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Original Paper

SEASONAL VARIATION ASSESSMENT IN THE CONCENTRATIONS OF HEAVY METALS IN WATER AND SEDIMENT SAMPLES FROM KOMADUGU RIVER BASIN, YOBE STATE, NIGERIA

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Abstract
Water and sediment samples were collected during the rainy and dry season from Komadugu river basin, Yobe State, Nigeria for the determination of some heavy metals which include Pb, Fe, Cu, Zn, Cd, Ni, Mn, As, Cr. Digestion of water and sediment samples were carried out using standard procedures, the concentrations of heavy metals were determined using Perkin-Elmer A Analyst 300 Atomic Absorption Spectroscopy (AAS) and X-Ray Fluoresces (XRF) to provide for comparative analysis between the methods. The concentrations of all the heavy metals in the water samples during the rainy and dry season ranged from 1.10E-04 to 7.74E-01 mg/L, Fe was observed to show the highest total concentrations (1.35E+02 mg/L) during the dry season, while as shows the total lowest concentration with a value of (1.00E-03 mg/L) during rainy season. The concentrations of all the heavy metals in the sediment samples were significantly higher at sampling point S8 with a value of (2.99E+04 mg/kg) during the dry season, while the lowest value was observed at sampling point S1 **(**4.00E-02 mg/kg). Fe was the most dominant in all the sampling points, while Pb shows the lowest concentration. The results further indicate that, the concentrations of all the heavy metals were significantly higher in the sediment samples when compared with the water samples.

1. Introduction

Heavy metals are natural trace components of the aquatic environment, but their levels have increased due to industrial wastes, geochemical structure, agricultural and mining activities [1,2]. All these sources of pollution affect the physiochemical characteristics of the water, sediment and biological components, and thus the quality and quantity of fish stocks [3,4]. Fish is generally

appreciated as one of the healthiest and cheapest sources of protein and it has amino acid compositions that are higher in cysteine than most other sources of protein. Heavy metals like copper, iron and zinc are essential for fish metabolism while some others such as mercury, cadmium, arsenic and lead have no known role in biological systems [5,6].

Studies from the field and laboratory experiments showed that accumulation of heavy metals in a tissue is mainly dependent on water concentrations of metals and exposure period; although some other environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation [1,6,7,8]. Ecological needs, size and age of individuals, their life cycle and life history, feeding habits and the season of capture were also found to affect experimental results from the tissues [9,10]. The obvious sign of highly polluted water and dead fish is readily apparent, but the sublethal pollution might result only in unhealthy fish. Very low levels of pollution may have no apparent impact on the fish itself, which would show no obvious signs of illness, but it may decrease the fecundity of fish populations, leading to a long-term decline and eventual extinction of this important natural resource [11,12]. Such low-level pollution could have an impact on reproduction, either indirectly via accumulation in the reproductive organs, or directly on the free gametes (sperm or ovum) which are released into the water. Control of reproduction in fish is complex and regulated by a wide range of factors and low-level pollution could affect any part of this pathway. Steroid hormones are very important and play essential roles in maintaining reproductive functions [9,10].

2. Experimental details

2.1 Sediment Sampling

Sediment samples were collected in accordance with the method described by Boyd and Tucker [13], from Komadugu river basin from Nguru to Gashua (points S_1 to S_{10}) using a plastic hand trowel sampler by scooping 1-5 cm of the top layer sediment. One kilogram (1kg) of sediment samples were collected at each sampling point and were placed in an amber glass bottle, labeled and stored in an iced box. The samples were transported to the Chemistry laboratory, University of Maiduguri and stored in a refrigerator at 4 °C for further analysis. Sediment samples were collected 10 meters away from the bank of the river on seasonal basis (dry and rainy seasons).

2.2 Digestion of Sediment Samples for Heavy Metals Determination

Digestion of sediment samples for heavy metals determination was carried out in accordance with the method described by Radojevic and Bashkin [14] and adopted by Akan *et al.* [15]. Two grammes of the sediment samples were weighed into acid washed glass beaker. Sediment samples were digested by the addition of 20 cm^3 of aqua regia (mixture of HCl and HNO_3, ratio 3:1) and 10 cm^3 of 30 % H_2O_2. The H_2O_2 was added in small portions to avoid any possible overflow, leading to loss of material from the beaker. The beakers were covered with watch glasses and heated over a hot plate at 90 ^{O}C for two hours. The beakers wall and watch glasses were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant. The volumes were adjusted to 100 cm^3 with distilled water.

3. Results and discussion

2.3 Mean Concentrations of Some Heavy Metals in Water Samples from Different Sampling Points of Komadugu River Basin, During the Rainy and Dry Seasons

The mean concentrations of some heavy metals in water samples from different sampling points of Komadugu River Basin, Yobe State during the rainy and dry seasons are as presented in Tables 1 and 2. The concentrations of Fe ranged from 3.00E-02 to 7.74E-01 mg/L; 8.00E-03 to 8.00E-03 mg/L Pb; 2.00E-02 to 2.00E-02 mg/L Cu; 2.00E-02 to 2.00E-02 mg/L Zn; 2.00E-03 to 6.00E-02 mg/L Cd; 6.00E-02 to 6.00E-02 mg/L Ni; 5.00E-02 to 1.10E-01 mg/L Mn; 1.10E-04 to 1.10E-04 mg/L As and 6.00E-03 to 6.00E-03 mg/L Cr. The total concentrations of Fe were significantly higher during the dry season with a value of 1.35E+02 mg/L, while as shows the lowest total concentrations with a value of 1.00E-03 mg/L during the rainy season.

Table 1: Mean Concentrations of Some Heavy Metals in Water Samples from Different Sampling Points of Komadugu River Basin, During the Rainy Season (AAS)

	Concentrations (mg/L)								
Sampling points	**Fe**	**Pb**	**Cu**	**Zn**	**Cd**	**Ni**	**Mn**	**As**	**Cr**
S1	3.00E-02	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S2	4.00E-02	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	7.00E-02	1.00E-04	6.00E-03
S3	3.00E-02	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S4	3.00E-02	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S5	5.50E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S6	5.80E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S7	4.00E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	1.10E-01	1.00E-04	6.00E-03
S8	2.20E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S9	3.00E-02	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S10	1.30E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	8.00E-02	1.00E-04	6.00E-03
Total	**2.04E+00**	**8.00E-02**	**2.00E-01**	**2.00E-01**	**2.00E-02**	**6.00E-01**	**6.10E-01**	**1.00E-03**	**6.00E-02**

Table 2: Mean Concentrations of Some Heavy Metals in Water Samples from Different Sampling Points of Komadugu River Basin, During the Dry Season (AAS)

	Concentrations (mg/L)								
Sampling points	**Fe**	**Pb**	**Cu**	**Zn**	**Cd**	**Ni**	**Mn**	**As**	**Cr**
S1	3.10E-01	8.00E-03	2.00E-02	2.00E-02	3.00E-02	6.00E-02	3.80E-01	1.00E-04	6.00E-03
S2	5.40E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	3.80E-01	1.00E-04	6.00E-03
S3	4.10E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S4	6.40E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	3.80E-01	1.00E-04	6.00E-03
S5	9.70E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S6	7.00E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	4.10E-01	1.00E-04	6.00E-03
S7	5.80E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	3.90E-01	1.00E-04	6.00E-03
S8	2.40E-01	8.00E-03	2.00E-02	2.00E-02	2.00E-03	6.00E-02	3.60E-01	1.00E-04	6.00E-03
S9	7.74E+01	8.00E-03	2.00E-02	2.00E-02	4.00E-02	6.00E-02	5.00E-02	1.00E-04	6.00E-03
S10	5.31E+01	8.00E-03	2.00E-02	2.00E-02	6.00E-02	6.00E-02	5.70E-01	1.00E-04	6.00E-03
Total	**1.35E+02**	**8.00E-02**	**2.00E-01**	**2.00E-01**	**1.44E-01**	**6.00E-01**	**3.02E+00**	**1.00E-03**	**6.00E-02**

2.4 Mean Concentrations of Some Heavy Metals in Sediment Samples from Different Sampling Points of Komadugu River Basin, During the Rainy and Dry Seasons

The mean concentrations of some heavy metals in sediment from different sampling points of Komadugu River basin, Yobe State during the rainy and dry seasons using AAS method are as presented in Tables 3 and 4. The concentration of Fe ranged from 1.40E+00 to 1.45E+05 mg/kg; 8.00E-03 to 9.90E+00 mg/kg Pb; 2.20E-02 to 2.23E+01 mg/kg Cu; 2.14E+00 to 2.61E+01 mg/kg Zn; 9.90E+00 to 6.00E+01 mg/kg Cd; 6.00E-02 to 2.48E+01 mg/kg Ni; 3.55E+00 to 2.02E+02 mg/kg Mn; 1.00E-04 to 5.00E-01 mg/kg As and 6.00E-03 to 1.36E+02 mg/kg Cr. The results revealed that Fe total concentrations were significantly higher during the rainy season with a value of 3.35E+04 mg/kg, while Pb shows the lowest total concentrations with a value of 8.00E-02 mg/kg during the dry season.

The concentrations of the heavy metals in sediment samples using XRF method are as presented in Tables 5 and 6. The concentration of Fe ranged from 1.73E+03 to 2.99E+04 mg/kg. mg/kg; 1.00E+00 to 1.14E+02 mg/kg Pb; 5.00E-01 to 1.74E+01 mg/kg Cu; 7.50E+00 to 6.00E+01 mg/kg Zn; 2.00E+00 to 2.30E+00 mg/kg Cd; 1.57E+01 to 2.74E+01 mg/kg Ni; 1.22E+01 to 7.50E+02 mg/kg Mn; 5.00E-02 to 1.34E+01 mg/kg As and 1.13E+01 to 6.73E+02 mg/kg Cr. From the results of the study Fe shows a significantly higher total concentration of 2.84E+05 mg/kg during the dry season, while Pb shows the lowest total concentration with a value of 1.00E+01 mg/kg during the dry season.

Table 3: Mean Concentrations of Some Heavy Metals in Sediment Samples from Different Sampling Points of Komadugu River Basin, During the Rainy Season (AAS)

	Concentrations (mg/kg)								
Sampling points	**Fe**	**Pb**	**Cu**	**Zn**	**Cd**	**Ni**	**Mn**	**As**	**Cr**
S1	7.53E+02	8.00E-03	1.13E+00	2.14E+00	5.60E+01	6.00E-02	6.23E+00	6.00E-02	1.12E+00
S2	1.40E+00	1.68E+00	1.24E+00	3.70E+00	3.10E+00	6.00E-02	9.19E+00	9.00E-02	2.28E+00
S3	1.11E+00	1.74E+00	1.41E+00	8.24E+00	9.40E-01	1.24E+00	4.38E+00	6.00E-02	6.00E-03
S4	4.02E+02	8.00E-03	6.20E-01	2.48E+00	1.21E+00	6.00E-02	1.47E+01	9.00E-02	1.04E+00
S5	7.34E+02	2.54E+00	1.78E+00	5.03E+00	6.06E+00	1.34E+00	1.76E+01	1.00E-01	3.13E+00
S6	3.13E+03	2.49E+00	2.32E+00	5.05E+00	6.00E+01	1.71E+00	1.50E+01	2.30E-01	4.52E+00
S7	2.64E+03	2.05E+00	2.26E+00	4.76E+00	2.08E+01	1.80E+00	1.18E+01	1.70E-01	4.45E+00
S8	2.04E+03	2.16E+00	2.29E+00	4.61E+00	3.93E+00	2.52E+00	1.19E+01	1.20E-01	3.68E+00
S9	1.45E+04	1.08E+01	4.20E+00	2.61E+01	2.00E+00	2.48E+01	9.81E+01	5.00E-01	1.36E+02
S10	9.18E+03	9.90E+00	7.10E+00	2.41E+01	2.00E+00	2.26E+01	6.11E+01	5.00E-01	6.01E+01
Total	**3.33E+04**	**3.34E+01**	**2.44E+01**	**8.62E+01**	**1.56E+02**	**5.62E+01**	**2.50E+02**	**1.92E+00**	**2.16E+02**

Table 4: Mean Concentrations of Some Heavy Metals in Sediment Samples from Different Sampling Points of Komadugu River Basin, During the Dry Season (AAS)

	Concentrations (mg/kg)								
Sampling points	Fe	Pb	Cu	Zn	Cd	Ni	Mn	As	Cr
S1	3.81E+02	8.00E-03	2.00E-02	2.21E+00	1.26E+00	6.00E-02	4.86E+00	1.00E-04	1.97E+00
S2	3.69E+02	8.00E-03	2.00E-02	2.26E+00	2.55E+00	6.00E-02	5.46E+00	1.00E-04	6.00E-03
S3	7.68E+02	8.00E-03	2.30E-01	3.50E+00	2.00E-03	1.05E+00	9.88E+00	1.00E-04	2.66E+00
S4	6.94E+00	8.00E-03	1.87E+00	1.02E+01	2.50E-01	1.15E+00	1.03E+01	1.00E-04	7.30E+00
S5	1.02E+03	8.00E-03	1.87E+00	7.16E+00	1.76E+00	3.78E+00	2.28E+01	1.00E-04	4.71E+00
S6	1.04E+03	8.00E-03	2.00E-02	6.97E+00	3.80E-01	4.39E+00	8.36E+01	1.00E-04	6.00E-03
S7	3.68E+03	8.00E-03	2.21E+00	1.32E+01	1.80E+00	5.06E+00	3.50E+01	1.00E-04	6.55E+00
S8	2.38E+03	8.00E-03	7.25E+00	1.70E+01	7.20E-01	8.15E+00	2.02E+02	1.00E-04	6.55E+00
S9	3.17E+03	8.00E-03	2.37E+00	9.26E+00	5.00E-01	6.81E+00	6.14E+01	1.00E-04	6.00E-03
S10	1.66E+03	8.00E-03	2.23E+01	1.15E+01	3.30E-01	1.30E+01	3.55E+00	1.00E-04	3.24E+00
Total	**1.45E+04**	**8.00E-02**	**3.82E+01**	**8.33E+01**	**9.55E+00**	**4.35E+01**	**4.39E+02**	**1.00E-03**	**3.30E+01**

Table 5: Mean Concentrations of Some Heavy Metals in Sediment Samples from Different Sampling Points of Komadugu River Basin, During the Rainy Season (XRF)

	Concentration (mg/kg)								
Sampling Points	Fe	Pb	Cu	Zn	Cd	Ni	Mn	As	Cr
S1	5.47E+03	6.30E+00	5.00E-01	1.13E+01	2.00E+00	2.13E+01	3.31E+01	5.00E-02	1.59E+01
S2	6.49E+03	7.80E+00	1.90E+00	1.51E+01	2.00E+00	1.92E+01	5.83E+01	5.00E-01	1.13E+01
S3	6.81E+03	9.00E+00	5.20E+00	2.25E+01	2.00E+00	1.95E+01	5.47E+01	5.00E-01	2.75E+02
S4	1.73E+03	4.90E+00	5.00E-01	7.50E+00	2.00E+00	1.57E+01	1.22E+01	5.00E-01	4.68E+02
S5	1.02E+04	1.04E+01	2.80E+00	2.52E+01	2.00E+00	2.30E+01	9.42E+01	5.00E-01	1.57E+01
S6	1.43E+04	1.19E+01	6.70E+00	3.00E+01	2.00E+00	2.37E+01	9.25E+01	5.00E-01	9.60E+01
S7	1.36E+04	1.14E+02	4.70E+00	2.68E+01	2.30E+00	2.25E+01	7.90E+01	5.00E-01	2.06E+02
S8	1.20E+04	1.06E+01	9.40E+00	2.48E+01	2.00E+00	2.74E+01	7.92E+01	5.00E-02	7.96E+01
S9	1.45E+04	1.08E+01	4.20E+00	2.61E+01	2.00E+00	2.48E+01	9.81E+01	5.00E-01	1.36E+02
S10	9.18E+03	9.90E+00	7.10E+00	2.41E+01	2.00E+00	2.26E-01	6.11E+01	5.00E-01	6.01E+01
Total	**9.44E+04**	**1.96E+02**	**4.30E+01**	**2.13E+02**	**2.03E+01**	**1.97E+02**	**6.62E+02**	**4.10E+00**	**1.36E+03**

Table 6: Mean Concentrations of Some Heavy Metals in Sediment Samples from Different Points of Komadugu River Basin, During the Dry Season (XRF)

	Concentrations (mg/kg)								
Sampling points	Fe	Pb	Cu	Zn	Cd	Ni	Mn	As	Cr
S1	2.97E+04	1.00E+00	8.30E+00	4.94E+01	2,00E+00	2.58E+01	4.26E+01	1.34E+01	1.23E+02
S2	2.60E+04	1.00E+00	1.20E+00	4.49E+01	2.00E+00	2.11E+01	4.89E+02	1.32E+01	5.76E+02
S3	2.96E+04	1.00E+00	1.33E+01	6.08E+01	3.30E+00	2.49E+01	6.78E+02	1.11E+01	5.26E+02
S4	2.93E+04	1.00E+00	1.49E+01	5.75E+01	2.00E+00	2.59E+01	6.76E+02	9.40E+00	6.73E+02
S5	2.90E+04	1.00E+00	1.45E+01	5.87E+01	2.30E+00	2.39E+01	6.63E+02	1.29E+01	4.41E+02
S6	2.91E+04	1.00E+00	1.74E+01	5.70E+01	2.00E+00	2.63E+01	7.07E+02	1.22E+01	8.02E+01
S7	2.98E+04	1.00E+00	1.33E+01	5.79E+01	2.00E+00	2.46E+01	7.50E+02	1.25E+01	1.17E+02
S8	2.99E+04	1.00E+00	1.24E+01	5.36E+01	2.00E+00	2.59E+01	7.03E+02	1.19E+01	4.72E+02
S9	2.74E+04	1.00E+00	1.06E+01	6.00E+01	2.00E+00	2.47E+01	6.73E+02	5.00E-01	7.57E+01
S10	2.40E+04	1.00E+00	9.20E+00	5.41E+01	2.00E+00	2.09E+01	5.78E+02	1.13E+01	7.45E+01
Total	**2.84E+05**	**1.00E+01**	**1.15E+02**	**5.54E+02**	**1.96E+01**	**2.44E+02**	**5.96E+03**	**1.08E+02**	**3.16E+03**

2.5 Discussion

The seasonal variation in the concentrations of heavy metals in water and sediment samples from Komadugu river basin for points S1 to S10 are in the following order dry season > rainy season. The higher levels of heavy metals during the dry season might be attributed to reduction in the volume of water and the addition of waste water from the river sources, while the low levels of these metals during the rainy season might be attributed to dilution of the waste water by fresh water. The levels of all the metals in the sediment samples were higher than that of the water sample. This variation may be attributed to the fact that sediments usually serve as a repository of elements in aqueous environment. This conforms to the report by Stephen *et al.*, [16], that sediments could act as sink for a wide range of contaminants including heavy metals from various sources.

The concentration of iron was generally detected in the entire samples analyzed. Although, iron is one of the essential elements in human nutrition, however its presence at elevated concentration in aquatic ecosystems, poses serious pollution and health problems. Toxicity of iron in humans has been found to bring about vomiting, cardiovascular collapse and diarrhea, while iron deficiency may lead to failure of blood clotting to replenish [17]. According to USEPA, (1987) [18] guideline value and maximum contaminant level, concentration values of 0.30 mg/l (water) and 30 mg/kg (sediment) Fe is acceptable [14]. Above 0.3 mg/l and 30 mg/kg a condition known as haemochromatosis could result. From the result of this study, the concentration of iron (5.80E-01 and 7.74E+01 mg/l) in water samples and that of sediment sample (1.45E+04 and 2.98E+04 mg/kg) in exceeded the guideline limit indicating severe pollution of the study area. However, point S3 (1.11E+00 mg/kg) using XRF methods did not exceed the USEPA maximum contamination levels of 30 mg/kg for sediment sample.

Lead is a non-essential trace element [19]. The toxicity of lead is dependent on the development stage of the organism and the presence of organic material. Decrease in water pH can increase the bioavailability of lead in the system [20]. Lead in aquatic environment is risky to life since aquatic organisms used as food are particularly very sensitive to lead and often retain about a percent of ingested lead which could be taken up by man through the food chain [19]. Lead can cause damage to the nervous system and the kidneys and it is suspected to be carcinogenic [14]. Children exposed to high lead levels are particularly at risk. The levels of lead in the analyzed water (8.00E-03 mg/l) and sediment (1.00E+00 and 1.14E+02 mg/kg) samples showed that the limiting values by USEPA (1987) [18] of 0.01 mg/l and 40 mg/kg respectively were not exceeded, indicating that the study area was not contaminated with lead and may not pose a hazard to the aquatic biota. The presence of lead in the study area may be attributed to anthropogenic discharge of lead waste from industrial processes within the source of the river which flows to the area of study [15].

Copper is a common environmental metal and is essential in cellular metabolism but at high concentrations it can be highly toxic to fish [21]. Copper is an essential substance to human life, however, in high concentrations, it can cause anemia, liver and kidney damage, stomach and intestinal irritation [17]. Copper is generally remobilized with acid-base ion exchange or oxidation mechanism [22]. Long term exposure to copper may lead to liver and kidney damage [23]. The

levels of copper in the water (2.00E-02 mg/l) and sediment (2.00E-02 to 2.23E+01 mg/kg) samples were below the (WHO, 2004) standard values of 1.00 mg/l and 25 mg/kg respectively for the survivor of aquatic organism (15,24].

Zinc is equally an essential element in the human diet. Zn deficiency in the diet may be more detrimental to human health than too much of it in the diet. In aquatic ecosystem, Zn is highly toxic to some aquatic organisms. Although Zn is not a human carcinogen, ingestion of large doses can cause death [25]. Zinc is also an essential micronutrient for all organisms and forms the active site for various metalloenzymes [26]. Excessive intake of Zn may lead to vomiting, dehydration, abdominal pain, nausea, lethargy and dizziness [25]. The levels of Zinc in the water (2.00E-02 mg/l) and sediment 2.14E+00 to 6.08E+01 mg/kg) samples did not exceed the WHO, (2004) guideline value of 3.00 mg/l and 123 mg/kg [15,24].

Cadmium is a non-essential trace element that enters the environment via anthropogenic activities such as industrial effluent, sewage-sludge, fertilizers and pesticides [26]. Cadmium adsorbs strongly to sediments and organic matter [27]. Cadmium has a range of negative physiological effects on organism, such as decreased growth rates and negative effects on embryonic development [28]. Although cadmium is a Sulphur seeking metal that tends to precipitate in anoxic sediments, experiments carried out at concentrations lower than the values found in this study, showed that cadmium can still be assimilated from anoxic sediments with high organic matter content [29-32]. The levels of Cadmium in the water (2.00E-03 mg/l) and sediment 2.00E-03 to 5.60E+01 mg/kg) samples were below the (WHO, 2004) [24] standard values of 0.01 mg/l and 6 mg/kg respectively for the survival of aquatic organism.

Nickel was detected in all the water and sediment samples. Long term exposure can cause decreased body weight, heart and liver damage and skin irritation. A comparison of Ni concentration in the water (6.00E-02 mg/l) and sediment (2.26E-01 to 2.74E+01 mg/kg) samples with WHO (2004) guideline values of 0.02 mg/l and 20 mg/kg respectively and USEPA (1987) maximum concentration level of 0.1 mg/l for water showed that the concentration of Ni in the study area was low [18,24]. However, nickel limit levels were not exceeded and the study area could probably not be contaminated with nickel.

Manganese is an essential element that is a functional component in nitrate assimilation and is used as a catalyst in many enzymatic systems in both plants and animals. Manganese is readily oxidizable and settles out of the water column as MnO [26,33]. The levels of manganese in the analyzed water (5.00E-02 to 5.70E-02 mg/l) and sediment (3.55E+01 to 7.50E+02 mg/kg) samples showed that the limiting values of USEPA, (1987) of 0.1 mg/l and 300 mg/kg respectively were not exceeded, indicating a possible free aquatic environment that may not pose hazard to the aquatic biota.

Arsenic is a highly toxic metalloid element [34,35]. It is widely distributed as a trace element in rocks and soils and is mainly mobilized by microbial activities [36]. The levels of arsenic in the analyzed water (1.00E-04 mg/l) and sediment 5.00E-02 to 1.34E+01 mg/kg) samples showed that the limit values of WHO (2004) [24] of 0.10 mg/l and 27 mg/kg respectively were not exceeded, indicating probably a contamination free environment. The presence of arsenic in the study area might

be attributed to anthropogenic discharge of wastewater from industrial processes from the source of the Komadugu River.

Chromium concentration was generally very high in all the water and sediment samples from the ten sampling points analyzed. Chromium is a relatively scarce metal that occurs in several states. The most toxic of these states is the chromium VI or hexavalent state. According to WHO, (2004); USEPA, (1987) guideline value, the concentration values of 0.1 mg/l (water) and 25 mg/kg (sediment) Cr is acceptable [14]. With values above 0.1 mg/l and 25 mg/kg, a condition known as allergic dermati could result [23]. From the result of these analyses, the concentrations of chromium in water (6.00E-03 mg/l) and sediment (6.00E-03 to 1.36E+02 mg/kg) samples did not exceed the regulating limits, with the exception of point S4 with a value of 6.73E+02 mg/kg which was higher than the WHO (2004); USEPA (1987) guideline value of 25 mg/kg, indicating pollution of the study area by chromium.

Conclusion

The study shows all the Heavy metals (Pb, Fe, Cu, Zn, Cd, Ni, Mn, As and Cr) were detected in both the water and sediment samples. Fe appeared to be the most predominant metal in all the sampling points, while Pb shows the lowest concentration. The results further indicate that, the concentrations of all the heavy metals were significantly higher in the sediment samples when compared with the water samples.

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