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EVALUATION OF LEVELS OF SOME CARCINOGENIC METALS IN THE WATER AND INCIDENCES OF CANCER ALONG HADEJIA-JAMA'ARE RIVER BASIN AREAS

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ABSTRACT

The determination of levels of some carcinogenic metals in the water and incidences of cancer was carried out in ten different local governments along Hadejia-Jama'are River Basin Areas, using standard procedures. Arsenic content was determined using UV Spectrophotometer after diazotization and heavy metals by atomic absorption spectrophotometry after acid digestion. The numbers of cancer patients were obtained from the Cancer Register of the health institutions along the basin after obtaining ethical approvals from the health institutions. The mean arsenic (As), of the water ranged from 3.35 – 10.60 μg/L, cadmium (Cd): 1.57 – 10.10 μg/L, chromium (Cr): 40.30 – 250.00 μg/L, nickel (Ni): 48.80 – 235.00 μg/L and lead (Pb): 19.50 – 38.20 μg/L. The metal concentrations in the water samples were higher in the dry season than the wet season. ANOVA showed significant differences at $p<0.05$ for Cd, Cr, Ni and Pb. The cancer levels were determined by matching the concentration of the heavy metals from each local government with number of cancer patients in the local government along the river basin route. The cancer cases along the basin were Bunkure- 13, Wudil- 16, Ajingi- 11, Ringim- 9, Taura- 8, K/Hausa- 10, Hadejia- 12, Jama'are- 3, Gashua- 14 and Nguru- 10. Using the principal component analysis (PCA) there was an excellent relationship between cancer burden and metal loads in the potable water of the basin while the hierarchical cluster dendrogram (HCD) analysis reveals that arsenic, chromium and cadmium may be the major contributors to cancer incidences along the basin.

INTRODUCTION

Water is vital to human existence and its importance in daily life makes it necessary that thorough physicochemical examinations be conducted on potable water sources (Shaibu and Audu, 2018). It is the most abundant chemical compound in the human body and other living organisms and dominates the earth taking approximately 70% of the surface.

Every living thing on earth needs water to survive and inadequate quantity and quality water have serious impact on sustainable development (Adewoye *et al.*, 2013). Today human activities are constantly adding industrial, domestic and agricultural wastes to ground water reservoirs at an alarming rate (Adefemi and Awokunmi, 2010). The increased use of metal-based fertilizer in agricultural practices results in continued rise in concentration of metal pollutions in fresh water reservoir due to run-offs from farm lands (Ambiga and Anna, 2013).

Similarly, industrial processes such as tannery effluents when discharged untreated, damage the normal life of the receiving water bodies. When allowed to percolate into the ground will pollute the groundwater permanently and make it unfit for drinking, irrigation and domestic consumption (Rahmanian *et al.*, 2015).

Khaled and Muhammad, (2016) reported that many metals form stable complexes with biomolecules, and their presence, even at low quantities, can be harmful to plants and animals. The problem of heavy metals entering the food chain requires systematic assessments to make timely decisions to avoid severe health effects because of the invisible mode of their toxicity (Mir *et al.*, 2016). According to Lohdip, (2013), contamination of heavy metals in the aquatic environment has attracted global attention owing to their abundance, persistence and environmental toxicity

Industrial liquid effluents are one of the principal sources of heavy metals responsible for environmental pollution (Solomon *et al.,* 2015). The wastewater from the treatment of hides and skin in industrial effluents contain high levels of

metals, toxic chemicals and other undesirable substances. As such, among all the industrial wastes, tannery effluents are ranked among the highest pollutants (Umar *et al.,* 2017). Tanneries have been found to discharge not only chromium as an inherent product of tanning process but also significant amount of Zn, Mn, Cu, Pb, Cd, Hg, As, Ni, B, Se, Mo as well as nitrogen and phosphorous in both organic and inorganic forms (Akan *et al.*, 2009). The International Agency for Research on Cancer (IARC, 2012) has classified arsenic, chromium, mercury, cadmium, lead, nickel and others and their compounds, as carcinogenic to humans. According to Shaibu and Audu (2019) these heavy metals are abundant in the tannery effluents that discharge the effluents into the Challawa River that feeds the Hadejia-Jama'are River Basin.

When cells are exposed to carcinogens, free radicals are formed that try to extract electrons from other molecules in the body. These free radicals damage cells and affect their ability to function normally (IARC, 2012; WHO, 2015). Exposure to toxic metals is closely associated with the formation of free radicals, directly or indirectly, in living organisms (Mates *et al.*, 2002; Jomova and Valko, 2011). The cumulative generation of free radicals, such as reactive oxygen species (ROS) and reactive nitrogen species (RNS), is termed oxidative stress and induces a cellular redox imbalance, which is linked to cancer incidence (Valko *et al.*, 2004; Valko *et al.*, 2006).

In Nigeria, freshwater systems are directly threatened by human activities and stand to be further affected by anthropogenic climate change (Amah 2015). One of the main sources of this water in Nigeria is Hadejia-Jama'are river basin, which receives textile and tannery waste effluents from the Sharada and Challawa industries in Kano (Akan *et al.*, 2007).

The research is aimed at determining the heavy metal load in the potable water and incidences of cancer along Hadejia-Jama'are river basin areas.

MATERIAL AND METHODS

Study area

Hadejia-Jama'are river basin area drains a catchment of about 45000 km^2 in the land area before discharging into Lake Chad. It covers the North west states of Kano, Jigawa and North east states of Bauchi, Yobe and Borno with irrigation potential of between 87000 hectares and 125000 hectares. The main activities taking place in the basin are agriculture, fishing, livestock keeping and water supply (Shaibu, 2020). (Table 1) showed coordinates of the sample sites

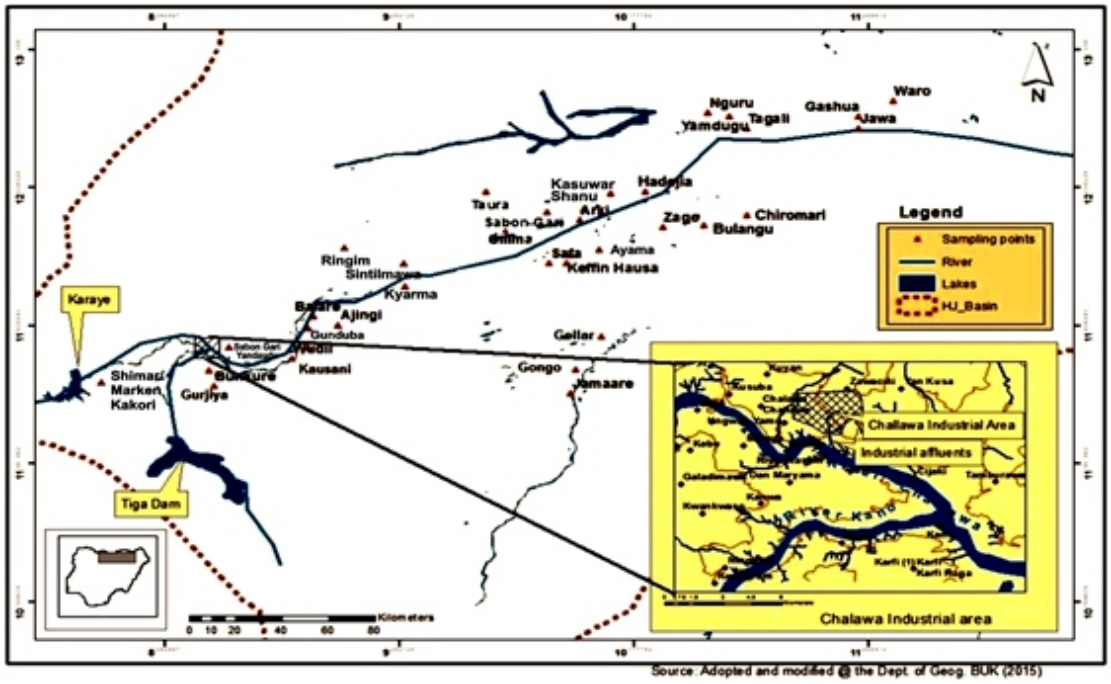

Figure 1: Map of the Study Area showing sampling sites

Sampling and Sample Pretreatment

Water samples from Hadejia-Jama'are river basin area, 6 samples each were collected from 10 local government areas; Bunkure [BKN], Wudil [WDL], Ajingi [AJN], Ringim [RGM], Taura [TAR], Kaffin-Hausa [KHS], Hadejia [HJA], Jama'are [JMR], Gashua [GSH] and Nguru [NGU].

Table1: Coordinate of the sample sites

Sample sites	Latitude	Longitude
BKN	11° 34′ 2.0″ N	8° 26′ 36.0″ E
WDL	11° 48′ 33.73″ N	8° 50′ 20.52″ E
AJN	11° 58′ 6.0″ N	9° 2′ 12″ E
RGM	12° 9′ 14.37″ N	9° 9′ 34.99″ E
TAR	12° 15′ 20.38″ N	9° 23′ 2.72″ E
KHS	12° 11′ 23.23″ N	9° 55′ 26.96″ E
HJA	12° 27′ 12.49″ N	10° 02′ 28.14″ E
JMR	12° 17′ 6.25″ N	10° 21′ 0.97″ E
GSH	12° 52′ 2.99″ N	11° 02′ 28.20″ E
NGU	12° 52′ 26.99″ N	10° 27′ 5.39″ E

Source: Adopted and modified @Dept. of Geog. BUK (2020)

Samples were collected from each local government, from three points; 2 samples each from river bank, 10 meters away and midpoint using 4 litre cleaned plastic containers in dry and wet seasons. 1cm^3 conc. HNO_3 was added to every 1L sample in 4L container to maintain the stability of the oxidation state of the metals in solution (APHA, 2011; Anuo *et al.,* 2012). One hundred and twenty (120) water samples in all were transported to the laboratory and subsequently used for the digestion. The samples for arsenic (UV/Visible spectrophotometer) analysis were collected separately in 2L cleaned plastic containers and stored in the refrigerator.

Digestion of Sample

To digest the sample, 750cm^3 of the water sample was transferred into a 1000cm^3 pyrex glass beaker and evaporated on a hot plate. When the volume had reduced to about half the original volume, the remaining 250cm^3 was added and heating continued until the volume reduced to about 50cm^3. The solution was allowed to cool and 5cm^3 of concentrated nitric acid was added to the beaker and the content reconstituted with 30cm^3 of distill deionized water and heated on a hot plate at 85^{o}C for few minutes. After a clear solution was obtained, it was allowed to cool and transferred into a 100cm^3 volumetric flask. It was then made up to 100cm^3 mark with distill deionized water and filtered into a 100cm^3 volumetric flask using Whatman 42 filter paper. The blank (distill deionized water) was prepared in a similar way by evaporating 1000cm^3 to 50cm^3 and subsequently digesting it using 5cm^3 concentrated nitric acid (Suleiman, 2015).

Each digested water sample was aspirated into the atomic absorption spectrophotometer (model: Varian AA240FS) and absorbance measured at the individual metal wavelength using the appropriate hollow cathode lamps of Cd, Cr, Ni and Pb. Calibration curves for the different metals were generated from metal standard solutions and concentrations of metals were calculated. The results were obtained from the standard calibration curve.

Determination of Arsenic Concentration in Water Samples

To determine arsenic, 3.60cm^3 of water sample was pipetted into a test tube, 5.0cm^3 of ammonium molybdate-hydrazine mixture and 2 drops of $Na_2S_2O_5$ were added. To this mixture 1.0cm^3 of KI_3 solution and 0.2cm^3 sodium hydrogen carbonate were added. This mixture was heated in a water bath at 95^{o}C. After cooling the absorbance reading was taken with UV-Visible

Spectrophotometer (Jenway 6505) at ëmax 840nm. The concentration of metals was extrapolated from standard calibration curve (Sholadoye and Elias, 2016).

$4N_2H_5^{2+} + 6HAsO_4^{2-} \rightarrow 4N_2 + 3As_2O_3 + 11H_2O + 4OH^-$ ---------- Equation 1

Cancer Data Collection

Application for ethical approval was written to all the major health institution around the study area. The approval was used to access the cancer register and the age, gender, address and part of the body affected were taken. The address of the individual cancer patient was used to correlate the cancer patient with the level of metals from the study area.

Statistical Analysis

All analyses were performed in triplicates and the results expressed as mean±SD. The excel data analysis was used. The difference in As, Cd, Cr, Ni and Pb concentrations among the different sampling points were tested by analysis of variance method, (ANOVA), a value of $p<0.05$ was considered statistically significant. Principal component analysis (PC) and Hierarchical cluster analysis were used to compare cancer, metals and sites.

RESULTS AND DISCUSSIONS

The Hadejia-Jama'are river basin water samples showed high arsenic levels in dry season than in wet season due to dilution in wet season (Tables 2 and 3). A significant difference was observed between the sites at $p<0.05$. In the dry season, three of the sites, BKN, GSH and RGM have arsenic levels slightly above the WHO permissible limit (WHO 2008).

The principal component analysis (PCA), (Fig. 2) placed arsenic in component 1 with BKN, WDL, RGM, HJA and AJN. BKN was clustered with AJN and HJA by hierarchical cluster analysis dendrogram, Cluster F, (Fig. 3). The clustering of these sites may be due to their similarities in levels of As, 9.65 – 10.40; 7.45 – 9.22; 6.90 – 9.14 µg/L, Cd, 2.73 – 7.87; 2.85 – 5.48; 2.70 – 5.54 µg/L, Cr, 165.00 – 190.00; 149.00 – 165.00; 132.00 – 133.00 µg/L with cancer incidences of 13.00, 11.00, 12.00 for BKN, AJN and HJA respectively. The PCA correlation chart (Fig. 4A) shows that arsenic, cadmium and chromium were positively correlated to cancer incidences with correlation coefficient, r = 0.359, 0.419 and 0.5347 respectively in dry season while contributions from Ni and Pb are very minimal as reveal by correlation chart (Fig. 4A and 4B). From the PCA analysis, arsenic cadmium and chromium may be the major contributor to cancer in these sites. This result is similar to the observations made by Aballay *et al*, (2012), Hamid *et al,* (2016), Mendez *et al,* (2017), and Steven *et al,* (2018) in which levels of As of 50.00 µg/L, 3.00 – 49.00 µg/L, 1.50 - 15.40 µg/L, and 1.00 - 950.00 µg/L respectively, in drinking water were found to have caused cancer among the inhabitants in their various study areas.

Table 2: Mean concentrations of Metals in the Water Samples in wet season

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L.G	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Ni (µg/Lt)	Pb (µg/L)
BKN	9.08±0.80	2.73±0.60	165±2.20	87.7±0.90	29.3±1.50
WDL	9.65±1.00	3.87±0.60	224±2.40	85.4±0.60	31.9±0.90
AJN	7.45±0.70	2.85±0.70	149±1.60	109±0.90	29.3±0.90
RGM	9.65±0.90	3.15±0.40	144±1.60	79.8±0.70	32.8±0.80
TAR	7.27±0.70	2.62±1.00	112±1.40	112±1.50	31.4±1.00
KSH	7.05±0.60	3.74±0.60	111±1.60	88.0±1.20	22.8±1.30
HJA	6.90±0.70	2.70±0.40	133±2.00	96.6±0. 60	28.0±1.20
JMR	3.35±0.30	1.57±0.40	40.3±1.00	48.8±1.10	19.5±0.70
GSH	10.10±0.70	6.55±0.50	122±1.60	95.2±1.30	28.0±0.80
NGU	7.13±0.70	4.88±0.40	123±1.80	81.4±0.90	30.5±1.30
WHO,2008	10.0	3.0	50.0	70.0	10.0

Table 3: Mean concentrations of Metals in the Water Samples in dry season

L.G.	As (μg/L)	Cd (μg/L)	Cr (μg/L)	Ni (μg/L)	Pb (μg/L)
BKN	10.40±0.90	7.87±1.30	190±1.80	107±1.80	38.20±1.70
WDL	9.80±1.00	9.30±1.10	250±2.40	112±2.10	30.20±1.80
AJN	9.22±1.00	5.48±1.10	165±2.30	120±2.40	34.70±2.80
RGM	10.20±1.00	6.77±1.00	186±1.00	235±1.80	36.50±2.00
TAR	8.93±0.80	7.43±1.10	137±2.20	122±2.00	36.80±2.20
KSH	9.32±0.80	9.59±1.20	117±2.00	96.7±2.10	24.40±1.80
HJA	9.14±0.80	5.54±0.90	132±1.90	111±2.00	33.40±1.90
JMR	4.20±0.60	2.40±1.10	44.4±2.00	69.7±2.40	21.10±2.30
GSH	10.60±1.00	10.10±1.50	144±2.10	111±1.50	34.90±2.30
NGU	8.95±0.80	9.30±1.80	136±2.10	98.10±2.20	36.30±2.10
WHO,2008	10.0	3.0	50.0	70.0	10.0

The cadmium levels in GSH, NGU, KHS and WDL in the wet season were found to be above WHO limit of 3.00 μg/L and much higher in all the sampling sites in the dry season. The much increase in the levels in the dry season can be attributed majorly to the decreased volume of water in the basin (Ejieji *et al*, 2016). ANOVA of the results showed significant differences ($p< 0.05$) among the sites between wet and dry seasons.

The PCA placed cadmium in component 2 with KHS, GSH and NGU (Fig. 2) having correlation values positively correlated with cancer at $r = 0.419$ and 0.874 (Fig. 4A and 4B). This confirms that cadmium is the major contributor to cancer incidences in these three sites. From the cluster analysis (Fig. 3) KHS and GSH are in Cluster C due to their closer cadmium levels and number of cancers 10.0 and 14.0 respectively.

Cluster A contains only NGU, this is due to the fact that the levels of Cd in this site was relatively high (4.88 – 9.30) μg/L above the WHO permissible limit of 3.00 μg/L Cd and positively correlated with the cancer incidence level of 10.0 in the LGA. The cluster showed that the possible cancer cases in this area within the basin may be as a result of the levels of Cd.

The result obtained is similar with the observations of Faijul (2013), Cd(10.00 – 30.00) μg/L; Nordberg (2010), Cd(25.00-50.00) μg/L; and Marouf (2018), Cd(25.00) μg/L which were indicated in the breast, prostate and renal cancers among people that drank water with these cadmium levels in Bangladesh and in Iran.

The Hadejia-Jama'are river basin water samples have high chromium levels in both wet and dry seasons which were above the WHO maximum permissible limit of 50.00 μg/L in all the sampling sites except JMR (Tables 2 and 3).

The PCA placed chromium in component 1 (Fig. 2) with BKN, WDL, AJN, RGM and HJA. The correlation chart (Fig. 4A) showed that chromium was positively correlated to cancer in these sites at $r = 0.585$ in dry season and this showed that chromium is the major contributor to cancer incidences at these sites. The cluster analysis placed BKN, AJN and HJA with Cr level (132.00-190.00) μg/L in the same cluster F (Fig. 3) as having similar cancer burden. This is similar to the observation of Cone (2009), where stomach and intestinal cancers were found among consumers of water with 57000 μg/L level of chromium.

The cluster analysis placed only WDL in Cluster D owing to its peculiarity in the high level of chromium (224.00-250.00) μg/L and cancer incidences of 14.0, the highest in the basin indicating that Cr is the major contributor to cancer in site WDL. Similarly, RGM and TAR were placed in cluster E due to their similarity in agricultural activities and levels of metals load except for Ni where the level for dry season in RGM was much higher than TAR (Tables 2 and 3) and similar cancer burden of 9.0 and 8.0 respectively.

The nickel concentration in the samples was above the WHO permissible limit of 70 µg/L for both wet and the dry seasons among all the sites. The PCA (Fig. 2) placed nickel in component 1 with very weak positive correlation to cancer at r = 0.190 (Fig. 4A) showing that nickel contributed minimally to cancer incidences in the study area.

Similarly, lead concentrations in the samples were found to be higher than the WHO permissible limit of 10.00µg/L in both dry and wet seasons. The PCA analysis (Fig. 2) placed lead in component 1 with BKN, WDL, AJN, RGM and HJA. The contribution to cancer from lead is less as revealed by correlation value, r = 0.201 as showed in (Fig. 4A).

Cluster B has JMR as the only site (Fig. 3) and has the least levels of metals though with high Pb (19.50 – 21.10)µg/L. These values were above the WHO maximum permissible limit of 10.00µg/L and has cancer incidence of 3.0. Adamu *et al*, (2015) reported 2330.00-4230.00µg/L Pb in soil and water samples around the mining site in Jos metropolis, Plateau State Nigeria. The 3.0 cancer incidences may have come from lead. This is similar to the observation of Olusengun and Schrauzer, (2010) in which a breast cancer woman was found to have been consuming water with 500.00µg/L Pb. The low levels of other metals apart from Pb in site JMR could be ascribed to the fact that the Jama'are River has it source from Jos, Plateau unlike the other sites that received their water from Challawa River (feeder river to the basin) with high pollution loads from tannery and textile effluents hence JMR served as control for this study.

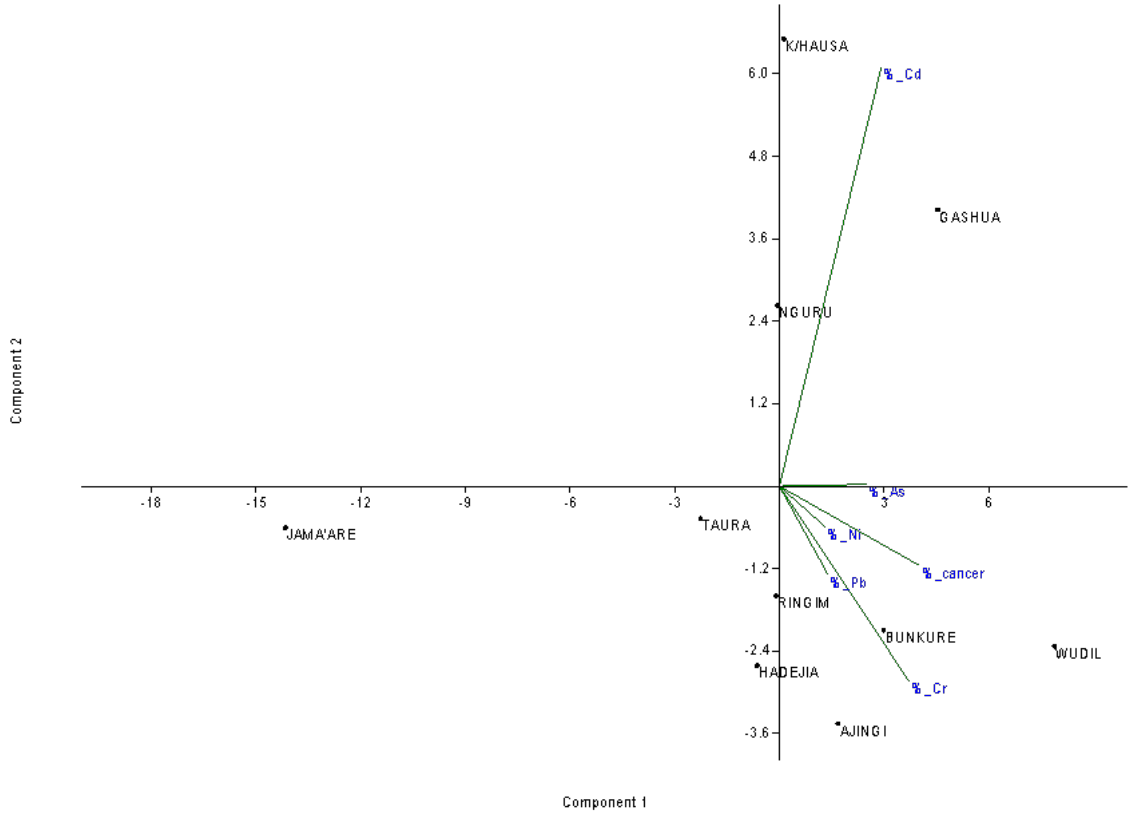

Figure 2: Principal Component Analysis of the Metals, Sites and Cancer Incidences

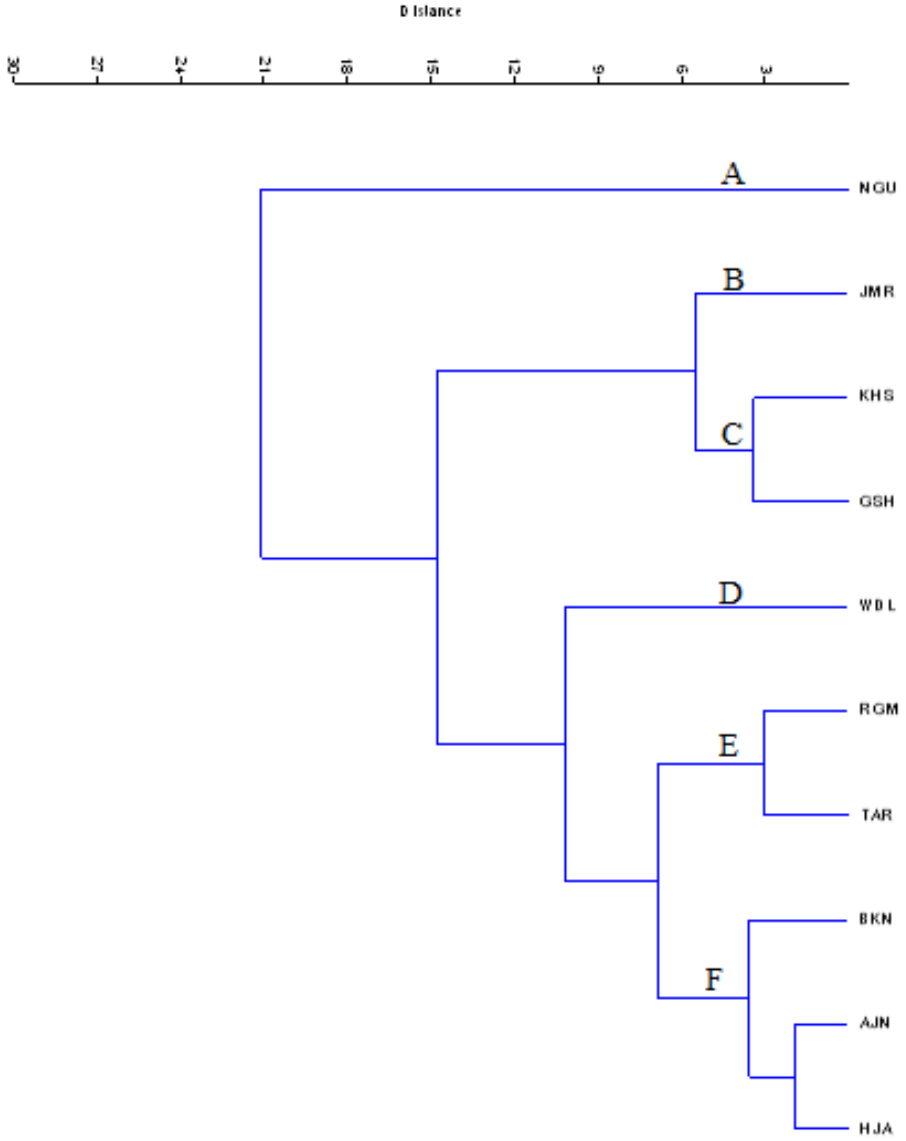

Figure 3: Hierarchical Cluster analysis dendrogram for Hadejia-Jama'are River Basin water sample.

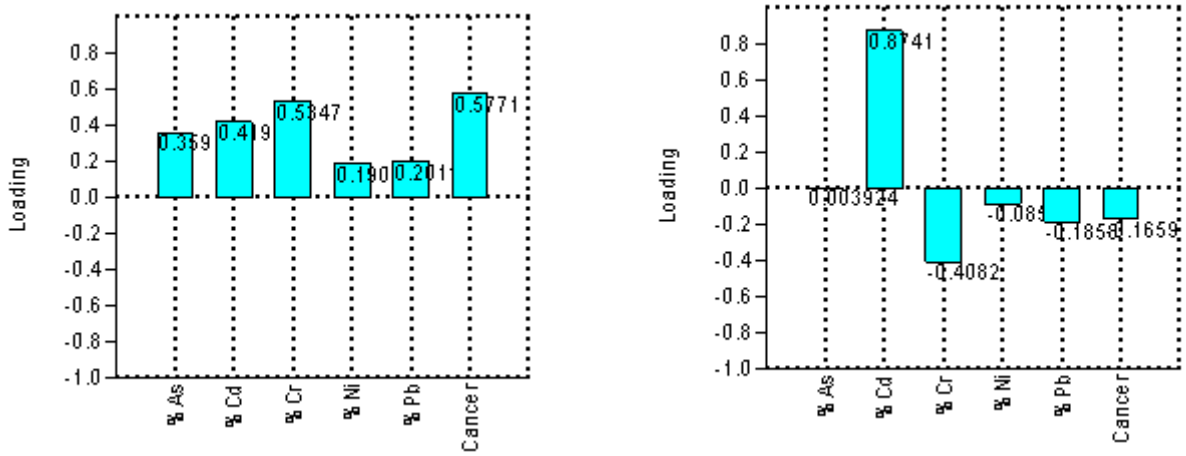

Figure 4: Principal Component Analysis Correlation chart
A: Dry season
B: Wet season

CONCLUSION

From the results, it was observed that heavy metals present in the water samples of Hadejia-Jama'are river basin were higher in dry season than the wet season which may be due to dilution as the volume of water increases during wet season. The results also showed that these heavy metals are from industrial effluents discharged into the Challawa river that feeds the Hadejia-Jama'are basin by the Sharada and Challawa industrial estate. The PCA and cluster analysis have implicated the heavy metals in the incidences of cancer among the inhabitants along the basin as a result of the use of the water for agricultural and other domestic activities.

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