



Preliminary Assessment of Some Selected Trace Elements' Concentrations in Asa River Water, North Central Nigeria

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Abstract

Preliminary assessment of some selected trace elements' concentrations in Asa River water has been established using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) technique. Eleven (11) out of about sixty trace elements were examined based on Contamination Factor, Degree of Contamination and Index of Geo-accumulation. The concentrations were also compared with WHO standard to determine its suitability for domestic consumptions. Al, Ba, Co, Cr, Cs, Cu, Fe, Pb, V, Zn and Mn ranged from 0.6 to 4.2ppm (average=0.79 ppm); 0.06 to 0.41 ppm (average=0.16ppm); 0.0002 to 0.02ppm (average=0.01pm); 0.0008 to 0.034ppm (average=0.002pm); 0.0015 to 0.023ppm (average=0.006pm); 0.58 to 15.02ppm (average=4.8ppm); 0.0017 to 0.019ppm (average=0.004ppm); 0.0008 to 0.034 ppm (average=0.0059pm); 0.004 to 0.044ppm (average=0.01 pm) and 0.048 to 6.26ppm (average=1.6ppm) respectively. The average values of the trace metals Al (0.79 ppm), Fe (4.8ppm) and Mn (1.6ppm) exceeded the maximum limit for drinking water making the water unfit for human consumption. Pb also exceeded the maximum limit in some samples. Positive correlation of Al with all the trace elements depicts sources from weathering of aluminosilicate minerals from the rock types in the study area and positive correlation of Pb with Al, Ba, Co, Cr, Cs, Cu, and Fe also depict contributions from various anthropogenic activities in the study area. The Contamination Factor values >1 for all the trace elements depict more contributions from anthropogenic activities over the geogenic activities within the study area. The values computed for the Degree of Contamination show that the samples are heavily contaminated/polluted with trace elements (range=67 to 1482). The values recorded for the Geo-accumulation Index also show that the water is contaminated/polluted with the trace elements. It is recommended that thorough treatment of Asa river water should be carried out to make the water suitable for human consumption.

Keywords: Asa River, trace elements, World Health Organization (WHO), Contamination Factor, Degree of Contamination, Geo-accumulation Index.

Introduction

River waters have been sources of portable water from ages. However, due to increase in industrialization, urbanization, mechanized farming and so on, rivers are indiscriminately being polluted overtime. More so, trace elements may be introduced into the river water system from chemical weathering of country rocks and from various anthropogenic sources. Once these trace elements are transported and dissolved into the rivers, element distributions are consistently being modified by complex geochemical and biological processes (Abdula'aly *et al.*, 2011; Newcomb and Rimstidt, 2002).

Abdula'aly *et al.*, 2011 reviewed the work done on trace metal levels by Botchway *et al.*, 1996 in Greater Accra region, Ghana on both surface and groundwater. It was discovered that greater percentage of the samples have Mn and Fe higher than the WHO recommended limits. They also reported the work done by Das *et al.*, 1996 on the measurement of Arsenic metal of six districts in West Bengal, India. The Arsenic metal in the samples was discovered above the recommended limit of 0.05mg/l. Moreover, Abu-Rukh and El-Aloosy (1997) carried out the various metal ions migration in the El-

Akader landfill site in north Jordan and concluded that there is migration of metal ions to the deep layers.

The area of study (Figure 1) is located within latitude $8^{\circ} 16' 45.97''$ E and $8^{\circ} 37' 40.2''$ N and longitude $4^{\circ} 16' 45.97''$ E and $4^{\circ} 53'49.20''$ E (Ilorin Topographical Sheet 223 N.W). Agricultural practices (like crop productions and fish farming- including fish ponds) and industrial activities are very prominent in the area. The location map showing the sampling points is presented in Figure 1. The study area is situated on the Precambrian Basement Complex Rocks

comprising: granite, granite gneiss, banded gneiss and migmatites (Alao and Ige, 2003; Omotoso *et al.*, 2011). Furthermore, Omotoso *et al.*, 2011 further reported that the gneisses are foliated with light and dark bands and the main minerals are suspected to be quartz, feldspar and mica as observed from the petrographic analysis of rock samples. Quartzite veins were seen cutting across one another as observed from the field mapping. In terms of structures, lineations, foliations, joints, fractures and folds are the essential features observed on the rocks. Figure 2 presents the Geological map of Nigeria.

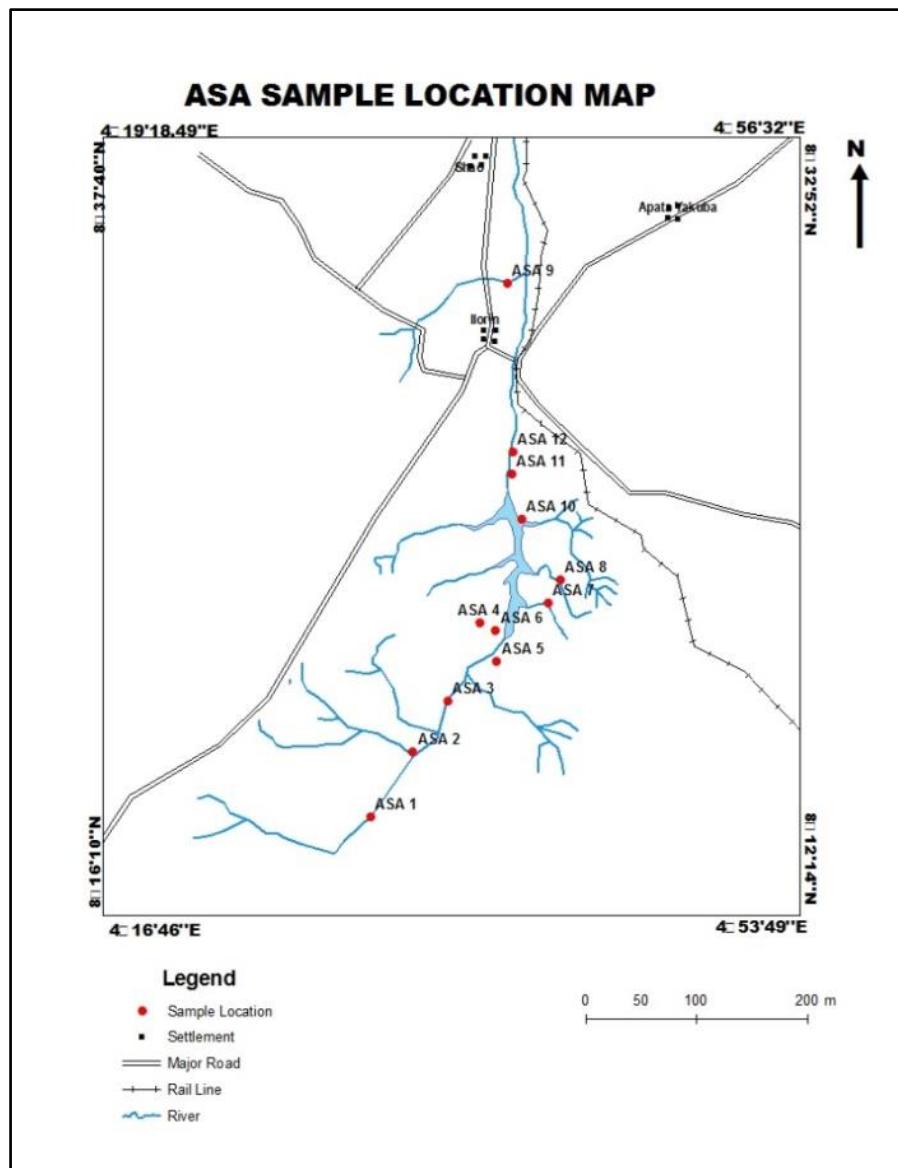


Figure 1: Location map of the study area showing the sampling points

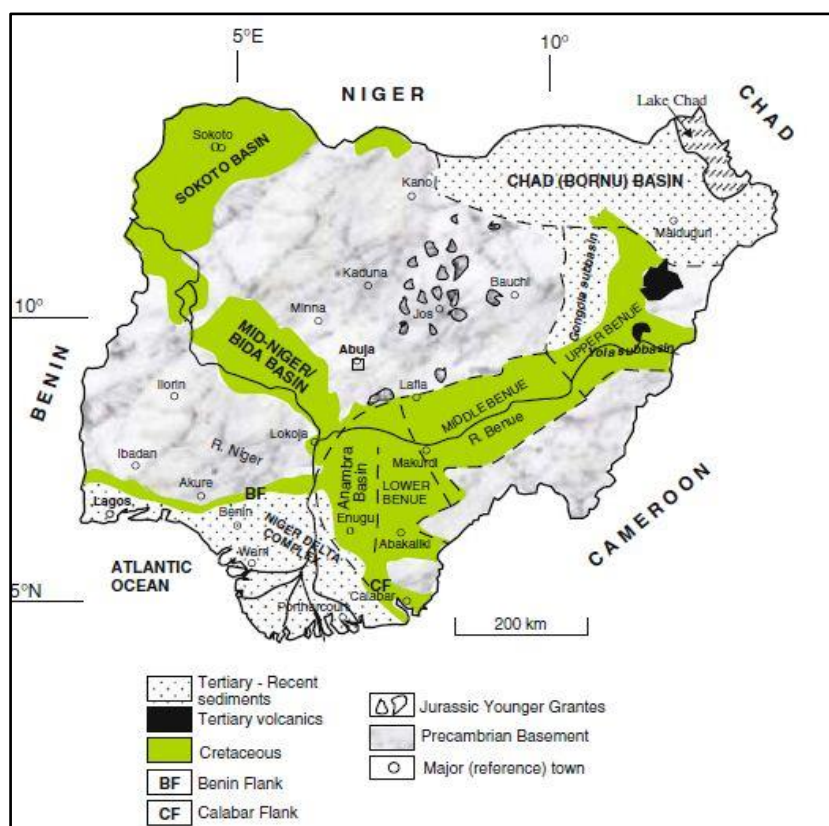


Figure 2: Geological map of Nigeria (After Obaje, 2009)

Materials and Methods

12 water samples were taken along the river channel randomly in order to determine the concentrations of some selected trace elements that are of health significant. The samples were taken using white plastic 60ml containers. The samples were acidified in-situ with nitric acid to prevent the precipitation of the cations from the water. ICP-MS technique was used for the analysis of the cations. Out of the hydrochemical result, only eleven (11) cations were selected for this research and they included: Al, Ba, Co, Cr, Cs, Cu, Fe, Pb, V, Mn and Zn ions. The hydrochemical analysis was carried out in ACME laboratory, Canada. Figure 1 presents the location map of the study area with the sampling points.

Assessment of Metal Contamination in Water samples

This research also carried out the contamination assessment of metals in the water of Asa river, central Nigeria using the following Contamination Indexes:

Contamination Factor (CF), Index of Geoaccumulation (Igeo) and Degree of Contamination (Cdeg).

Contamination Factor (CF)

This is the single index determined by the relation:

$$C_F = C_M / B_M$$

C_F = Contamination Factor of the element of interest; B_M = background concentration; C_M = concentration of the element in the sample. Contamination factor has four categories which include: < 1 low contamination factor; 3-6 = considerable contamination factor; > 6 = very high contamination factor (Atiemo *et al.*, 2011). The background concentration used in this research is that of the average dissolved phase concentration from the global elemental flux carried by riverine suspended sediments to the oceans (Viers *et al.*, 2009).

Degree of Contamination (C_{deg})

This is the sum of all the Contamination Factors in the sample. It is indicated as:

$$C_{deg} = \sum (C_M/B_M)$$

C_M =measured concentration of in soil or water; B_M =local background concentration (value) of metal, m within the pristine area of the catchment.

Four categories have been defined for the degree of contamination which includes: < 8 = low degree of contamination; 8 – 16 = considerable degree of contamination; > 32 = very high degree of contamination (Atiemo *et al.*, 2011).

Index of Geo-Accumulation (Igeo)

This is widely used in the assessment of contamination by comparing the level of trace metal obtained to a background levels originally used with bottom sediments (Muller, 1979) which can also be adopted to water contamination (Tijani *et al.*, 2007; Omotoso *et al.*, 2011). It is calculated by:

$$I_{geo} = \log_2 [(C_m) / (1.5 * B_m)]$$

C_m = measured concentration in water; B_m = background concentration (value) of metal. 1.5 is a factor for possible variation in the background concentration due to lithologic differences. The following classification is given for geo-accumulation index (Huu *et al.*, 2010; Muller, 1979): <0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3= moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and > = extremely polluted.

Results and Discussions

Trace Elements concentration

Table 1 presents the statistical summary of the results of Asa river water, central Nigeria Ilorin. Figure 3 also presents the selected trace metals/elements profile in the study area. Al ranged from 0.6ppm in ASA-12 to 4.24 ppm in ASA-4(average=0.79ppm). On the average, the value is higher than the prescribed limit of 0.2ppm by WHO. Ba ranged from 0.06ppm in ASA-11 to 0.4 ppm in ASA-4 (average=0.16ppm). Based on the average value, Ba ion is below the recommended limit of 0.7 ppm by WHO. Furthermore, Co ranged from 0.00022ppm in ASA-11 to 0.021ppm in ASA-4 (average=0.006ppm). Cr ranged from 0.0008ppm in ASA-11 to 0.0072ppm in ASA-4 (average=0.0022ppm). The average value is below the recommended value of 0.05 ppm by WHO. Cu ranged from 0.0015ppm in ASA-12 to 0.023ppm in ASA-4 (average=0.006ppm). the values are below the recommended limits. Fe ranged from 0.58ppm in ASA-1 to 15ppm in ASA-9 (average=4.8ppm). The average value is above the prescribed limit of 1ppm by WHO. Pb ion gives a range of 0.0017 ppm in ASA-1 to 0.019ppm in ASA-4 (average=0.0043ppm). it is below the prescribed limit of 0.01 ppm. However, ASA-4 exceeded the prescribed limit having Pb value of 0.02 ppm and ASA-6 and ASA-7 have a potential Pb-hazard with values of 0.01ppm respectively. V also ranged from 0.0008ppm to 0.034 ppm (average=0.006ppm). Zn ranged from 0.004 to 0.044 ppm (average=0.011ppm). Mn ions ranged from 0.05 ppm in ASA-11 to 6.26ppm in ASA-3 (average=1.6ppm). The average value exceeds the prescribed limit of 0.1 ppm by WHO.

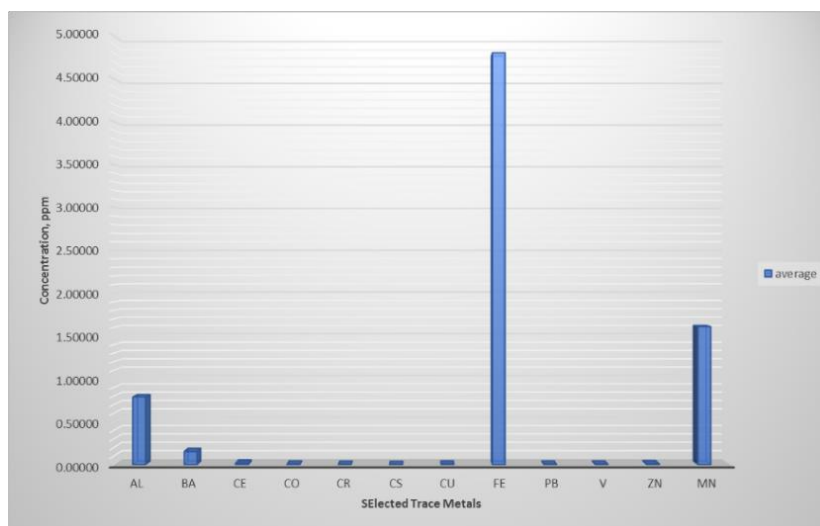


Figure 3: Selected trace metals/elements profile

Trace Elements Contamination Indexes

Table 1 also presents the computed results of the Contamination Factor (CF), Degree of Contamination (Deg. Cont.) and Index of Geo-accumulation (I-geo) of the selected trace elements in the studied river water. Figures 4, 5 and 6 also present the Contamination Factor, Degree of Contamination and Geo-Accumulation Index profiles of the selected trace elements. The average Contamination Factors of Al, Ba, Co, Cr, Cs, Cu, Fe, Pb, V, Zn and Mn are: 25, 7, 39, 3, 12, 4, 72, 53, 8, 18 and 47 respectively. Based on the average CF values of the trace elements, the CF ranged from 3 (in Cu) to 72 (in Fe). That is, the trace elements ranged from moderate contamination factor to very high contamination factor. More

so, the degree of contamination ranged from 67 to 1483 (average=357; very high degree of contamination). Figure 1 also presents the Degree of Contamination profile of the samples. From the profile, it is clearly seen that ASA-4 has the highest value. This location is very close to fish pond area. This is an indication that fish pond farming system possibly contributed to the metal load of the river water. The average values of geo-accumulation index for the selected trace elements are: 2.9 (Al), 1.9 (Ba), 3.7 (Co), 0.8 (Cr), 2.5 (Cs), 1 (Cu), 4.8 (Fe), 4.7 (Pb), 1.5 (V), 3.2 (Zn) and 3.8 (Mn). They ranged from moderately polluted (in Cu) to strongly polluted in Fe and Pb respectively.

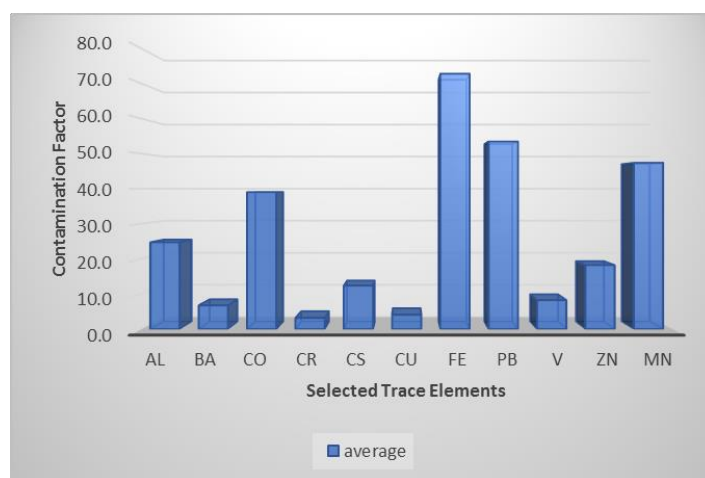


Figure 4: Contamination factor profile for the trace elements

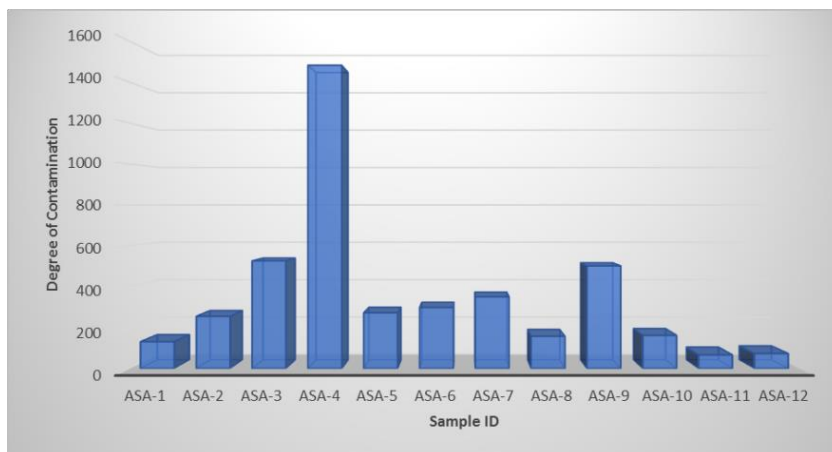


Figure 5: Degree of Contamination Profile of individual sample

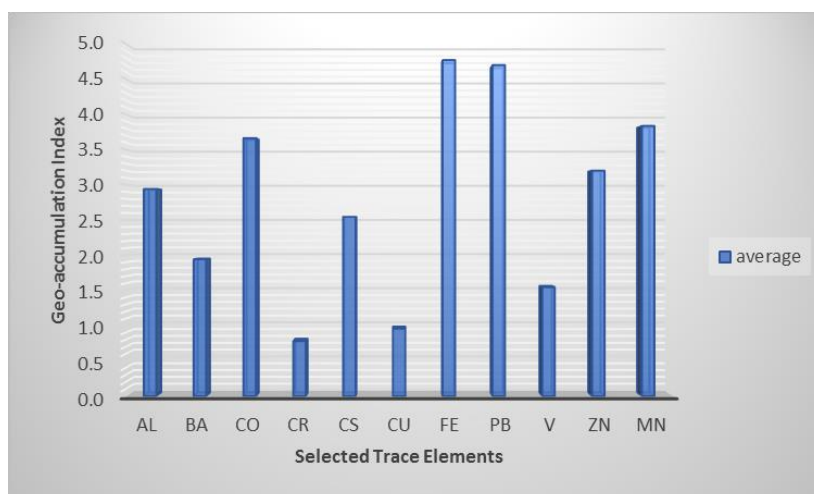


Figure 6: Geo-accumulation index profile

Correlations between Trace Elements and common sources

Table 2 presents the correlation matrixes of the trace elements. Al has positive correlation with Ba (0.66), Co (0.60), Cr (0.96), Cs (0.99), Cu (0.93), Fe (0.45), Pb (0.95), V (0.98), Zn (0.90) and Mn (0.01) respectively. This shows that they share common source from weathering of aluminosilicate silicate minerals from the rock type of the study area. Positive correlation of Pb with Al (0.95), Ba (0.80), Co (0.71), Cr (0.89), Cs (0.92), Cu (0.87), and Fe (0.52) also shows an input of various anthropogenic activities (agricultural practices e.g. fish farming-fish ponds, fertilizer applications, manuring and bush burning;

industrial waste discharge and municipal wastes) in the study area into the water system.

Trace Elements (implication on human’s health)

From the results of the concentrations of selected trace elements, it has been discovered that Al, Fe and Mn are quite above the prescribed limits of WHO based on the average values. Also, in some samples (ASA-6 and ASA-7; ASA-4), Pb also has a value equals or higher than the prescribed limit of 0.01ppm by WHO standard. This is an indication of potential hazard in the river water.

It has been reported that Manganese in large doses causes headaches, apathy, irritability, insomnia, and weakness of the legs and long-term heavy exposure may result in a nervous system disorder. Also, Pb has been reported to be a cumulative poison, meaning that it remains in the body following exposure. Consequently, children under age three are most susceptible to lead poisoning. Symptoms may include abdominal pains, decreased appetite, constipation, fatigue, and decreased physical fitness. Long-term exposure may result to kidney damage, anemia, nerve and brain damage, and finally death. Fe in water may increase the hazard of pathogenic

organisms, since many of these organisms require iron to grow. Aluminum may be formed during chemical weathering of feldspars such as orthoclase, anorthite, albite, micas and bauxite (Oke and Tijani 2012). Fe may be derived from solid phase rock minerals such as goethite and hematite (Elueze, 2004; Oke and Tijani 2012). Sources of the high level of Mn in the water is from both geogenic (weathering of silicate minerals) and anthropogenic (e.g. agriculture practices, fertilizers usage, sewage and animal waste disposal) contributions (Ramesh and Elango, 2011; Pauer and Nikumbh, 1999).

Table 1: The statistical summary of selected trace elements (in ppm), contamination factors, Degree of contaminations and geo-accumulation indexes

Statistical Summary of Selected Trace Elements (ppm) in Asa River water											
	Al	Ba	Co	Cr	Cs	Cu	Fe	Pb	V	Zn	Mn
WHO	0.2	0.7	-	0.05	-	0.5	1	0.01	-	3	0.1
average	0.79142	0.15537	0.00585	0.00223	0.00012	0.00603	4.80100	0.00428	0.00587	0.01093	1.61086
min	0.06000	0.05725	0.00022	0.00080	0.00003	0.00150	0.58200	0.00170	0.00080	0.00400	0.04789
max	4.24100	0.40601	0.02078	0.00720	0.00045	0.02300	15.02000	0.01930	0.03400	0.04410	6.25600
stdev	1.18502	0.10074	0.00671	0.00182	0.00013	0.00614	5.13762	0.00494	0.00921	0.01114	1.87591

Contamination Factor											Deg. Cont.	
	Al	Ba	Co	Cr	Cs	Cu	Fe	Pb	V	Zn	Mn	
average	24.7	6.8	39.0	3.2	12.4	4.1	72.7	53.4	8.3	18.2	47.4	356.5
min	1.9	2.5	1.5	1.1	3.0	1.0	8.8	21.3	1.1	6.7	1.4	66.6
max	132.5	17.7	138.5	10.3	45.0	15.5	227.6	241.3	47.9	73.5	184.0	1482.6
stdev	37.0	4.4	44.7	2.6	12.8	4.1	77.8	61.7	13.0	18.6	55.2	385.1

Geo-accumulation Index											
	Al	Ba	Co	Cr	Cs	Cu	Fe	Pb	V	Zn	Mn
average	2.9	1.9	3.7	0.8	2.5	1.0	4.8	4.7	1.5	3.2	3.8
min	0.3	0.7	-0.1	-0.4	1.0	-0.6	2.6	3.8	-0.4	2.2	-0.1
max	6.5	3.6	6.5	2.8	4.9	3.4	7.2	7.3	5.0	5.6	6.9
stdev	1.8	0.8	2.0	0.9	1.2	1.2	1.7	1.0	1.5	1.0	2.2

Table 2: Correlation matrixes within the trace elements from the study area

Trace Elements	Al	Ba	Ce	Co	Cr	Cs	Cu	Fe	Pb	V	Zn	Mn
Al	1.00											
Ba	0.66	1.00										
Ce	0.96	0.76	1.00									
Co	0.60	0.93	0.69	1.00								
Cr	0.96	0.64	0.92	0.63	1.00							
Cs	0.99	0.60	0.93	0.55	0.96	1.00						
Cu	0.93	0.64	0.90	0.53	0.88	0.93	1.00					
Fe	0.45	0.78	0.51	0.95	0.48	0.39	0.32	1.00				
Pb	0.95	0.80	0.99	0.71	0.89	0.92	0.87	0.52	1.00			
V	0.98	0.72	0.99	0.65	0.94	0.96	0.92	0.47	0.98	1.00		
Zn	0.90	0.69	0.95	0.58	0.83	0.88	0.95	0.34	0.92	0.94	1.00	
Mn	0.01	0.70	0.13	0.58	-0.01	-0.07	0.12	0.52	0.21	0.09	0.15	1.00

Conclusion

Water samples were randomly collected along Asa river banks. The minimum and maximum trace elements concentrations in Al, Ba, Co, Cr, Cs, Cu, Fe, Pb, V, Zn and Mn ranged from 0.6 to 4.2 ppm; 0.06 to 0.41 ppm; 0.0002 to 0.02 ppm; 0.00003 to 0.00045 ppm; 0.0015 to 0.023 ppm; 0.58 to 15.02 ppm; 0.002 to 0.02 ppm; 0.0008 to 0.034 ppm; 0.004 to 0.044 ppm and 0.048 to 6.26 ppm respectively.

On the average, the trace metals Al, Fe and Mn exceeded the maximum limit for drinking water. Pb also exceeded the maximum limit in some samples.

Positive correlation of Al with all the trace elements depicts sources from weathering of aluminosilicate minerals from the rock types in the study area. Also, positive correlation of Pb with Al (0.95), Ba (0.80), Co (0.71), Cr (0.89), Cs (0.92), Cu (0.87), and Fe (0.52) depict contributions from various anthropogenic activities in the area of study.

The Contamination Factor values >1 for all the trace elements depict more contributions from anthropogenic activities over the geogenic activities within the study area. The values computed for the Degree of Contamination show that the samples are heavily contaminated/polluted with trace elements (range=67 to 1482). The values recorded for the Geo-accumulation Index also show that the water is really contaminated/polluted with the trace elements.

Hence, both geogenic and anthropogenic activities contributed to the metal loading in the river water. Based on the elevated concentrations of Al, Mn and Fe the water is not fit for direct human consumption. It is recommended that detailed hydrochemistry of the river should be carried out and based on the preliminary assessment carried out in this research, thorough treatment of Asa river water should be carried out to make the water suitable for human consumption.

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