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Preliminary Health Risk Assessment of Water from Asa River, Ilorin, North-Central Nigeria

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Abstract

This study was carried out to establish health impacts of some trace elements (Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in Asa-river, using Inductively Coupled Plasma-Mass Spectrometer technique for the chemical analysis. Laboratory results show that Al, Fe and Mn average concentrations are higher than prescribed limits unlike others. The Contamination Indexes reveal that the elements are heavily loaded in the water. The exposure dose in both adults and children ranges from 0.021 in As to 181 in Fe (in adults) and from 0.068 in As to 576 in Fe (in children). The average Hazard Quotient (HQ) values for adults and children are generally lower than one except Mn that has average value greater than one in both age groups. However, for children, individual HQ in Fe in some of the locations are >1. The Hazard Index (HI)for adults and children ranged from low to high. The average values of Chronic Daily Intake (CDI) are generally <1. However, in children, values for Fe in some locations are >1. The average Carcinogenic Risk (CR) of Cr and Pb computed for adults and children indicated that the values are greater than the risk limit of 10^{-6} and 10^{-4}. This could result in potential health risk to the consumers. The sources of these trace elements are largely from various anthropogenic activities and slightly from weathering of rocks in the study area. It is recommended that adequate and well monitored precautions need to be taken to safeguard the health of the consumers especially the children with low immunity.

Keynotes: Health Risk Assessment, Asa River, Hazard Index, Chronic Daily Intake, Carcinogenic Risk.

Introduction

The ravaging of various diseases across the globe in recent times calls for global consideration and intervention because millions of people are being plagued and this has geometrically increased the mortality rate. In developing world like Nigeria there are also problems of indiscriminate disposal of wastes (industrial wastes, agricultural wastes, domestic wastes, municipal wastes) and this scenario cuts across the rural and urban areas of the country. These waste materials find their ways into near or faraway streams, rivers and groundwater, thereby increasing the elemental compositions of toxic elements in the consumable water phases (Hynds *et al*., 2014; Lindgren *et al*., 2016; Edokpayi *et al*., 2018). This directly or indirectly affects the quality of the sources of water and ultimately impairs the health of the consumers.

Similar works have been carried out across the globe by several researchers. Edokpayi *et al.*, 2018 evaluated water quality and human risk assessment due to heavy metals in groundwater around Muledane area of Vhembe District, Limpopo Province, South Africa. Inductively Coupled Plasma Optical Atomic Spectrophotometer (ICP-OES) was used to analyze the water samples. The results of their study revealed that ingestion of the investigated boreholes water poses carcinogenic risk

regarding the estimated Mn, Fe and Cu for adults and children after Quantitative Health Risk Assessment of the water**.**

The study area is underlain by the basement complex of south western part of Nigeria, which is of Precambrian to lower Paleozoic in age (Rahaman, 1976; Oluyide, 1979). This consists of gneisses and migmatites, metasediments (schists, quartzites and metavolcanics and older Pan-African granite and late-stage minor pegmatitic and aplitic intrusives (Oluyide *et al*., 1998; Omotoso *et. al*., 2011). According to the work of Olasehinde *et al*. (1998), Ilorin is situated on the undifferentiated Precambrian Basement Complex rocks of granitic and metamorphic origin. It is also reported that the oldest rocks in the area comprise gneiss complex whose principal member is biotite-hornblende gneiss with intercalated amphibolites and other rock types in the area are the older granite mainly porphyritic granite, gneiss and granite-gneiss and quartz schist.

Asa river is one of the major sources of drinking water supply in Ilorin metropolis which was dammed around Asa township of Ilorin city. The water supplies industrial, agricultural and domestic sectors of the city. This same water resources serves as a source of irrigation for the farming system in the area. It also serves as a source of water for Fish ponds in the area. Consequently, as a result of various anthropogenic and natural weathering of rocks in the area, there is the need to critically examine the qualitative and quantitative health risks of the water resources so as to safeguard the health of the consumers.

Methodology

Environmental Settings of the Study Area

According to NOAA, 2016, the study area is situated in the savannah region of Nigeria which also lies within longitudes 4° 30’ E, 4° 40’E and latitudes 8° 19’N, 8° 29’N. The weather condition in the region is of two main types namely rainy season and dry season. The rainy season starts in the month of late March and ends around October, while dry season begins in November and ends in early March. The average annual rainfall ranges between 4.6 mm in November and 211.1 mm in September while the average relative humidity ranges from 29% in February to 70.2% in August. The mean annual temperature falls within 27°C to 30°C.
The location map of the study area is presented in Figure 1 and this also shows the sampling points.

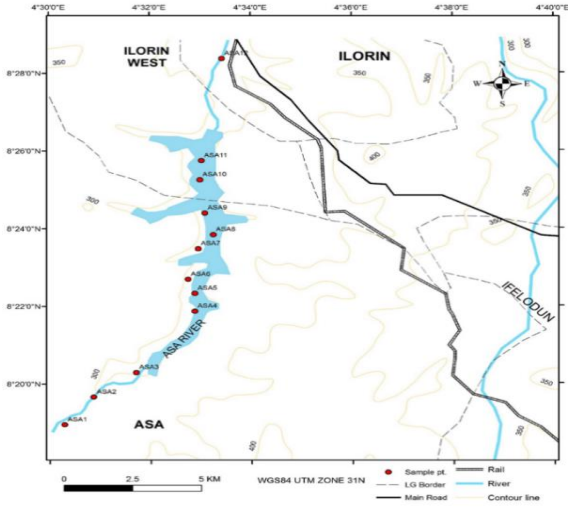

Figure 1: Location Map of the Study area showing Sampling Points (*carved from topographical map sheet 223 NW, Ilorin, Nigeria, Published by Federal Survey, Nigeria, 1966***)**

The study was carried out during the dry season (that is, January, 2017). Random sampling method was employed in the collection of the water samples. 60ml white bottle containers with white cover were used to collect the water samples. Topographical map sheet 223 NW, Ilorin was used as base map to navigate the sampling points with the aid of GPS. With the aid of the location map, 12 sampling points were randomly mapped out because of the challenge of accessibility in some areas which did not support systemic sampling technique or gridding.

At each proposed sampling point, water sample was taken randomly. Before sampling, the white bottle container was rinsed severally to remove every dirt from the container, then the containers were filled with the water samples to the brim respectively. Air space was prevented to make the water in the container airtight. Few drops of concentrated nitric acid were added to the water samples respectively and covered tightly immediately. Nitric acid prevents the precipitation of the cations from solution. After each sampling, the bottle was labelled accordingly. The samples were shipped to the laboratory for hydrochemical analysis. The water samples were analyzed in ACME laboratory, Vancouver, Canada, North America, using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) laboratory technique.

Data Evaluation

The selected trace elements (Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were examined by: comparing their respective concentrations with WHO (2006) and NSDWQ (2007); determining some of their contamination indexes (i.e. contamination factor and degree of contamination); health risk assessment using the average daily dose, hazard quotient, hazard index, chronic daily intake and carcinogenic risk. The WHO standard, Nigerian standard for drinking water qualities and the Mean Composition of World Rivers (MCWR) were presented in Table 1 respectively. The MCWR was adopted to normalize the results of the Contamination Indexes.

Table 1: WHO and Nigerian Standards for Drinking Water Quality for potable water and mean composition of world rivers.

Trace Elements	WHO Standard (ppm), 2006	NSDWQ, 2007 (ppm)	Mean composition of world rivers in ppm, (*after* Viers *et al.,* 2009*)*
Aluminum, Al	0.2	0.2	0.32
Arsenic, As	0.01	0.01	0.00062
Barium, Ba	0.3	0.7	0.023
Chromium, Cr	0.05	0.05	0.0007
Copper, Cu	2	1	0.00148
Iron, Fe	0.3	0.3	0.066
Manganese, Mn	0.5	0.2	0.00042
Nickel, Ni	0.02	0.001	0.0008
Lead, Pb	3	0.01	0.00008
Cadmium, Cd	0.003	0.003	0.0006

(WHO, 2006; NSDWQ, 2007; Vier et al., 2009)

Contamination Factor: This can be expressed as the single index usually determined using equation 1:

$$Cf = \frac{Cm}{Bm} \quad (1)$$

C*f* is the contamination factor of the trace element of interest; Cm is the concentration of the trace element in the sample; Bm is the background concentration of the trace element in the sample. MCWR was used for the value of Bm in this research. Atiemo *et al.*, 2011 presented four categories of contamination factors which include the following:

< 1= low contamination factor;
1-3=moderate contamination factor;
3-6=considerable contamination factor;
> 6=very high contamination factor

Degree of Contamination (C_{deg}): This is the addition of all the contamination factors in the sample and it can be expressed as indicated in equation 2:

$$C_{deg} = \sum {}^{C_m}/_{B_m} \quad (2)$$

Cm is the concentration of water; Bm is the local background concentration of trace element, m within the pristine area of catchment. Atiemo *et al*., 2011 also identified four categories namely: < 8=low degree of contamination, 8-16=moderate degree of contamination, 16-32=considerable degree of contamination and > 32=very high degree of contamination.

Quantitative Health Risk Assessment:

The Average Daily Dose*:* The Average Daily Dose was computed using equation 3 shown below to estimate the health risk of the water samples from the study area.

$$ADD = \frac{Cwater * IR * EF * ED}{BW * AT} \quad (3)$$

where, ADD is the Average Daily Dose similar to the exposure dose through ingestion of water (µg/kg/day); C_{water} is the average concentration of the estimated metals in water (µg/L); IR is the ingestion rate in this research (2.72 L/day for adults; 1.8 L/day for children); EF is the exposure frequency (365 days/year); ED is the exposure duration (70 years for adults; and 6 years for children); BW is the average body weight (70 kg for adults; 15 kg for children); AT is the averaging time (365 days/year × 70 years for an adult; 365 days/year × 6 years for a child), Edokpayi, *et al*. (2018). Hazard Quotient (HQ): The non-carcinogenic health risk as a result of the exposure to surface water resources consumption was computed as the hazard quotient (HQ). Equation 4 is used to calculate the HQ of Asa river:

$$HQ = \frac{ADD}{RfD} \quad (4)$$

ADD is the average daily dose similar to the exposure dose through ingestion of water (µg/kg/day); R_fD is the reference dose of a specific element. The reference dose for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 1 mg/kg/day, 0.0003 mg/kg/day, 0.2 mg/kg/day, 1.5 mg/kg/day, 0.04 mg/kg/day, 0.7 mg/kg/day, 0.046 mg/kg/day, 0.02 mg/kg/day, 0.0035 mg/kg/day and 0.3 mg/kg/day respectively (USEPA, 2001). If the value of HQ is greater than unity, that is, 1, there is possibility of non-carcinogenic negative effects on health while HQ value less than unity infers that the

exposure to the surface water consumption would not likely have any practical effect on the consumers (USEPA 2001, Yuan *et al.,* 2017; Maxwell *et al*., 2018; Joel *et al*., 2018).

Hazard Index (HI): To assess the overall potential non-carcinogenic health effects posed by more than one metal and pathway, the addition of the computed HQs across metals/trace elements was expressed as hazard index (HI) using the equation 5 according to USEPA (1989):

$$HI = \sum_{i=1}^{n} HQ \quad (5)$$

HI > 1 is an indication of a potential adverse effect on human health (Li SY and Zhang, 2010; Naveedullah *et al*., 2014). Table 2 presents the classification of non-carcinogenic risk.

Table 2: Classification of non-carcinogenic risk

Risk Level	Hazard Index (HI)	Chronic Risk
1	<0.1	Negligible
2	≥ 0.1 <1	Low
3	≥ 1 < 4	Medium
4	≥ 4	High

(*USEPA, 1989)*

Chronic Daily Intake (CDI*):* Edokpayi *et al* (2018) calculated Chronic daily intake (CDI) of trace elements through ingestion using equation 6 below:

$$CDI = C_{water} * \frac{DI}{BW} \quad (6)$$

where C_{water}, DI and BW denote the concentration of trace elements in water (measured in mg/kg), average daily intake of water (2.72 L/day for adults; 1.8 L/day for children) and body weight (70 kg for adults; 15 kg for children), respectively.

Carcinogenic Risk (CR): Edokpayi *et al (*2018) also used equation 7 below to estimate the carcinogenic risk (CR) through ingestion and this was also adopted in this research:

$$CR_{ing} = \frac{Exping}{SF_{ing}} \quad (7)$$

where, CR_{ing} =carcinogenic risk via ingestion route and SF_{ing} = carcinogenic slope factor where Pb is 8.5E, Cd is 6.1E+03 and Cr is 5.0E+02 µg/kg/day (Iqbal and Shah, 2013; Naveedullah *et al*., 2014; Asare-Donkor *et al.*, 2016). The CR_{ing} values for other trace elements were not computed in this study because of unobtainability of the SF_{ing} values.

Results and Discussion

Hydrochemical results

The results of some of the trace elements in the samples analyzed are presented in Table 3 and Figure 2 illustrates the profile of the average concentrations of the selected trace elements compared with WHO (2006) and NSDWQ (2007. Fe ranges from 0.58 to 15.02 ppm (average=4.80ppm), Mn ranges from 0.048 to 6.256 ppm (average=1.61 ppm), Al ranges from 0.06 to 4.24 ppm (average=0.79), Ba ranges from 0.057 to 0.406 ppm (average=0.155 ppm), Zn ranges from 0.004 to 0.0441ppm (average=0.011ppm), Cu ranges from 0.0015 to 0.023 ppm (average=0.006 ppm), Pb ranges from 0.0017 to 0.0193ppm (average=0.0043), Ni ranges from 0.0015 to 0.0078 ppm (average=0.0026 ppm), Cr ranges from 0.0004 to 0.0072 ppm (average=0.0021ppm) and As ranges

from 0.0004 to 0.0011 ppm. Based on average values, their concentration sequence is as follows: Fe>Mn>Al>Ba>Zn>Cu>Pb>Ni>Cr>As.

Table 3: Hydrochemical Analysis Data of Selected Trace Elements in Asa River and their Statistical Summary

	Trace Elements (ppm)									
	Al	**As**	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
WHO, 2006	**0.2**	**0.01**	**0.3**	**0.05**	**2**	**0.3**	**0.5**	**0.02**	**0.01**	**3**
NSDW, 2007	**0.2**	**0.01**	**0.7**	**0.05**	**1**	**0.3**	**0.2**	**0.001**	**0.01**	**3**
ASA-1	0.145	0.0004	0.14593	0.0011	0.0025	0.582	1.31908	0.0022	0.0021	0.0048
ASA-2	0.173	0.0006	0.16798	0.0012	0.0098	1.335	3.82324	0.0023	0.0017	0.0165
ASA-3	0.132	0.0011	0.27743	0.0011	0.0018	10.092	6.256	0.0015	0.0047	0.004
ASA-4	4.241	0.001	0.40601	0.0072	0.023	12.943	2.72348	0.0078	0.0193	0.0441
ASA-5	0.633	0.0006	0.11083	0.0018	0.0035	6.639	1.05894	0.0024	0.0023	0.0053
ASA-6	0.785	0.0004	0.1137	0.0013	0.0041	2.864	0.30175	0.0017	0.0053	0.0111
ASA-7	1.709	0.0004	0.11163	0.0029	0.0111	3.273	0.23498	0.0029	0.0055	0.0125
ASA-8	0.855	0.0004	0.07089	0.0033	0.0056	1.676	0.08038	0.0024	0.0024	0.0051
ASA-9	0.314	0.0007	0.21374	0.0021	0.0025	15.02	2.18184	0.0022	0.0022	0.0043
ASA-10	0.36	0.0004	0.10938	0.0017	0.0034	1.726	0.81115	0.0018	0.0022	0.009
ASA-11	0.09	0.0004	0.05725	0.0008	0.0036	0.693	0.04789	0.0021	0.0019	0.0088
ASA-12	0.06	0.0004	0.07961	0.0004	0.0015	0.769	0.49172	0.002	0.0017	0.0057
average	0.7914	0.0006	0.15541	0.0021	0.0060	4.8010	1.61096	0.0026	0.0043	0.0109
min.	0.060	0.0004	0.05725	0.0004	0.0015	0.5820	0.04789	0.0015	0.0017	0.0040
max.	4.241	0.001	0.40601	0.0072	0.023	15.020	6.25604	0.0078	0.0193	0.0441
stdev.	1.1850	0.0002	0.10071	0.0018	0.0061	5.1376	1.87594	0.0017	0.0049	0.0111
var.	1.4043	0.0000	0.01014	0.0000	0.0000	26.395	3.51902	0.0000	0.0000	0.0001
med.	0.3370	0.0004	0.11273	0.0015	0.0036	2.2950	0.93503	0.0022	0.0023	0.0073

(*after WHO 2006; NSDWQ 2007; Omotoso and Ojo, 2017*)

Based on the average concentrations computed, it was discovered that Al, Fe and Mn are above the recommended values of 0.2, 0.3 and 0.5 ppm of WHO (2006) and NSDWQ (2007) respectively while others are quite below the prescribed values. These three elements are of health significant which could hamper human health leading to shortage of the consumers' life span. It has been reported that excess iron in water constitute health hazard to consumers. It leads to gene mutation resulting in haemochromatosis whose symptoms include fatigue, weight loss, joint pains and ultimate heart disease, liver problems and diabetes (Ekere *et al*., 2014). In addition, excess Fe in water also leads to severe allergic reaction (e.g. rashes and itching), breathing difficulty, tightness in chest, swelling of the mouth, lips and face, black tarry stools as well as blood or streaks of blood in the stool including severe vomiting or stomach pain (Ekere *et al*., 2014). The elevated values could be as a result of agricultural practices (fish ponding, growing of crops using fertilizers, pesticides and herbicides) carrying out in the study area. It can be suggested that weathering of aluminosilicate minerals in the rocks and sediments from the area can contribute to elemental compositions of the water (Omotoso *et al*, 2018).

Computed Contamination Indexes of Al, Fe and Mn:

The contamination indexes of the three trace elements were computed to support the sources of the elevated values in the water (Table 4). Figures 3 and 4 present the profiles of the contamination indexes for the average values of the three trace elements. The computed contamination factor of Al ranges from 0.19 to 13.25, Fe ranges from 8.82 to 227.58 and Mn ranges from 114.02 to 14895. Values of contamination factor greater than unity implies that the sources of ions are both from geogenic (weathering of rock materials in the area of study) and heavy anthropogenic factors while values less than unity indicate mainly from weathering of aluminosilicate minerals and rock materials in the area (Tijani, 2007, Omotoso et al., 2017; Omotoso 2018).
The Degree of contamination of Al, Fe and Mn in the samples analyzed ranges from 124.81 in sample ASA 11 to 15048.56 in sample ASA 3. The average is 3910.61. This means that the samples are heavily contaminated with these elements/metals. Most especially according to Figure 5, ASA 2, ASA 3 and ASA 4 are the most heavily contaminated areas probably because of various agricultural practices in the area.

Table 4: Statistical Summary of Contamination Factors and Degree of Contamination of Al, Fe and Mn in the sampled Water

	Contamination Factor			Degree of Contamination	
	Al	Fe	Mn		
average	2.5	72.7	3835.4	average	3910.606
min	0.2	8.8	114.0	min	124.8051
max	13.3	227.6	14895.2	max	15048.56
stdev	3.7	77.8	4466.5	stdev	4507.29
var	13.7	6059.5	19949255.3	var	20315665
med	1.1	34.8	2226.3	med	2291.22

(*after Tijani 2007; Omotoso and Ojo, 2017*)

Human Health Risk Assessment:

Exposure dose through ingestion for adults: The computed statistical values of the exposure dose through ingestion for adults are presented in Table 5 and Figure 5 presents the profile of the exposure

dose. On the average, Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn have the following values respectively: 29.898 µg/kg/day, 0.02 µg/kg/day, 5.87 µg/kg/day, 0.078 µg/kg/day, 0.228 µg/kg/day, 181.37 µg/kg/day, 60.855 µg/kg/day, 0.099 µg/kg/day, 0.162 µg/kg/day and 0.413 µg/kg/day. The average values computed are greater than unity in Al, Ba, Fe and Mn while others are less than unity. Values below unity are generally recommended for a safe water quality. However, Al, Ba, Fe and Mn that has values higher than 1 are of health risk in adults' consumers.

Table 5: Statistical Summary of the Exposure Dose through Ingestion in Adults (in µg/kg/day)

Exposure Dose through Ingestion in Adults (Exping)										
Sample ID	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ASA-1	5.478	0.015	5.513	0.042	0.094	21.987	49.832	0.083	0.079	0.181
ASA-2	6.536	0.023	6.346	0.045	0.370	50.433	144.434	0.087	0.064	0.623
ASA-3	4.987	0.042	10.481	0.042	0.068	381.253	236.338	0.057	0.178	0.151
ASA-4	160.216	0.038	15.338	0.272	0.869	488.958	102.884	0.295	0.729	1.666
ASA-5	23.913	0.023	4.187	0.068	0.132	250.807	40.004	0.091	0.087	0.200
ASA-6	29.656	0.015	4.295	0.049	0.155	108.196	11.399	0.064	0.200	0.419
ASA-7	64.562	0.015	4.217	0.110	0.419	123.647	8.877	0.110	0.208	0.472
ASA-8	32.300	0.015	2.678	0.125	0.212	63.316	3.037	0.091	0.091	0.193
ASA-9	11.862	0.026	8.075	0.079	0.094	567.422	82.425	0.083	0.083	0.162
ASA-10	13.600	0.015	4.132	0.064	0.128	65.204	30.643	0.068	0.083	0.340
ASA-11	3.400	0.015	2.163	0.030	0.136	26.180	1.809	0.079	0.072	0.332
ASA-12	2.267	0.015	3.007	0.015	0.057	29.051	18.576	0.076	0.064	0.215
average	29.898	0.021407	5.869344	0.078389	0.227926	181.3711	60.85487	0.098537	0.161537	0.413037
min	2.266667	0.015111	2.162778	0.015111	0.056667	21.98667	1.809078	0.056667	0.064222	0.151111
max	160.2156	0.041556	15.33816	0.272	0.868889	567.4222	236.3378	0.294667	0.729111	1.666
stdev	44.76727	0.009439	3.805608	0.068686	0.231864	194.088	70.86781	0.063306	0.186519	0.420772
var	2004.108	8.91E-05	14.48265	0.004718	0.053761	37670.14	5022.247	0.004008	0.034789	0.177049
med	12.73111	0.015111	4.256233	0.056667	0.134111	86.7	35.32392	0.083111	0.085	0.273889

Exposure Dose through Ingestion for Children*:* The statistical values of the exposure dose through ingestion in children are presented in Table 6 and the profile is illustrated in Figure 6. The average values for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 94.97 µg/kg/day, 0.068 µg/kg/day, 18.64 µg/kg/day, 0.249 µg/kg/day, 0.724 µg/kg/day, 576.12 µg/kg/day, 193.304 µg/kg/day, 0.313 µg/kg/day, 0.513 µg/kg/day and 1.312 µg/kg/day respectively. The average values of Al, Ba, Fe,

Mn and Zn are greater than unity while others are less than unity. The higher values indicate health risk in children which must not be overlooked.

Table 6: Statistical Summary of the Exposure Dose through Ingestion in Children (in µg/kg/day)

Sample ID	Exposure Dose through Ingestion in Children (Exping)									
	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ASA-1	17.400	0.048	17.512	0.132	0.300	69.840	158.290	0.264	0.252	0.576
ASA-2	20.760	0.072	20.158	0.144	1.176	160.200	458.789	0.276	0.204	1.980
ASA-3	15.840	0.132	33.292	0.132	0.216	1211.040	750.720	0.180	0.564	0.480
ASA-4	508.920	0.120	48.721	0.864	2.760	1553.160	326.808	0.936	2.316	5.292
ASA-5	75.960	0.072	13.300	0.216	0.420	796.680	127.073	0.288	0.276	0.636
ASA-6	94.200	0.048	13.644	0.156	0.492	343.680	36.210	0.204	0.636	1.332
ASA-7	205.080	0.048	13.396	0.348	1.332	392.760	28.198	0.348	0.660	1.500
ASA-8	102.600	0.048	8.507	0.396	0.672	201.120	9.646	0.288	0.288	0.612
ASA-9	37.680	0.084	25.649	0.252	0.300	1802.400	261.821	0.264	0.264	0.516
ASA-10	43.200	0.048	13.126	0.204	0.408	207.120	97.338	0.216	0.264	1.080
ASA-11	10.800	0.048	6.870	0.096	0.432	83.160	5.747	0.252	0.228	1.056
ASA-12	7.200	0.048	9.553	0.048	0.180	92.280	59.006	0.240	0.204	0.684
average	94.97	0.068	18.6438	0.249	0.724	576.12	193.3037	0.313	0.513	1.312
min	7.2	0.048	6.87	0.048	0.18	69.84	5.7468	0.18	0.204	0.48
max	508.92	0.132	48.7212	0.864	2.76	1802.4	750.72	0.936	2.316	5.292
stdev	142.2019	0.029982	12.0884	0.218078	0.736508	616.5147	225.1095	0.201089	0.592472	1.33657
var	20221.38	0.000899	146.1295	0.047602	0.542444	380090.4	50674.33	0.040437	0.351023	1.786242
med	40.44	0.048	13.5198	0.18	0.426	275.4	112.2054	0.264	0.27	0.87

Hazard Quotient and Hazard Index for Adults: The computed hazard quotient, hazard index together with their statistical summary are presented in Table 7 and their graphical profiles are illustrated in Figures 7 and 8. The computed average values of hazard quotient for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 0.0.299, 0.00153, 0.0293, 5.23E-05, 0.005698, 0.259, 1.32, 0.00493, 0.0461 and 0.00138 respectively. Only average value of Mn is greater than the recommended value of unity while others are less than unity (USEPA 1989; Su *et al*., 2017).

However, the Hazard index ranges from 0.12 in sample ASA-12 to 5.798 in ASA-3 with an average of 1.7. That is, the range is from low to high (USEPA, 1989). This is an indication of health risk for the adults' consumers.

Table 7: Computed Hazard Quotient, Hazard Index and their Statistical Descriptions in Adults' Consumers

	Hazard Quotient (Adults)										Hazard Index	
	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn		
ASA-1	0.005478	0.001079	0.027565	2.77E-05	0.002361	0.03141	1.083302	0.004156	0.022667	0.000604	ASA-1	1.18
ASA-2	0.006536	0.001619	0.03173	3.02E-05	0.009256	0.072048	3.139859	0.004344	0.018349	0.002078	ASA-2	3.29
ASA-3	0.004987	0.002968	0.052403	2.77E-05	0.0017	0.544648	5.137778	0.002833	0.05073	0.000504	ASA-3	5.80
ASA-4	0.160216	0.002698	0.076691	0.000181	0.021722	0.698511	2.236609	0.014733	0.208317	0.005553	ASA-4	3.43
ASA-5	0.023913	0.001619	0.020935	4.53E-05	0.003306	0.358295	0.869661	0.004533	0.024825	0.000667	ASA-5	1.31
ASA-6	0.029656	0.001079	0.021477	3.27E-05	0.003872	0.154565	0.247814	0.003211	0.057206	0.001398	ASA-6	0.52
ASA-7	0.064562	0.001079	0.021086	7.3E-05	0.010483	0.176638	0.192979	0.005478	0.059365	0.001574	ASA-7	0.53
ASA-8	0.0323	0.001079	0.01339	8.31E-05	0.005289	0.090451	0.066013	0.004533	0.025905	0.000642	ASA-8	0.24
ASA-9	0.011862	0.001889	0.040373	5.29E-05	0.002361	0.810603	1.791849	0.004156	0.023746	0.000541	ASA-9	2.69
ASA-10	0.0136	0.001079	0.020661	4.28E-05	0.003211	0.093149	0.666162	0.0034	0.023746	0.001133	ASA-10	0.83
ASA-11	0.0034	0.001079	0.010814	2.01E-05	0.0034	0.0374	0.03933	0.003967	0.020508	0.001108	ASA-11	0.12
ASA-12	0.002267	0.001079	0.015037	1.01E-05	0.001417	0.041502	0.403828	0.003778	0.018349	0.000718	ASA-12	0.49
average	0.029898	0.001529	0.029347	5.23E-05	0.005698	0.259102	1.322932	0.004927	0.046143	0.001377	average	1.70
min	0.002267	0.001079	0.010814	1.01E-05	0.001417	0.0374	0.03933	0.002833	0.018349	0.000504	min	0.12
max	0.160216	0.002968	0.076691	0.000181	0.021722	0.810603	5.137778	0.014733	0.208317	0.005553	max	5.80
stdev	0.044767	0.000674	0.019028	4.58E-05	0.005797	0.277269	1.540605	0.003165	0.053291	0.001403	stdev	1.74
var	0.002004	4.55E-07	0.000362	2.1E-09	3.36E-05	0.076878	2.373463	1E-05	0.002841	1.97E-06	var	3.03
med	0.012731	0.001079	0.021281	3.78E-05	0.003353	0.123857	0.767911	0.004156	0.024286	0.000913	med	1.00

Hazard Quotient and Hazard Index for Children*:* The computed hazard quotient, hazard index together with their descriptive statistical summary are presented in Table 8 and their graphical profile illustrated in Figures 9 and 10 respectively. The average computed values of hazard quotient

for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 0.09497, 0.004857, 0.0932, 0.000166, 0.0181, 0.823, 4.202, 0.0157, 0.147 and 0.00437 respectively.

Table 8: Computed Hazard Quotient, Hazard Index and Statistical Summary in Children Consumers

Sample ID	Hazard Quotient (Children)											Hazard Index
	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn		
ASA-1	0.0174	0.003429	0.087558	0.000088	0.0075	0.099771	3.441078	0.0132	0.072	0.00192	ASA-1	3.74
ASA-2	0.02076	0.005143	0.100788	0.000096	0.0294	0.228857	9.97367	0.0138	0.058286	0.0066	ASA-2	10.44
ASA-3	0.01584	0.009429	0.166458	0.000088	0.0054	1.730057	16.32	0.009	0.161143	0.0016	ASA-3	18.42
ASA-4	0.50892	0.008571	0.243606	0.000576	0.0698	2.218522	7.104	0.0468	0.661714	0.01764	ASA-4	10.88
ASA-5	0.07596	0.005143	0.066498	0.000144	0.0105	1.138114	2.762452	0.0144	0.078857	0.00212	ASA-5	4.15
ASA-6	0.09402	0.003429	0.068022	0.000104	0.0123	0.490971	0.787174	0.0102	0.181714	0.00444	ASA-6	1.65
ASA-7	0.20508	0.003429	0.066978	0.000232	0.0333	0.561086	0.612991	0.0174	0.188571	0.0055	ASA-7	1.69
ASA-8	0.10206	0.003429	0.042534	0.000264	0.0168	0.287314	0.209687	0.0144	0.082286	0.00204	ASA-8	0.76
ASA-9	0.03768	0.006	0.128244	0.000168	0.0075	2.574857	5.691757	0.0132	0.075429	0.00172	ASA-9	8.54
ASA-10	0.04302	0.003429	0.065628	0.000136	0.0102	0.295886	2.116043	0.0108	0.075429	0.0036	ASA-10	2.62
ASA-11	0.01088	0.003429	0.03435	0.000064	0.0108	0.1188	0.12493	0.0126	0.065143	0.00352	ASA-11	0.38
ASA-12	0.00772	0.003429	0.047766	0.000032	0.0045	0.131829	1.282748	0.012	0.058286	0.00228	ASA-12	1.55
average	0.09497	0.004857	0.093219	0.000166	0.0181	0.823029	4.202254	0.0157	0.147571	0.00437	average	5.40
min	0.00772	0.003429	0.03435	0.000032	0.0045	0.099771	0.12493	0.009	0.058286	0.0016	min	0.38
max	0.50892	0.009429	0.243606	0.000576	0.0698	2.574857	16.32	0.0468	0.661714	0.01764	max	18.42
stdev	0.14202	0.002142	0.060442	0.000145	0.0184	0.880735	4.893685	0.0105	0.169278	0.00455	stdev	5.53
var	0.02021	4.59E-06	0.003653	2.12E-08	0.0003	0.775339	23.94695	0.0001	0.028655	1.98E-05	var	30.55
med	0.04044	0.003429	0.067599	0.000012	0.0065	0.393429	2.439248	0.0132	0.077143	0.0029	med	3.18

Based on the average value, Mn only has hazard quotient value of 4.2 above the recommended value of 1 (USEPA 1989; Su *et al*., 2017).

However, the individual computed hazard quotient values for Fe in samples ASA-3, ASA-4, ASA-5 and ASA-9 are: 1.7, 2.2, 1.1 and 2.6 respectively greater than recommended value of unity. This

is an indication of health risk to the consumers. The range of the computed hazard index for children in the samples is from 0.38 in sample ASA-11 to 18.4 in sample ASA-3 with an average of 5.4. This shows that the hazard index ranges from low to high health risk to the consumers.

Chronic Daily Intake of Trace Elements in Adults: Table 9 presents the computed chronic daily intake and its statistical summary for Adults consumers.

Table 9: Chronic Daily Intake computed for the Adult Consumers

Chronic Daily Intake (CDI) for Adults										
Trace Elements	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
ASA-1	0.005634	1.55E-05	0.00567	4.27E-05	9.71E-05	0.022615	0.051256	8.55E-05	8.16E-05	0.000187
ASA-2	0.006722	2.33E-05	0.006527	4.66E-05	0.000381	0.051874	0.14856	8.94E-05	6.61E-05	0.000641
ASA-3	0.005129	4.27E-05	0.01078	4.27E-05	6.99E-05	0.392146	0.24309	5.83E-05	0.000183	0.000155
ASA-4	0.164793	3.89E-05	0.01576	0.00028	0.000894	0.502928	0.105824	0.00033	0.00075	0.001714
ASA-5	0.024597	2.33E-05	0.004307	6.99E-05	0.000136	0.257973	0.041147	9.33E-05	8.94E-05	0.000206
ASA-6	0.030503	1.55E-05	0.004418	5.05E-05	0.000159	0.111287	0.011725	6.61E-05	0.00026	0.000431
ASA-7	0.066407	1.55E-05	0.004338	0.00013	0.000431	0.127179	0.009131	0.00013	0.00014	0.000486
ASA-8	0.033223	1.55E-05	0.002755	0.00028	0.000218	0.065125	0.003123	9.33E-05	9.33E-05	0.000198
ASA-9	0.012201	2.72E-05	0.008305	8.16E-05	9.71E-05	0.583634	0.084778	8.55E-05	8.55E-05	0.000167
ASA-10	0.013989	1.55E-05	0.00425	6.61E-05	0.000132	0.067067	0.031519	6.99E-05	8.55E-05	0.00035
ASA-11	0.003497	1.55E-05	0.002225	3.11E-05	0.00014	0.026928	0.001861	8.16E-05	7.38E-05	0.000342
ASA-12	0.002331	1.55E-05	0.003093	1.55E-05	5.83E-05	0.029881	0.019107	7.77E-05	6.61E-05	0.000221
average	0.030752	2.2E-05	0.006037	8.06E-05	0.000234	0.186553	0.062594	0.000101	0.000166	0.000425
min	0.002331	1.55E-05	0.002225	1.55E-05	5.83E-05	0.022615	0.001861	5.83E-05	6.61E-05	0.000155
max	0.164793	4.27E-05	0.015776	0.00028	0.000894	0.583634	0.243099	0.00033	0.00075	0.001714
stdev	0.046046	9.71E-06	0.003914	7.06E-05	0.000238	0.199633	0.072893	6.51E-05	0.000192	0.000433
var	0.00212	9.43E-11	1.53E-05	4.99E-09	5.69E-08	0.039853	0.005313	4.24E-09	3.68E-08	1.87E-07
med	0.013095	1.55E-05	0.004378	5.83E-05	0.000138	0.089177	0.036333	8.55E-05	8.74E-05	0.000282

The average values computed for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn are: 0.03, 2.2E-05, 0.006, 8.06E-05, 0.000234, 0.187, 0.063, 0.000101, 0.000166 and 0.000425 respectively.
Values computed for Fe are generally higher than other elements. In general, the average values of the trace elements are less than unity below the recommended value. Figures 11 and 12 illustrate the profiles of chronic daily intakes in Adults.

Chronic Daily Intake of Trace Elements in Children*:* The computed chronic daily intake for children is presented in Table 10 and the graphical profiles are illustrated in Figures 13 and 14.

Table 10: Chronic Daily Intake computed for the Children

Chronic Daily Intake (CDI) for Children										
Sample ID	**Al**	**As**	**Ba**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
ASA-1	0.0174	0.000048	0.017512	0.000132	0.0003	0.06984	0.15829	0.000264	0.000252	0.000576
ASA-2	0.02076	0.000072	0.020158	0.000144	0.00176	0.1602	0.458789	0.000276	0.000204	0.00198
ASA-3	0.01584	0.000132	0.033292	0.000132	0.00016	1.2110 4	0.75072	0.000128	0.000564	0.00048
ASA-4	0.50892	0.000122	0.048721	0.000864	0.00276	1.55316	0.326808	0.000936	0.002316	0.005292
ASA-5	0.07596	0.000072	0.013316	0.000216	0.00042	0.79668	0.127073	0.000288	0.000276	0.000636
ASA-6	0.09424	0.000048	0.013644	0.000156	0.00092	0.34368	0.036201	0.000204	0.000636	0.001332
ASA-7	0.20508	0.000048	0.013396	0.000348	0.00132	0.39276	0.028198	0.000348	0.00066	0.00156
ASA-8	0.10264	0.000048	0.008507	0.000396	0.00072	0.20112	0.009646	0.000288	0.000288	0.000612
ASA-9	0.03768	0.000084	0.025649	0.000252	0.00036	1.80244	0.261821	0.000264	0.000264	0.000516
ASA-10	0.04324	0.000048	0.013126	0.000204	0.00048	0.20712	0.097338	0.000216	0.000264	0.00108
ASA-11	0.01084	0.000048	0.006807	0.000096	0.00032	0.08316	0.005747	0.000252	0.000228	0.001056
ASA-12	0.00724	0.000048	0.009553	0.000048	0.00018	0.09228	0.059006	0.000264	0.000204	0.000684
average	0.09497	0.000068	0.018644	0.000249	0.00074	0.57612	0.193304	0.000313	0.000513	0.001312
min	0.00724	0.000048	0.006807	0.000048	0.00018	0.06984	0.005747	0.000128	0.000204	0.000484
max	0.50892	0.000132	0.048721	0.000864	0.00276	1.80244	0.75072	0.000936	0.002316	0.005292
stdev	0.14202	3E-05	0.012088	0.000218	0.00037	0.61651	0.225101	0.000201	0.000592	0.001337
var	0.02021	8.99E-10	0.000146	4.76E-08	5.42E-07	0.38009	0.050674	4.04E-08	3.51E-07	1.79E-06
med	0.04044	0.000048	0.013522	0.000188	0.00042	0.27546	0.112205	0.000264	0.000264	0.000867

The following are the average values for Al, As, Ba, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively: 0.095, 0.000068, 0.017, 0.00025, 0.00072, 0.58, 0.19, 0.00031, 0.00051 and 0.0013. Based on the average values, they are lower than the recommended values of unity.

However, individual values computed for Fe have chronic daily intake higher than unity above the recommended values in samples: ASA-3 (1.2), ASA-4 (1.6) and ASA-9 (1.8). As illustrated by Figure 13, samples ASA-3, ASA-4 and ASA-9 are more loaded with the trace elements, while Fe generally takes the lead in the three samples. Hence, care must be taken for children consuming the water in the area.

Carcinogenic Risk for Adults and Children*:* Two carcinogenic elements are considered in this research namely Cr and Pb. The computed values are presented in Table 11 together with their statistical summary and their graphical profiles are also presented in Figures 15 and 16. In adults, Cr ranges from 0.00003 to 0.0005 with an average of 0.0002 while Pb ranges from 0.008 to 0.09 with an average of 0.02. From the values computed for children, Cr ranges from 0.0001 to 0.002 with an average of 0.00005 while Pb ranges from 0.02 to 0.3 with an average of 0.06. However, the average carcinogenic risk values exceeded the prescribed limit of 10^{-6} and 10^{-4} respectively (Edokpayi *et al.,* 2018). This is likely to pose potential carcinogenic health risk hazard to both adults and children consuming the water in the investigated area. Hence, adequate precaution needs to be taken to avoid potential carcinogenic risk of people in the area especially, children consuming the water resources.

Table 11: Computed Carcinogenic Risk values and their Descriptive Statistical Summary in Adults and Children

Sample ID	Carcinogenic risk (Adult)		Carcinogenic risk (Children)	
	Cr	Pb	Cr	Pb
ASA-1	8E-05	9E-03	3E-04	3E-02
ASA-2	9E-05	8E-03	3E-04	2E-02
ASA-3	8E-05	2E-02	3E-04	7E-02
ASA-4	5E-04	9E-02	2E-03	3E-01
ASA-5	1E-04	1E-02	4E-04	3E-02
ASA-6	1E-04	2E-02	3E-04	7E-02
ASA-7	2E-04	2E-02	7E-04	8E-02
ASA-8	2E-04	1E-02	8E-04	3E-02
ASA-9	2E-04	1E-02	5E-04	3E-02
ASA-10	1E-04	1E-02	4E-04	3E-02
ASA-11	6E-05	8E-03	2E-04	3E-02
ASA-12	3E-05	8E-03	1E-04	2E-02
average	2E-04	2E-02	5E-04	6E-02
min	3E-05	8E-03	1E-04	2E-02
max	5E-04	9E-02	2E-03	3E-01
stdev	1E-04	2E-02	4E-04	7E-02
var	2E-08	5E-04	2E-07	5E-03
med	1E-04	1E-02	4E-04	3E-02

Correlation Matrix: The correlation matrix between elements in water samples establish the interrelationship between the elements and this can be used to predict the source of the elements in the sampled water. Table 12 presents the correlation matrix of the selected trace elements in the

water samples. Al has positive correlations with all the other trace elements ranging from 0.01 in Mn to 0.96 in Cr and this is an indication of interrelationship. Fe has positive correlations with all the other trace elements ranging from 0.32 in Cu to as high as 0.80 in As. Moreover, Mn has positive correlations with all other trace elements ranging from 0.01 in Al to 0.86 in As. The results of the correlation matrix support the findings from the computed contamination factor of some of the selected trace elements, that the elements are sourced from both weathering of surrounding rock types and various anthropogenic activities in the area of study.

Table 12: Correlation Matrix of the Selected Trace Elements in the Analyzed Water Samples of ASA River Water

parameters (ppb)	Al	As	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.40	1.00								
Ba	0.66	0.89	1.00							
Cr	0.96	0.43	0.66	1.00						
Cu	0.93	0.38	0.64	0.89	1.00					
Fe	0.45	0.80	0.78	0.52	0.32	1.00				
Mn	0.01	0.86	0.70	0.05	0.12	0.52	1.00			
Ni	0.95	0.46	0.71	0.93	0.92	0.46	0.09	1.00		
Pb	0.95	0.57	0.80	0.89	0.87	0.52	0.21	0.93	1.00	
Zn	0.90	0.43	0.69	0.83	0.95	0.34	0.15	0.93	0.92	1.00

(*after Omotoso and Ojo, 2017*)

Conclusion and Recommendations

The preliminary health risk assessment of Asa river water has been established in this research using ten selected trace elements from the hydrochemical data analyzed from the water samples in the area of study. The following conclusions were drawn:

i. The average concentrations of Al (0.79 ppm), Fe (4.8) and Mn (1.6) show elevated values above the prescribed values of WHO (2006) and NSDWQ (2007), other trace elements are less than the prescribed values.
ii. The computed contamination factors of Al (0.2 - 13.3), Fe (8.8 - 227.6) and Mn (114 - 14895.2) ranged from low contamination factor to very high contamination factor and the degree of contamination is extremely high (average = 3910.6)).
iii. The exposure dose through ingestion in adults and children has high average values greater than unity in Al (adults=29.9 µg/kg/day, children= 95 µg/kg/day), Ba(adults=5.9 µg/kg/day, children= 18.6 µg/kg/day), Fe(adults=181 µg/kg/day, children=576 µg/kg/day) and Mn(adults=60.9 µg/kg/day, children=193 µg/kg/day) while other selected trace elements have values below unity except Zn (1.3 µg/kg/day) in children that has values greater than unity.
iv. The computed hazard quotient in Mn is higher than unity while others are less than unity in both adults and children.
v. The average values of hazard index for both age groups are greater than unity, above the prescribed standard of USEPA, which makes the water practically non-carcinogenic health risky to the consumers.

vi. The average chronic daily intake computed are generally less than unity. However, in children, the computed values for Fe in some samples are higher than unity making the water of potential health risk for the consumers, especially the children.

vii. The average carcinogenic risk values computed for Cr and Pb exceeded the recommended values of 10^{-6} and 10^{-4} respectively. This could pose serious health hazard to the consumers most especially the children having low immunity.

viii. The results of the correlation matrix and contamination factors show that the sources of the trace elements in the river is mainly from both weathering of rock types and anthropogenic activities in the area of study.

Hence, it is recommended that the use of agrochemical by farmers and indiscriminate channeling and dumping of wastes (industrial, domestic and agricultural) into the river should be monitored and regulated.

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Appendix

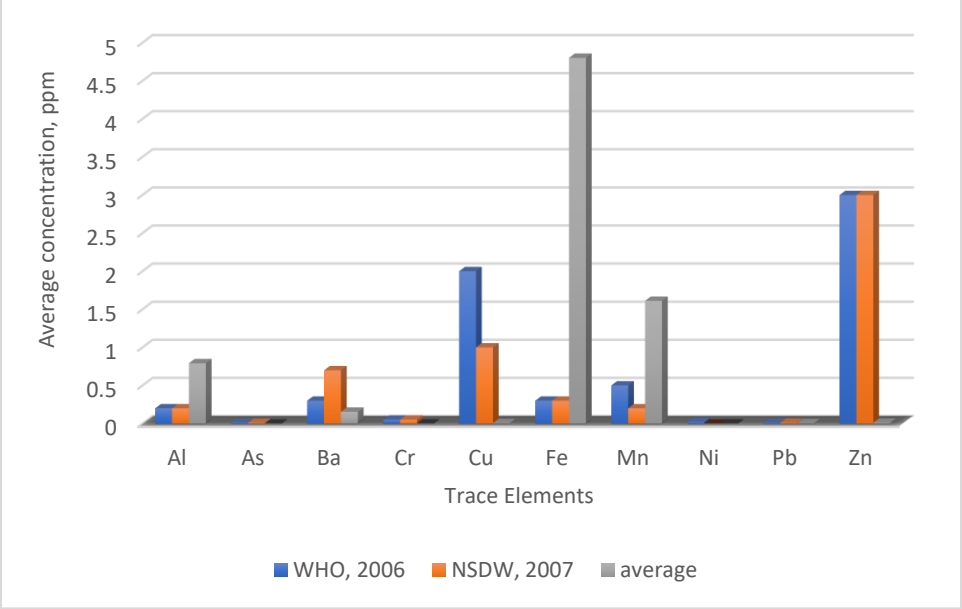

Figure 2: Profile of the Average Concentrations of the Selected Trace Elements Compared with WHO (2006) and NSDWQ (2007)

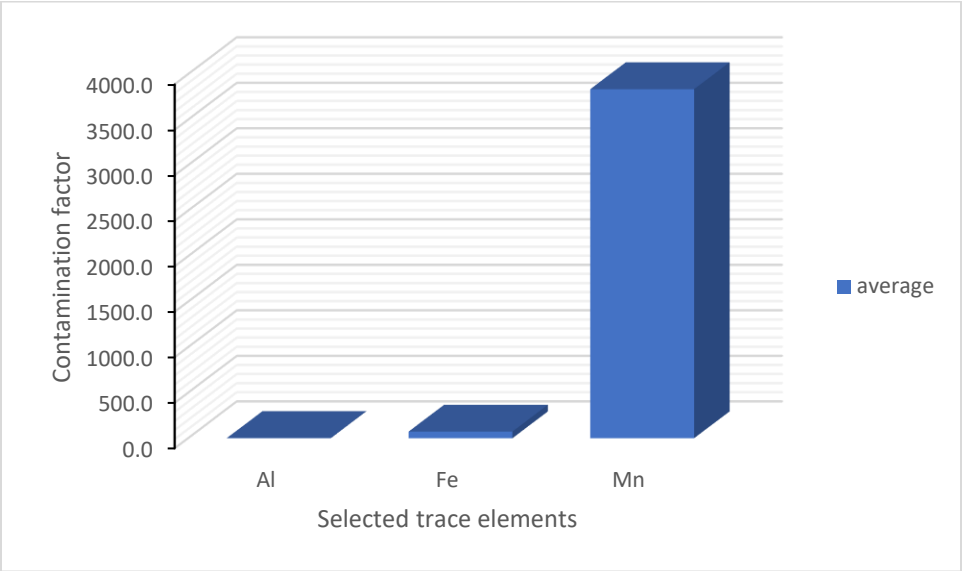

Figure 3: Profile of Average Contamination Factor of Al, Fe and Mn

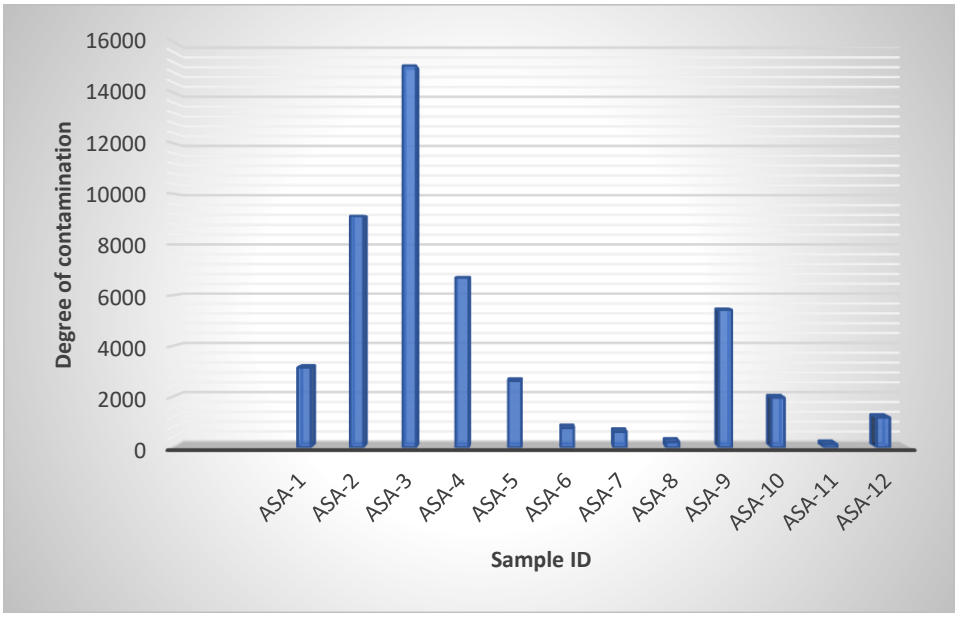

Figure 4: Profile of Degree of Contamination of Al, Fe and Mn

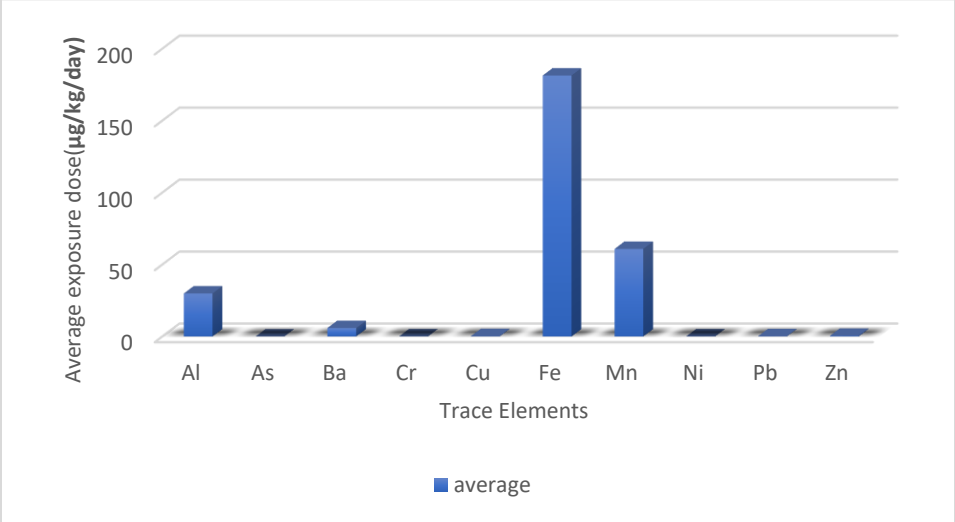

Figure 5: Profile of Exposure Dose through Ingestion in Adults

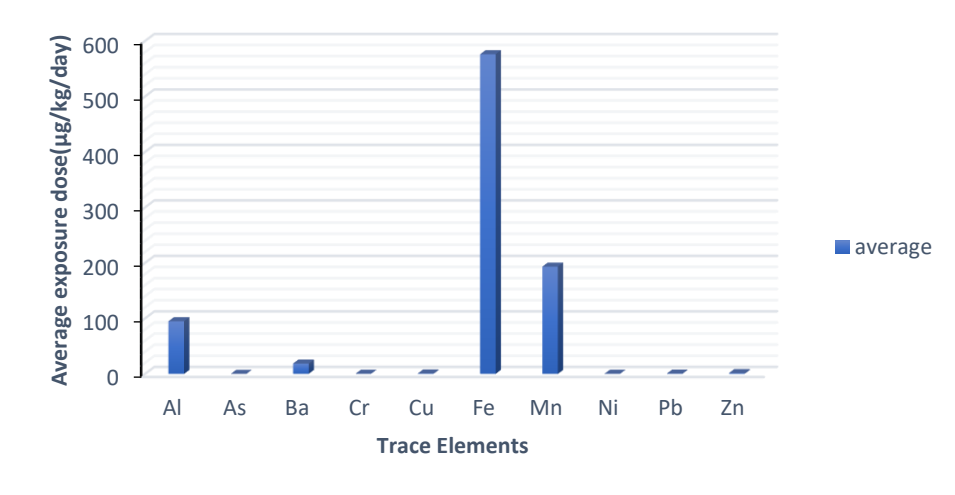

Figure 6: Profile of Exposure Dose through Ingestion in Children

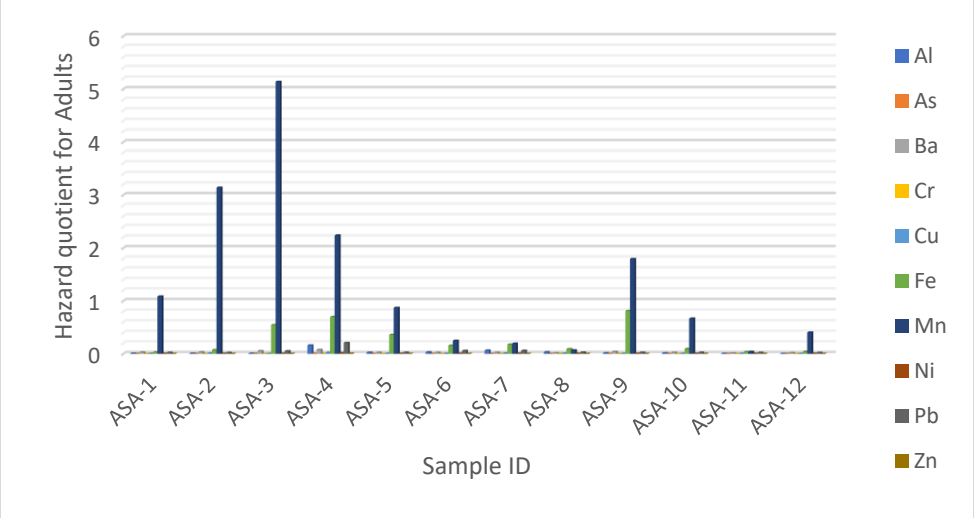

Figure 7: Profile of Hazard Quotient in the Water Samples for Adults

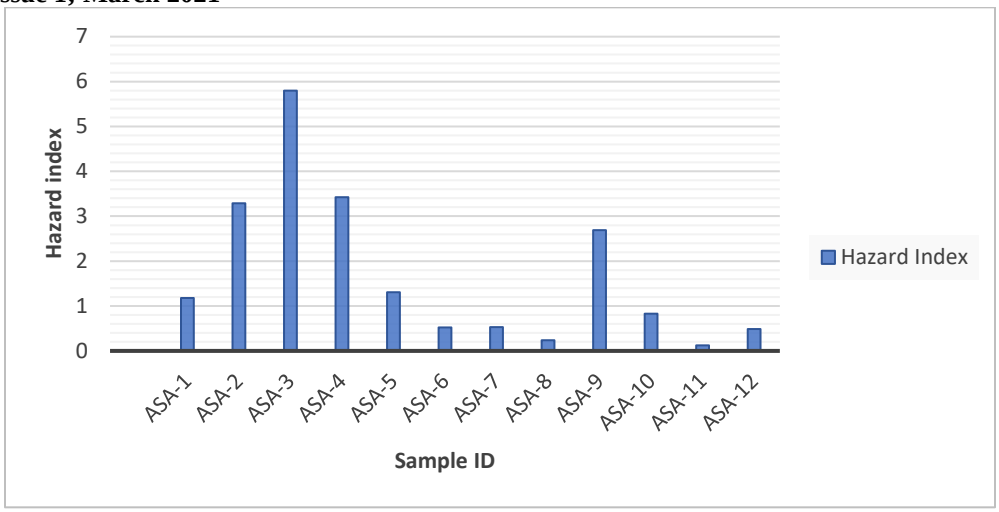

Figure 8: Hazard Index of the Samples Water in Adults

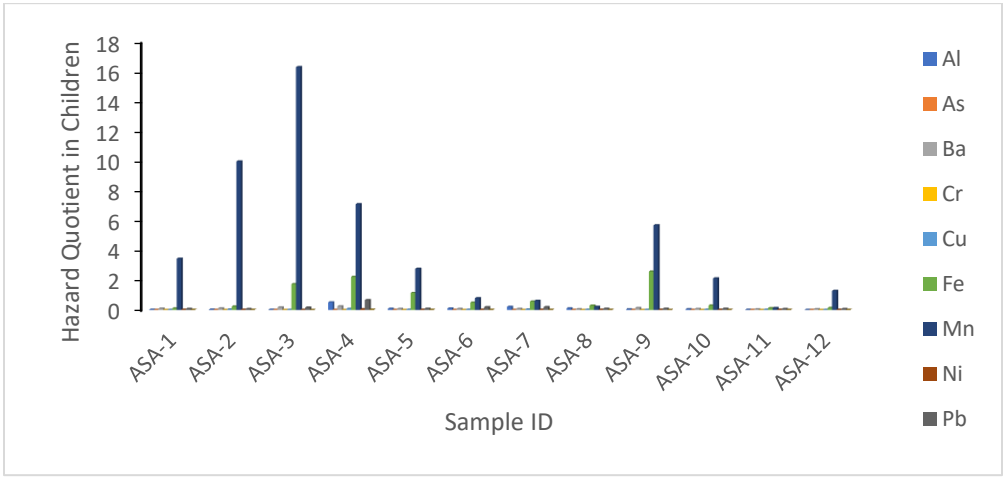

Figure 9: Profile of Hazard Quotient for Children

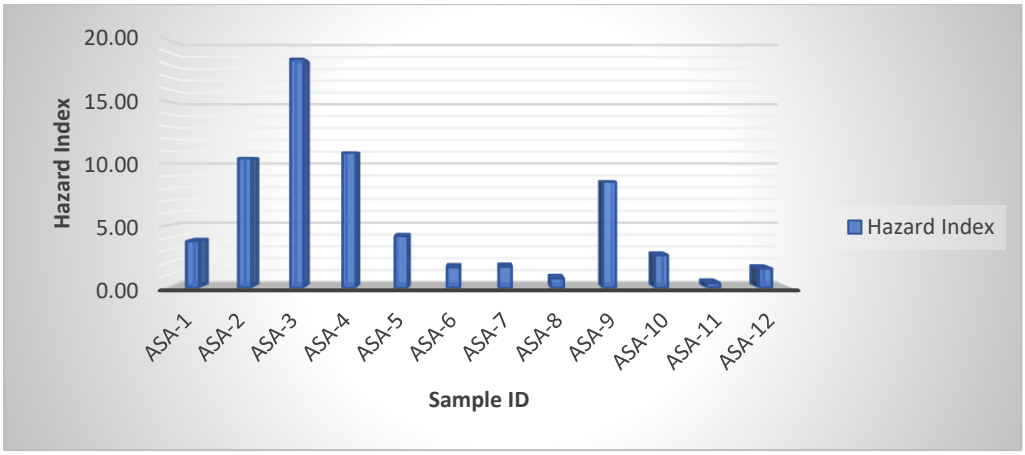

Figure 10: Profile of Hazard Index of the Water Samples for Children

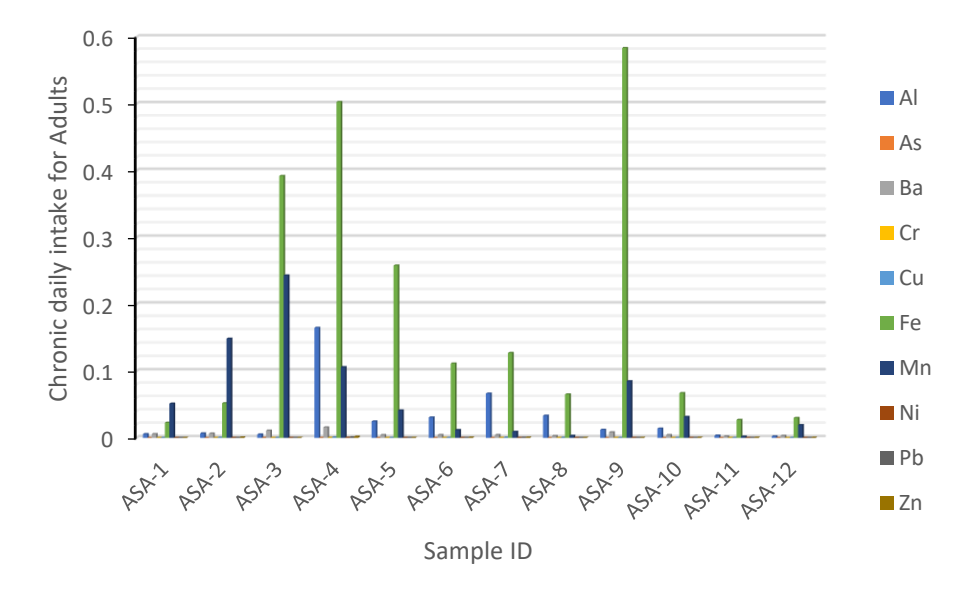

Figure 11: Profile of Chronic Daily Intake for Adults

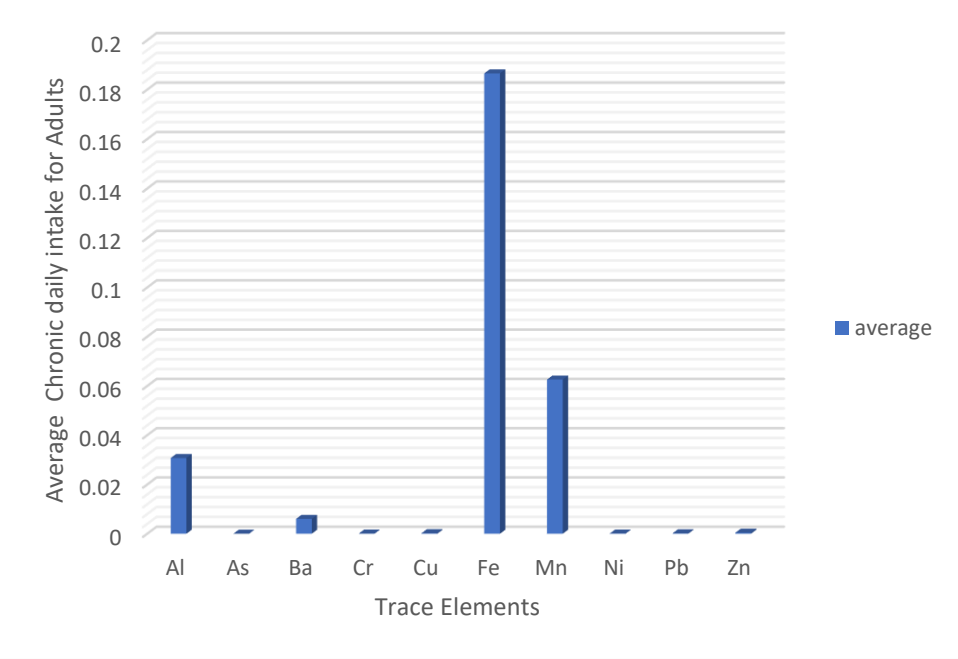

Figure 12: Profile of Average Chronic Intake for Adults

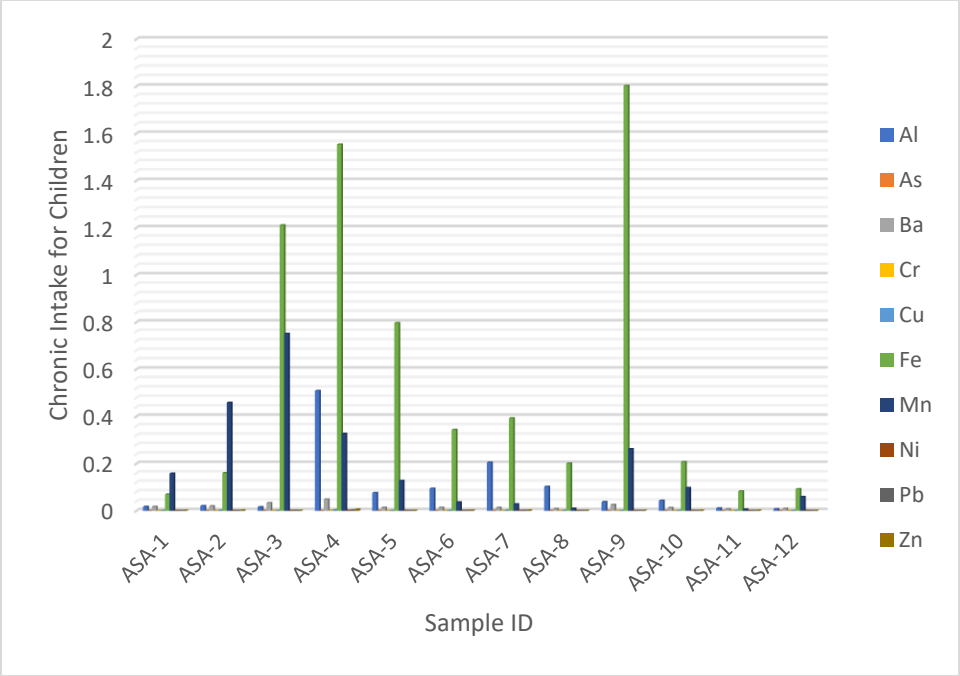

Figure 13: The Profile of Chronic Daily Intake of each of the Samples for Children

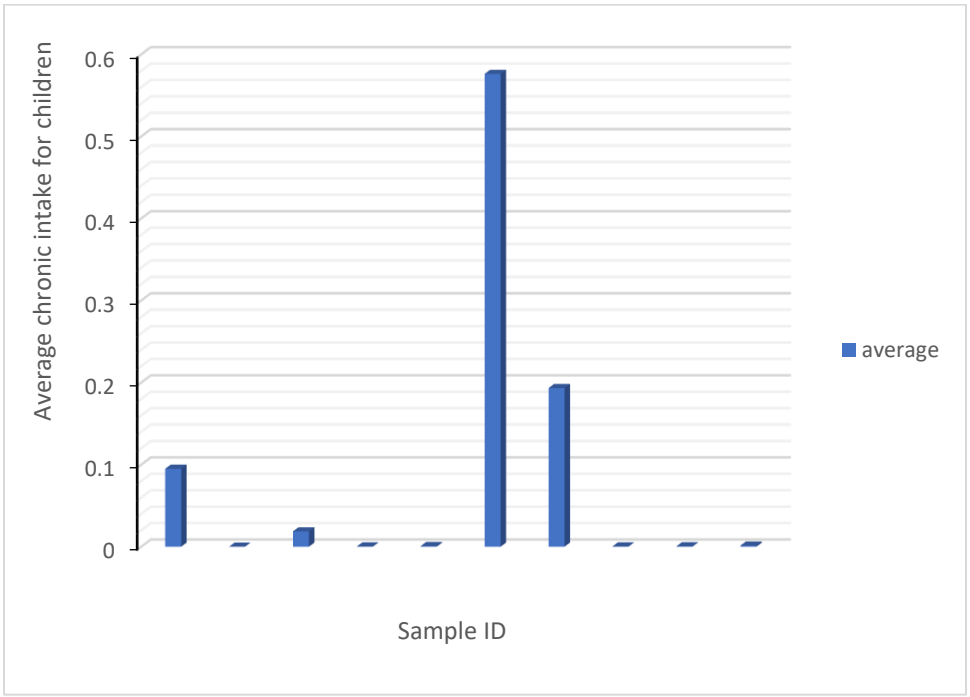

Figure 14: The Profile of Average Chronic Intake for Children

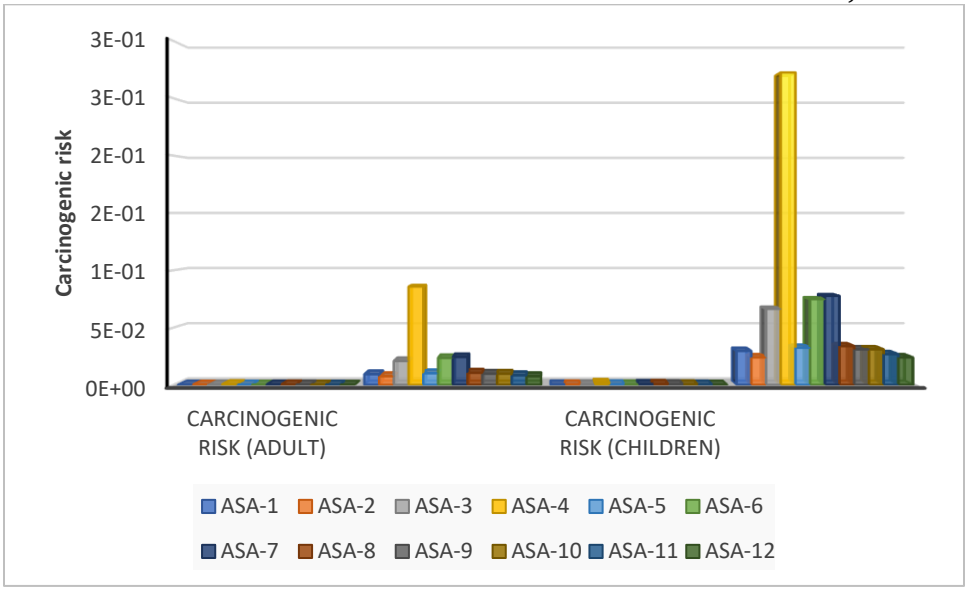

Figure 15**:** Profile of Carcinogenic Risk for Adults and Children

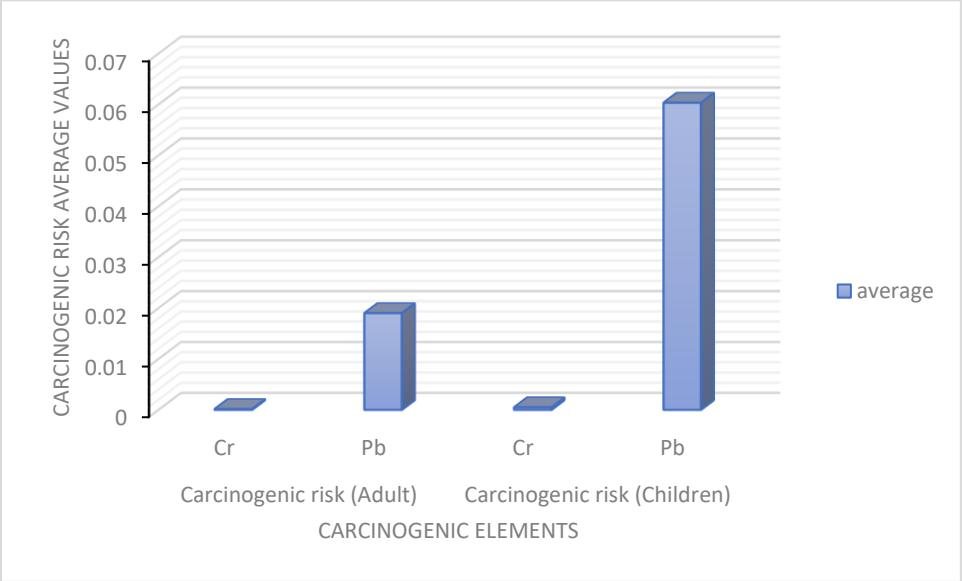

Figure 16: Profile of Average Carcinogenic risk for Adults and Children

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