, Zn, Fe, K, Al, Mn, Ni, Cr, V, As, and Na all exceeded the permissible limits with the exceptions of Na, Cr, and Ba, which were within the limits, while Cu and Zn was below the permissible levels as shown in Figure 2.

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The heavy metals detected in June were Na, Mg, K, Ca, Ba, Be, V, Mn, Fe, Co, Ni, Cu, Zn, Al, Cd, Ag, As, Se, Th, U, and Pb, as depicted in Figure.3. Similar to May, most concentrations exceeded permissible limits, except for Zn, Ba, Cu, and Ni, which were below those limits.

The metal of Mg, Mn, Fe, Al, and Cd had concentrations that exceeded the permissible in the month of July while other metals were within acceptable limits.

Table3. Physicochemical results for samples collected in April

Parameters	US	MS	LS	WHO STD (2017)	NESREA STD
pH	6.5	6.5	6.3	7.5-8.5	6.5-8.5
Temp (⁰ c)	28	28	28	<30	<30
EC (μ/cm)	484.7±1.15	382.8±2.12	336.4±0.49		1000
Alkalinity (mg/L)	76.5±0.05	45.6±0.01	78.6±0.00	200	
Chloride (mg/L)	8.86±0.01	8.66±0.01	12.3±0.01	250	350
Turbidity (NTU)	2.32±0.01	1.69±0.01	7.25±0.01	5	10
TDS (ppm)	259.6±0.57	229.3±1.15	276.3±58.3	600	500
DO (mg/L)	8.42±0.01	7.52±0.00	8.83±0.01		<4.0
Hardness (mg/L)	112.3±0.03	94.14±0.42	128.56±0.98	500	150

Table4. Physicochemical results for samples collected in May

Parameters	US	MS	LS	WHO STD (2017)	NESREA STD
pH	6.3	7.1	6.8	7.5-8.5	6.5-8.5
Temp (⁰ c)	30	30	32	<30°C	<30
EC (μ/cm)	325.0±0.05	460.0±0.00	70.3±0.15		1000
Alkalinity (mg/L)	61.3±0.02	39.4±0.11	82.7±1.05	200	
Chloride (mg/L)	5.06±0.02	4.64±0.01	4.39±0.02	250	350
Turbidity (NTU)	1.43±0.11	1.06±0.57	2.33±0.11	5	10
TDS (ppm)	176.3±0.20	201.3±1.21	185.1±0.05	600	500
DO (mg/L)	5.66±0.00	5.16±0.03	9.76±0.00		<4.0
Hardness (mg/L)	88.62±0.02	77.61±0.01	106.60±0.21	500	150

Table5. Physicochemical results for samples collected in June

Parameters	US	MS	LS	WHO STD (2017)	NESREA STD
pH	6.7	7.1	7.4	7.5-8.5	6.5-8.5
Temp (⁰ c)	32	32	30	<30	<30
EC (μ/cm)	558.3±1.52	483.0±1.00	438.0±1.00		1000
Alkalinity (mg/L)	57.4±0.02	42.3±0.03	67.3±0.05	200	
Chloride (mg/L)	1.13±0.05	0.93±0.05	0.86±0.05	250	350
Turbidity (NTU)	2.16±0.05	1.30±0.00	2.46±0.05	5	10
TDS (ppm)	278.0±1.00	232.6±1.52	219.3±0.57	600	500
DO (mg/L)	5.14±0.03	4.70±0.04	7.24±0.01		<4.0
Hardness (mg/L)	114.31±0.09	95.40±0.11	113.33±0.07	500	150

Table6. Physicochemical results for samples collected in July

Parameters	US	MS	LS	WHO STD (2017)	NESREA STD
pH	7.5	7.6	6.5	7.5-8.5	6.5-8.5
Temp (⁰ c)	28	28	28	<30	<30

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EC (μcm)	420.3 \pm 1.52	477.6 \pm 1.52	628.3 \pm 1.52		1000
Alkalinity (mg/L)	48.6 \pm 0.01	37.2 \pm 0.01	49.7 \pm 0.03	200	
Chloride (mg/L)	0.83 \pm 0.05	0.90 \pm 0.00	1.20 \pm 0.10	250	350
Turbidity (NTU)	2.36 \pm 0.05	1.36 \pm 0.05	2.33 \pm 0.05	5	10
TDS (ppm)	206.3 \pm 1.52	236.3 \pm 1.52	308.6 \pm 1.15	600	500
DO (mg/L)	3.66 \pm 0.11	4.00 \pm 0.10	5.60 \pm 0.01		<4.0
Hardness (mg/L)	120.56 \pm 0.16	98.65 \pm 0.01	126.27 \pm 0.12	500	150

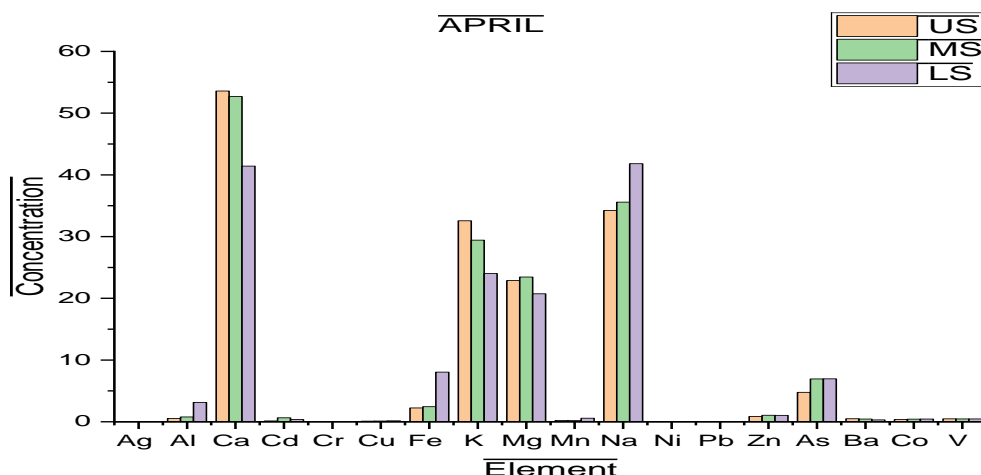


Fig1. Graphical representation of recorded heavy metals in the samples collected in the month of April

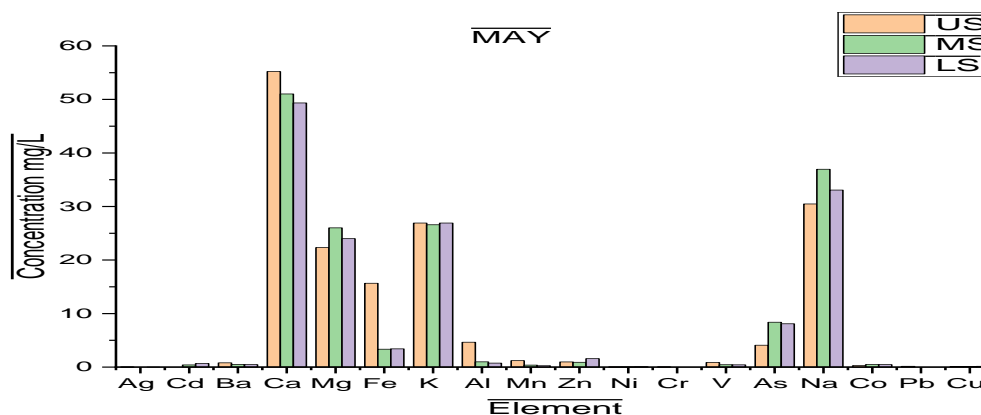


Fig2. Graphical representation of recorded heavy metals in the samples collected in the month of May

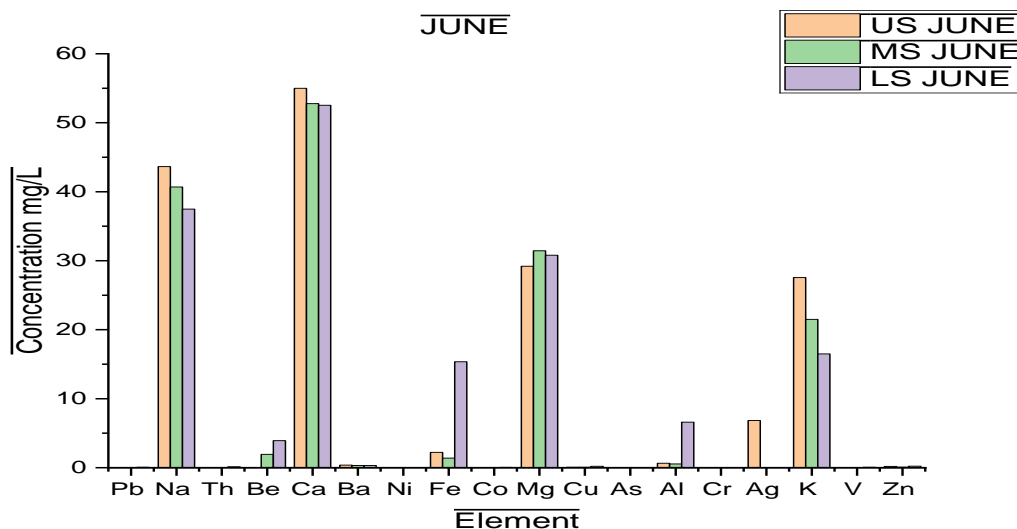


Fig3. Graphical representation of recorded heavy metals in the samples collected in the month of June

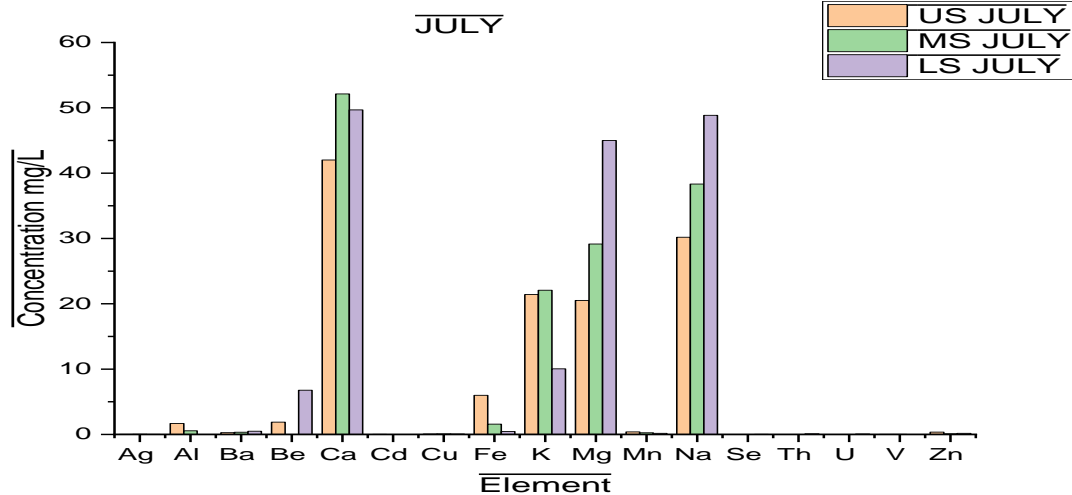


Fig4. Graphical representation of recorded heavy metals in the samples collected in the month of July

3.3. Health Risk Assessment

The results of CDI, HQ and HI of heavy metals; Pb, Cd, Cr, As, Cu, Zn, Fe, Ni, Mn, and Co in the collected samples in the region of study for adults and children collected in April and May through ingestion route are represented in Table 7, while that of the samples collected in June and July are represented in Table 8.

The value of those recorded through Dermal route are represented in Table 9 and 10. All of the heavy metals' HQ via ingestion and dermal routes, for both adults and children, showed only Pb, Cd, As, Co, Fe and Mn were above the stipulated limit while estimations for other metals were below the limit (< 1) for the two age sets. In addition, in both contact routes, the HQ values estimated for children were greater than those for adults. Through ingestion and dermal pathways, HI, a marker of non-cancer-inducing risk, was notably higher than the acceptable threshold for both adults and children.

CRI calculated for Pb, Cd, Cr and As via ingestion and dermal route of contact for both children and adult were outside the acceptable cancer risk range as represented in Table 11. But, in June MS the CRI of Pb was $\leq 10^{-6}$. In samples where the metals used to calculate the CRI were not detected such as June US and July MS, the CRI also was undetected.

Table7. Chronic Daily Impact, Hazard Quotient and Hazard Indices of Heavy Metals in samples Collected in April and May from different sampling sites Through Ingestion Route of Exposure

Receptor	H Ms	April						May					
		US	HQ US	MS	HQ MS	LS	HQ LS	US	HQ US	MS	HQ MS	LS	HQ LS
Adult	Pb	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0048	1.3703	0.0000	0.0000	0.0000	0.0000
	Cd	0.0044	4.4440	0.0202	20.1505	0.0114	11.436	0.0000	0.0000	0.0129	12.879	0.0212	21.245
	Cr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0009	0.3132	0.0000	0.0000	0.0000	0.0000
	As	0.1498	499.33	0.2180	726.61	0.2184	727.99	0.1285	428.29	0.2635	878.37	0.2546	848.60
	Cu	0.0034	0.0860	0.0039	0.0973	0.0050	0.1248	0.0038	0.0962	0.0034	0.0852	0.0047	0.1178
	Zn	0.0271	0.0903	0.0331	0.1103	0.0325	0.1084	0.0304	0.1015	0.0280	0.0935	0.0496	0.1655
	Fe	0.0706	0.1009	0.0770	0.1100	0.2529	0.3613	0.4922	0.7031	0.1048	0.1498	0.1070	0.1528
	Ni	0.0010	0.0484	0.0015	0.0729	0.0016	0.0794	0.0011	0.0542	0.0012	0.0610	0.0017	0.0850

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	Mn	0.00 68	0.04 83	0.00 61	0.043 3	0.01 83	0.13 05	0.03 79	0.27 07	0.01 19	0.085 2	0.00 81	0.05 80
	Co	0.01 10	0.55 09	0.01 33	0.662 8	0.01 38	0.69 22	0.00 86	0.42 77	0.01 49	0.744 7	0.01 43	0.71 28
HI			504. 69		747.8 6		740. 92		431. 63		892.4 7		871. 14
Childr en	Pb	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.01 02	2.90 67	0.00 00	0.000 0	0.00 00	0.00 00
	Cd	0.00 94	9.42 67	0.04 28	42.75 3	0.02 43	24.2 60	0.00 00	0.00 00	0.02 73	27.32 0	0.04 51	45.0 67
	Cr	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 20	0.66 44	0.00 00	0.000 0	0.00 00	0.00 00
	As	0.31 78	1059 .2	0.46 24	1541. 3	0.46 33	1544 .2	0.27 26	908. 51	0.55 90	1863. 2	0.54 00	1800 .1
	Cu	0.00 73	0.18 25	0.00 83	0.206 3	0.01 06	0.26 47	0.00 82	0.20 40	0.00 72	0.180 7	0.01 00	0.24 98
	Zn	0.05 74	0.19 15	0.07 02	0.233 9	0.06 90	0.23 00	0.06 46	0.21 53	0.05 95	0.198 2	0.10 53	0.35 10
	Fe	0.14 98	0.21 40	0.16 33	0.233 3	0.53 65	0.76 64	1.04 40	1.49 15	0.22 24	0.317 7	0.22 69	0.32 42
	Ni	0.00 21	0.10 27	0.00 31	0.154 7	0.00 34	0.16 83	0.00 23	0.11 50	0.00 26	0.129 3	0.00 36	0.18 03
	Mn	0.01 44	0.10 25	0.01 29	0.092 0	0.03 88	0.27 68	0.08 04	0.57 41	0.02 53	0.180 7	0.01 72	0.12 30
	Co	0.02 34	1.16 87	0.02 81	1.406 0	0.02 94	1.46 83	0.01 81	0.90 73	0.03 16	1.579 7	0.03 02	1.51 20
HI			1070 .5		1586. 3		1571 .6		915. 58		1893. 1		1847 .8

Table8. Chronic Daily Impact, Hazard Quotient and Hazard Indices of Heavy Metals in samples Collected in June and July from different sampling sites Through Ingestion Route of Exposure

Recep tor	H Ms	June						July					
		US	HQ US	MS	HQ MS	LS	HQ LS	US	HQ US	MS	HQ MS	LS	HQ LS
Adult	Pb	0.00 00	0.00 00	0.00 08	0.240 7	0.00 19	0.53 97	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Cd	0.00 00	0.00 00	0.00 01	0.122 6	0.00 01	0.10 06	0.00 03	0.27 03	0.00 00	0.000 0	0.00 01	0.08 80
	Cr	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	As	0.00 00	0.00 00	0.00 07	2.430 5	0.00 00	0.00 00	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Cu	0.00 19	0.04 68	0.00 20	0.048 8	0.00 63	0.15 83	0.00 22	0.05 47	0.00 26	0.064 5	0.00 22	0.05 55
	Zn	0.00 60	0.02 00	0.00 29	0.009 6	0.00 69	0.02 30	0.01 12	0.03 74	0.00 34	0.011 5	0.00 53	0.01 78
	Fe	0.06 98	0.09 97	0.04 35	0.062 2	0.48 29	0.68 98	0.18 82	0.26 88	0.04 97	0.071 0	0.01 45	0.02 07
	Ni	0.00 00	0.00 00	0.00 00	0.000 0	0.00 02	0.00 83	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Mn	0.00 49	0.03 48	0.00 47	0.033 8	0.02 14	0.15 27	0.01 25	0.08 93	0.00 83	0.059 0	0.00 53	0.03 82
	Co	0.00 00	0.00 00	0.00 00	0.000 0	0.00 14	0.06 91	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	HI		0.20 13		2.948 1		1.74 16		0.72 05		0.206 0		0.22 01
Childr en	Pb	0.00 00	0.00 00	0.00 18	0.510 5	0.00 40	1.14 48	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Cd	0.00 00	0.00 00	0.00 00	0.260 0	0.00 00	0.21 00	0.00 00	0.57 00	0.00 00	0.000 0	0.00 00	0.18 00

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		00	00	03	0	02	33	06	33	00	0	02	67
	Cr	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	As	0.00 00	0.00 00	0.00 15	5.155 6	0.00 00	0.00 00	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Cu	0.00 40	0.09 92	0.00 41	0.103 5	0.01 34	0.33 58	0.00 46	0.11 60	0.00 55	0.136 8	0.00 47	0.11 77
	Zn	0.01 27	0.04 24	0.00 61	0.020 4	0.01 47	0.04 89	0.02 38	0.07 93	0.00 73	0.024 3	0.01 13	0.03 77
	Fe	0.14 81	0.21 16	0.09 23	0.131 9	1.02 43	1.46 33	0.39 91	0.57 02	0.10 55	0.150 7	0.03 08	0.04 40
	Ni	0.00 00	0.00 00	0.00 00	0.000 0	0.00 04	0.01 77	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	Mn	0.01 03	0.07 39	0.01 00	0.071 7	0.04 53	0.32 39	0.02 65	0.18 95	0.01 75	0.125 2	0.01 13	0.08 10
	Co	0.00 00	0.00 00	0.00 00	0.000 0	0.00 29	0.14 67	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00
	HI		0.42 70		6.253 6		3.69 43		1.52 83		0.437 0		0.46 70

Table9. Chronic Daily Impact, Hazard Quotient and Hazard Indices of Heavy Metals in samples Collected in April and May from different sampling sites Through Dermal Route of Exposure

Recep tor	H Ms	April						May					
		US	HQ US	MS	HQ MS	LS	HQ LS	US	HQ US	MS	HQ MS	LS	HQ LS
Adult	Pb	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 27	5.08 67	0.00 00	0.000 0	0.00 00	0.00 00
	Cd	0.00 25	247. 45	0.01 12	1122. 3	0.00 64	636. 82	0.00 00	0.00 00	0.00 72	717.1 5	0.01 18	1183 .0
	Cr	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 05	8.72 08	0.00 00	0.000 0	0.00 00	0.00 00
	As	0.08 34	678. 13	0.12 14	986.8 1	0.12 16	988. 67	0.07 15	581. 66	0.14 67	1192. 9	0.14 18	1152 .4
	Cu	0.00 19	0.15 97	0.00 22	0.180 5	0.00 28	0.23 16	0.00 21	0.17 85	0.00 19	0.158 1	0.00 26	0.21 86
	Zn	0.01 51	0.25 13	0.01 84	0.307 0	0.01 81	0.30 18	0.01 70	0.28 25	0.01 56	0.260 2	0.02 76	0.46 07
	Fe	0.03 93		0.04 29		0.14 08		0.27 41		0.05 84		0.05 96	
	Ni	0.00 05	0.17 97	0.00 08	0.270 7	0.00 09	0.29 46	0.00 06	0.20 13	0.00 07	0.226 3	0.00 09	0.31 56
	Mn	0.00 38	2.04 77	0.00 34	1.836 5	0.01 02	5.52 87	0.02 11	11.4 67	0.00 66	3.608 4	0.00 45	2.45 57
	Co	0.00 61	0.38 35	0.00 74	0.461 3	0.00 77	0.48 18	0.00 48	0.29 77	0.00 83	0.518 3	0.00 79	0.49 61
HI		928. 60		2112. 1		1632 .3		607. 90		1914. 8		2339 .4	
Childr en	Pb	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 57	10.8 52	0.00 00	0.000 0	0.00 00	0.00 00
	Cd	0.00 53	527. 89	0.02 39	2394. 3	0.01 36	1358 .6	0.00 00	0.00 53	0.01 53	1529. 9	0.02 52	2523 .7
	Cr	0.00 00	0.00 00	0.00 00	0.000 0	0.00 00	0.00 00	0.00 11	18.6 04	0.00 00	0.000 0	0.00 00	0.00 00
	As	0.17 79	1446 .7	0.25 89	2105. 2	0.25 94	2109 .2	0.15 26	1240 .8	0.31 30	2544. 8	0.30 24	2458 .6
	Cu	0.00 41	0.34 07	0.00 46	0.385 2	0.00 59	0.49 40	0.00 46	0.38 08	0.00 40	0.337 2	0.00 56	0.46 64
	Zn	0.03 22	0.53 61	0.03 93	0.655 0	0.03 86	0.64 39	0.03 62	0.60 27	0.03 33	0.555 1	0.05 90	0.98 29

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	Fe	0.08 39		0.09 14		0.30 04		0.58 47		0.12 45		0.12 71	
	Ni	0.00 11	0.38 33	0.00 17	0.577 4	0.00 19	0.62 84	0.00 13	0.42 93	0.00 14	0.482 8	0.00 20	0.67 32
	Mn	0.00 80	4.36 84	0.00 72	3.918 0	0.02 17	11.7 95	0.04 50	24.4 65	0.01 42	7.698 0	0.00 96	5.23 88
	Co	0.01 31	0.81 81	0.01 57	0.984 2	0.01 64	1.02 78	0.01 02	0.63 51	0.01 77	1.105 8	0.01 69	1.05 84
HI			1981 .0		4505. 9		3482 .3		1296 .8		4084. 9		4990 .7

Table10. Chronic Daily Impact, Hazard Quotient and Hazard Indices of Heavy Metals in samples Collected in June and July from different sampling sites Through Dermal Route of Exposure

Recept or	HM s	June						July					
		US	HQU S	MS	HQM S	LS	HQL S	US	HQU S	MS	HQM S	LS	HQL S
Adult	Pb	0.00 00	0.000 0	0.00 05	0.893 3	0.00 11	2.003 3	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Cd	0.00 00	0.000 0	0.00 01	6.825 0	0.00 01	5.600 0	0.00 02	15.05 0	0.00 00	0.000 0	0.00 00	4.900 0
	Cr	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	As	0.00 00	0.000 0	0.00 04	3.300 8	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Cu	0.00 10	0.086 8	0.00 11	0.090 6	0.00 35	0.293 9	0.00 12	0.101 5	0.00 14	0.119 7	0.00 12	0.103 0
	Zn	0.00 33	0.055 6	0.00 16	0.026 8	0.00 38	0.064 1	0.00 62	0.104 1	0.00 19	0.031 9	0.00 30	0.049 4
	Fe	0.03 89		0.02 42		0.26 89		0.10 48		0.02 77		0.00 81	
	Ni	0.00 00	0.000 0	0.00 00	0.000 0	0.00 01	0.030 9	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Mn	0.00 27	1.476 1	0.00 26	1.432 3	0.01 19	6.468 3	0.00 70	3.784 4	0.00 46	2.500 4	0.00 30	1.617 8
	Co	0.00 00	0.000 0	0.00 00	0.000 0	0.00 08	0.048 1	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	HI			1.618 5		12.56 9		14.50 8		19.03 9		2.652 0	
Childr en	Pb	0.00 00	0.000 0	0.00 10	1.905 8	0.00 22	4.273 8	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Cd	0.00 00	0.000 0	0.00 01	14.56 0	0.00 01	11.94 6	0.00 03	32.10 6	0.00 00	0.000 0	0.00 01	10.45 33
	Cr	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	As	0.00 00	0.000 0	0.00 09	7.041 7	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Cu	0.00 22	0.185 1	0.00 23	0.193 2	0.00 75	0.626 9	0.00 26	0.216 5	0.00 31	0.255 4	0.00 26	0.219 6
	Zn	0.00 71	0.118 7	0.00 34	0.057 2	0.00 82	0.136 8	0.01 33	0.222 0	0.00 41	0.068 1	0.00 63	0.105 5
	Fe	0.08 29		0.05 17		0.57 36		0.22 35		0.05 91		0.01 72	
	Ni	0.00 00	0.000 0	0.00 00	0.000 0	0.00 02	0.066 0	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	Mn	0.00 58	3.149 0	0.00 56	3.055 7	0.02 54	13.79 9	0.01 49	8.073 3	0.00 98	5.334 2	0.00 64	3.451 3
	Co	0.00 00	0.000 0	0.00 00	0.000 0	0.00 16	0.102 7	0.00 00	0.000 0	0.00 00	0.000 0	0.00 00	0.000 0
	HI			3.452 8		26.81 3		30.95 1		40.61 8		5.657 7	

Table11. Cancer Risk Index of Heavy Metals in samples Collected from different sampling sites Through Ingestion and Dermal Route of Exposure

Receptor	H M s	April			May			June			July		
CRIning		US	MS	LS	US	MS	LS	U S	MS	LS	US	M S	LS
Adult	P	0	0	0	4.08E ⁻⁰⁵	0	0	0	7.16E ⁻⁰⁶	1.61E ⁻⁰⁵	0	0	0
	C	0.0271	0.1229	0.0697	0	0.0785	0.1295	0	0.0008	0.0006	0.0017	0	0.0005
	C	0	0	0	0.0005	0	0	0	0	0	0	0	0
	A	0.2247	0.3269	0.3275	0.1927	0.3952	0.3818	0	0.0011	0	0	0	0
Children	P	0	0	0	8.65E ⁻⁰⁵	0	0	0	1.52E ⁻⁰⁵	3.41E ⁻⁰⁵	0	0	0
	C	0.0575	0.2607	0.1479	0	0.1666	0.2749	0	0.0015	0.0013	0.0035	0	0.0011
	C	0	0	0	0.0009	0	0	0	0	0	0	0	0
	A	0.4766	0.6935	0.6949	0.4088	0.8385	0.8100	0	0.0023	0	0	0	0
CRIderm													
Adult	P	0	0	0	0.0040	0	0	0	0.0007	0.0015	0	0	0
	C	0.0150	0.0684	0.0388	0	0.0437	0.0721	0	0.0004	0.0003	0.0009	0	0.0003
	C	0	0	0	0.0105	0	0	0	0	0	0	0	0
	A	0.3052	0.4442	0.4450	0.2618	0.5370	0.5188	0	0.0014	0	0	0	0
Children	P	0	0	0	0.0086	0	0	0	0.0015	0.0034	0	0	0
	C	0.0322	0.1460	0.0828	0	0.0933	0.1539	0	0.0008	0.0007	0.0019	0	0.0006
	C	0	0	0	0.0223	0	0	0	0	0	0	0	0
	A	0.6512	0.9477	0.9495	0.5586	1.1456	1.1068	0	0.0032	0	0	0	0

4. DISCUSSION

When the pH value of a water body decreases compared to the neutral pH state, it indicates an increase in acidity. A more acidic water body poses greater risks for living organisms when used or ingested as it has been known to contain high levels of heavy metals (Arhin *et al.*, 2023). The pH values of the surface water samples collected were within the acceptable standard limits in all the months. This means the surface water can support biological and chemical activities without issues (Afriyie *et al.*, 2022).

Water temperature is a crucial factor that directly influences the chemical and biochemical reactions necessary for the survival of various organisms (Dallas, 2009). From this research, it shows that surface water that exceeded the standard can be attributed to intense solar radiation and the absence of large trees to provide essential shade due to the removal of these trees by artisanal miners along the riverbed causing detrimental impact on the thermal conditions of the surface water.

The conductivity of water is a factor that impacts its salinity levels, which in turn affects its suitability for irrigation and domestic use (Ogunfowokan *et al.*, 2013). In this study, it was observed that the conductivity values recorded from all sampled locations were notably lower than the established standards, suggesting that the water is only weakly conductive, which may positively influence its suitability for agricultural and household purposes.

The assessment of total alkalinity for the water samples taken from the river indicated that the sample values fell comfortably within the permissive limits established by the WHO. This is significant as it

implies that the water can be safely utilized for a range of applications, including irrigation, and other domestic uses. An adequate level of alkalinity serves as a natural buffer system that stabilizes pH levels in the water, thereby preventing drastic shifts that can be detrimental to the environment and human health (Samuel *et al.*, 2015).

Chloride is an anion present in all natural waters, with concentrations that can vary significantly. Measuring chloride levels helps indicate salt pollution and assess how this pollution could affect the water's beneficial uses for agriculture and domestic purposes (Tadesse *et al.*, 2024). The chloride values recorded were within the standard limits.

In terms of turbidity, the values recorded were below the standard limits, except at the LS in April, which exceeded the permissible limit which may be attributed to low dissolved solids in the water body, likely due to the good flow capacity of the river.

Total Dissolved Solids (TDS) consists of trace amounts of organic materials and inorganic salts dissolved in water (Tadesse *et al.*, 2024). TDS is an important parameter for assessing water suitability. The samples collected from the surface water had values below the permissible limit, this indicates that the water contains little to no contaminant which makes it suitable for usage.

The maximum dissolved oxygen in surface water was 9.76 mg/L at point LS. All collected samples exceeded the standard limits, indicating a high level of aeration at the sampling sites, which makes the water suitable for all purposes.

Soft water is classified as having a calcium carbonate concentration between 75 and 150 mg/L according to the commonly accepted categorization for water hardness while water is deemed hard when the concentration exceeds 150 mg/L (Ayandiran *et al.*, 2018). The analysis of the surface water samples revealed that concentrations was below the permissible limit of 150 mg/L, which suggests that the water sample is a soft water.

Toxic metals like lead (Pb), arsenic (As), and cadmium (Cd) pose significant health risks. Their accumulation has been linked to various health issues in the body, including neurological disorders, cancer, and damage to vital organs, highlighting the importance of monitoring and managing vulnerability to these harmful heavy metals (Odukoya *et al.*, 2017).

Odukoya *et al.* (2017) studied the health hazards related to toxic metals present in the surface water of Ilesha gold mine sites. It was discovered that mining is the primary factor contributing to the discharge of harmful metals such as manganese (Mn), lead (Pb), cadmium (Cd), arsenic (As), copper (Cu), chromium (Cr), nickel (Ni), and vanadium (V), which accounted for 47.73% of the variance in his data. The release of these toxic elements is linked to both mineral dissolution and anthropogenic processes stemming from leachates produced by gold mining activities.

In a review, Laker (2023) concluded that gold mining has a devastating impact on environmental health. The study pointed out that contaminants from Gold Mine Tailing Storage Facilities can persist at high rates for decades, sometimes continuing unabated for over fifty years.

Cadmium (Cd), on the other hand, is found in high concentrations in the surface water, and its presence in large amounts poses a serious health risk. Nishijo *et al.* (2017) evaluated the factors behind the deaths of Itai-itai disease patients and discovered the cause to be severe chronic Cd poisoning. It was found that there is no dose-related effect of Cd poisoning on mortality. Presence of Cd in surface water can bring about severe health problems among the users.

Kamunda *et al.* (2016) estimated the human health risks related to the heavy metals in the Witwatersrand gold mining area. It was discovered that the concentrations of chromium (Cr), nickel (Ni), and arsenic (As) exceeded permissible levels. These three potentially toxic elements were also noted as hazards in the long-defunct New Machavie gold mine in another location. This study executed by Kamunda *et al.* (2016) supports the analysis of Cr and As in the surface water samples conducted in this research work, which showed that the levels of Cr and As were higher than permissible limits, this may present a serious health risk to adults and an even more serious risk to children.

Lead is a major contaminant in mining sites and a non-essential heavy metal that is frequently discovered with gold. It can seriously harm brain and nerve cells and has been identified as a possible

human carcinogen. During pregnancy, lead can be passed from mother to child, and it builds up in the human body (Wasiu *et al.*, 2016). The recorded values of water samples from the study area exceed the specified limit of 0.01 mg/L set by WHO and NESREA, which suggests that the continuous use of the water samples for domestic purposes can lead to Lead poisoning by the users.

The analysis conducted by Adeniyi *et al.* (2019) on the Anka area in Northwest Nigeria, revealed that lead poisoning linked with artisanal gold mining has resulted in the deaths of more than 400 children in the region.

Amadi *et al.* (2017) reported on the merits and demerits of iron (Fe) and manganese (Mn) in the water around the Galadima Koko mining site. It was noted that a lack of Fe in water can lead to goiter, while high concentrations can result in turbid, colored, and unpleasant-tasting water, potentially causing hemochromatosis. Additionally, the study indicated that elevated levels of Mn can impose neurological disorders in animals. The surface water sample collected in April for this study has the highest concentration of Fe which resulted in the high turbidity value recorded for the month.

Investigations in environmental toxicology have shown that Al can pose a significant threat to organisms, leading to various diseases (Monisha *et al.*, 2014). Factors such as pH levels and organic matter content greatly influence the toxicity of aluminum. As pH decreases, the toxicity of aluminum increases (Monisha *et al.*, 2014).

The health risk assessment result of this study throughout the month of sample collection and the points of collection reveals definite cancer risks for both adults and children from the usage of the water over a lifetime. The cancer risk index showed that children are more at risk than adult. The report of Emmanuel *et al.*, 2022 is in support of this conclusion, seeing as the value recorded were above the acceptable range (10^{-6} to 10^{-4}) set by regulatory bodies. The concentration of heavy metals present in the sample influences the degree of the carcinogenic and non-carcinogenic effects of the heavy metals (Emmanuel *et al.*, 2022).

Shaffiudin *et al.* 2021 reported that the ingestion contact route usually have more carcinogenic and non-carcinogenic effect, and the ingestion pathway of contact is considered the major route of exposure to heavy metals. This study conducted is in support of this report, as the ingestion route pronounced more cancer risk in adult and children than dermal contact route.

5. CONCLUSION

This study's primary objective was to evaluate the levels of heavy metals in the Ilahun River as a result of mining operations there and the risks to both adults and children's health. The findings of this investigation proved that the river is contaminated with heavy metals whose value are above the standard limit. The physico-chemical analysis showed variation throughout the months of sample collection, most likely as a result of mining operations and naturally occurring changes in geology. The value of the parameters analyzed were within the permissible limit. There are risks to public health since the levels of heavy metals are typically higher than the WHO-recommended threshold. The month with the highest level of contamination was May, having the highest number of both essential and heavy metals in concentrations above the standard limit. The heavy metal with the highest concentration recorded was As and the essential metal with the highest value recorded was Ca, both in the month of May. The health risk assessment conducted showed that the metals are able to cause both carcinogenic and non-carcinogenic effect when ingested orally and absorbed through dermal contact route. These effects are more pronounced in children than adults.

RECOMMENDATION

The research's conclusions suggest that miners should refrain from engaging in gold extraction and other mining activities in regions where rivers are mostly used for household purposes. Additionally, it is crucial to inform the miners and the society at large about the risks and harm associated with consuming these metals.

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