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Assessment of Physicochemical Parameters and Heavy Metal Speciation Study of Water and Bottom Sediments From River Jibam in Chip District of Pankshin Local Government Area, Plateau State, Nigeria

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Abstract: *The physicochemical parameters and heavy metal species of Water and bottom sediment samples from river Jibam in Chip district of Pankshin L.G.A. were investigated in the dry and wet seasons. The analysis was done using standard procedures. The result for the physical parameters revealed the following ranges of values, 6.61 – 7.57 for pH, 24.5 – 24.7 ^{0}C for temperature, 0.97 – 29.4 NTU for turbidity, 60 – 150 uS/cm for electrical conductivity, 26.3 – 166.5 mg/l for total solids, 17.5 – 18.3 mg/l for dissolved solids, 8.0 – 149.0 mg/l for suspended solids, and 5.0 – 6.4 HZ for colour. The chemical parameters revealed 50.1 – 123.89 mg/l for total hardness, 0.002 – 0.004 mg/l for sulphate, 0.06 – 0.08 mg/l for phosphate, 0.00 – 0.002 mg/l for nitrate. 11.17 – 19.17 mg/l for total acidity, 37.35 – 78.5 mg/l for total alkalinity, 16.05 – 16.38 mg/l for chloride, 0.03 - 0.03 mg/l for copper, 0.00 – 0.12 mg/l for lead, 0.02 - 0.03 mg/l for manganese, 0.02 – 0.11 mg/l for cadmium, 0.00 – 0.03 mg/l for nickel but zinc was not detected within the limits used. The total metal concentration of metals analysed (Cu, Pb, Mn, Cd, Zn, and Ni) in the sediments revealed a generally higher concentration in the wet season except for cadmium which revealed a higher concentration in the dry season. Speciation of the metals was also carried out on the sediments using Tessier et al., 1979 method to determine their distribution in the sediment of the river. The percentage ranges of the fractions for the dry season are, 8.58 – 31.93%, 6.39 – 20.50%, 7.61 – 34.78%, 5.39 – 21.97%, and 21.90 – 33.04% for exchangeable , Fe-Mn oxide, organic, carbonate and residual fractions respectively. Ni was not detected in all the fractions. The range of fractions for the wet season are, 11.87 – 22.83%, 8.92 – 32.67%, 5.68- 21.78%, 18.62 – 32.18%, and 18.66 – 33.59% for exchangeable, Fe-Mn oxide, organic, carbonate and residual fractions respectively. Ni was not detected in the first two fractions. With change in the environmental conditions Cadmium and lead bound to such labile phases in both the dry and wet season, can easily remobilize in the water system*

Keywords: *speciation studies, physico - chemical parameters,bioavailability, metals, sediments, river jibam,*

I. Introduction

The earth is very special among other planets because of the presence of water in abundance, which among other factors is primarily responsible for the existence of life.[1, 2]. Also its availability has been responsible for the pattern of human settlements in history [3]. Water quality is a major prerequisite governing the health of human beings, animals as well as plants. [4].Water quality is the physical, chemical and biological characteristics of water. It depends on both natural processes, such as precipitation, erosion, weathering of crystal materials and anthropogenic processes like urbanization, manufacturing, mining and agricultural activities [5, 6].The different sources of water around the world are increasingly been polluted. This occurs in both rural and urban areas. In most rural communities, the major source of drinking water is rivers and streams. The pollutants are mostly organic substances from upstream users who may also use water for some agricultural and industry related activities and natural deposits (geochemical components). These can be described as nonpoint source pollutants [7, 8]. Polluted drinking water causes many diseases such as diarrhoea, vomiting, gastroenteritis, dysentery, kidney problems, typhoid etc [9] Important physical and chemical parameters affecting the aquatic environment are temperature, rainfall, pH, salinity, dissolved oxygen, carbon dioxide, total suspended and dissolved solids, total alkalinity and acidity, and heavy metal contaminants.[10]

Heavy metals among other indicators of water pollution has remained a major source of concern to researchers.[4, 8, 11]. This is because they have assumed a perilous dimension to mankind. Heavy metals are persistent in nature, toxic , and have a very high tendency to accumulate in living organisms and adsorbed on sediment particles.[12, 13]. So many researchers [8, 14, 15,16] have reported that Sediments are important sinks for pollutants, particularly, heavy metals and they play a significant role in re-mobilization of contaminants in aquatic systems when certain conditions prevail. Therefore it is very appropriate to study it, to know its level of contamination with metals and to determine its interaction with the water body. The determination of total metal concentration of metals in sediments is often grossly insufficient to providing proper information regarding their bioavailability, mobility, toxicity and reactivity [15] Hence, the need to use speciation analysis (sequential extraction), to investigate their geochemical composition and distribution in the sediments. [17, 18] whereby, components loosely held in the soil are extracted first, followed by those that are more tightly bonded.ie the sequential solubilisation of the various layers that make up the sediments. [19]. It has the following advantages over the determination of total metal concentration as it tells the source of metal, weather natural (lithogenic) or anthropogenic [16], its toxicity to living organism (biota) and a superior knowledge of metal-sediment interaction.[20] The aim of the present research is to study the status of the physicochemical parameter and heavy metal speciation of river jibam. The results obtained from this study will provide information on the level of concentration of heavy metals in water and sediment, contributing to the effective monitoring of environmental quality and ecosystem health.

II. Materials and Methods

2.1 Study Area

Mhiship community or Chip community is comprised of people whose tribe is called Mhiship or Chip. It is located around the hills in southern part of Pankshin local government area of Plateau state. it is located between kilometers 50 and 58 along Panyam – Shendam road. They are surrounded by hills and mountains in the north, which has the local government council secretariat/headquarters and plain land that leads to Shendam and Quan-Pan local government areas in the south. [21] The main occupation of the inhabitants is farming and tapping of palm wine. The major sources of water in Chip are the rivers with a very few boreholes. The sources of water identified for this project work is river Jibam. The source of water is under consistent attack by human and animal activities such as washing, bathing, excreting, urinating, agricultural activities, cattle rearing and herdsmen activities .The length of river under investigation is at its youthful stage, near its watershed where the river takes its own source. It is V-shaped, has steep sides and gradient fast moving during the rainy season.

The Map, Topography and Pictures of the sample site is shown below.

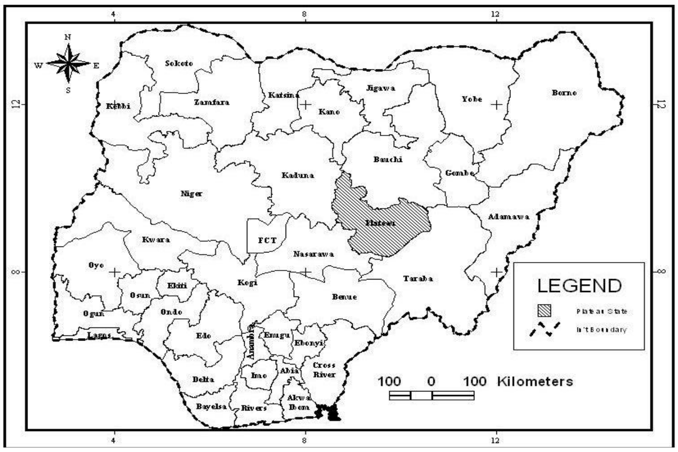

Fig 1. Map of Nigeria showing Plateau State

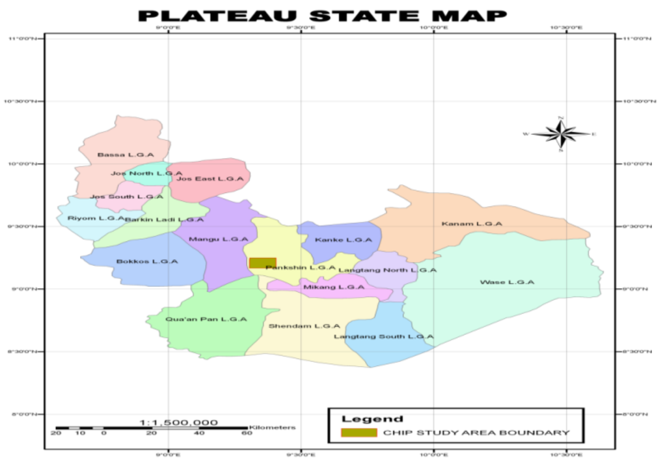

Fig 2. Map of Plateau State showing Pankshin L.G.A.

Fig 3: River Jibam in the dry season

Fig 4 : River Jibam in the wet season

2.2 Sample Collection

2.2.1Water Sample Collection

The sample containers (2 litre plastic containers with a screw cap) were washed with detergent, leached with concentrated $HNO_{3,}$ rinsed with distilled water until acid free and finally with the water sources. And were labelled appropriately. Grap samples of water were collected from four different locations singly (at about 500 meters) along the rivers into the prepared containers manually. This was done in January, Febuary and March for the dry season and June, July and August for the wet season. The samples were collected and the temperature and pH were measured at the sampling site using standard mercury thermometer and pocket pH meter and then preserved at 4^0C prior further analysis. For heavy metal determination, some were preserved by adding a few drops of Hydrogen Trioxonitrate (vi) acid at the point of collection. [11, 22]

2.2.2 Sediment Sample Collection and Treatment

Sediments samples were collected alongside the water samples using a stainless steel scoop into a polyethylene bags previously soaked with dilute nitric acid for 24 hrs, rinsed with distilled water and dried. The grab samples of surface sediments were taken at a depth of 0-5 cm for the various months for the dry and wet seasons [23]. These samples were then transported to postgraduate chemistry laboratory and air dried for about two weeks at room temperature and grinded with mortar and pestle. The ground soil samples were sieved using 0.2mm sieve size and kept in a poly ethylene bottle for further analysis.

2.3 Experimental

Water samples were tested for different physicochemical parameters. Temperature was measured with glass mercury thermometer, conductivity was measured using Hanna Potable conductivity meter, turbidity was determined by absorbance method, pH was measured using a digital pH metre and total solids, dissolved solids and suspended solids was measured using gravimetric methods. Colour was determined using Lovibond comparator. Total hardness, total acidity, total alkalinity and chloride were determined by titrimetric method. Sulphate, nitrate and phosphate were determined using absorbance method. Metallic elements were analysed using Atomic Absorbtion Spectrophotometric method. [11] The determination of total metal in the sediment sample was done using aqua regia. The sequential method was used to determine the speciation of the metals studied in the sediments [24]. The five sequential procedure was used [25], which were:

1. Exchangeable Fraction: A 1.00g triplicate dried sieved soil sample from each dumpsite was shaken with 20ml of 1M $MgCl_2$ at pH 7 for 1hr, filtered and analysed.
2. Carbonate Fraction: the residue of the soil sample from fraction 1 was shaken with 20ml CH_3COONa at room temperature for 5hrs at pH 5, then filtered and analysed.
3. Fe-Mn Oxide/Reducible Fraction: The residue of soil sample from fraction 2 was digested with a mixture of 10ml 0.04M $NH_2OH.HCl$ and 10ml of 25% CH_3COOH at 96 ^{0}C for 6hrs, then filtered and analysed.
4. Organic Fraction: The residue of soil sample from fraction 3 was transferred into 250ml beaker and 9ml of 0.02M HNO_3 and 15ml of 30% H_2O_2 were added, the mixture was heated for 5hrs at 85 ^{0}C on a water bath after 2hrs of heating, another 15ml of 30% H_2O_2 was added. This was then filtered and analysed.
5. Residual Fraction: The residue of soil sample from fraction 4 was digested with aqua regia (7.5ml of 37% HCl and 2.5ml of HNO_3) at 85 ^{o}C for 1hr and then filtered and analysed.

III. Result and Discussion

Table 1: Physical Parameters of the water samples from River Jibam

Parameters	Dry season	Wet season	WHO	SON
Temperature (^{0}C)	24.7 ± 0.33	24.5 ± 0.61	25	25
Turbidity (NTU)	0.97 ± 0.03	29.4 ± 2.2	5	5
pH	6.61 ± 0.28	7.57 ± 0.23	6.5-8.5	6.5-8.5
Conductivity (uS/cm)	150 ± 1.32	60 ± 2.90	500	1000
Total solids (mg/l)	26.3 ± 1.95	166.5 ± 3.72		
Dissolved solids (mg/l)	18.3 ± 0.55	17.5 ± 0.5	1200	500
Suspended solids (mg/l)	8.0 ± 1.4	149 ± 4.0		
Colour (Hz)	5.0	6.4	15	

Table 2 The chemical parameters of the water samples from River Jibam.

Parameters(Mg/l)	Dry season	Wet season	WHO	SON
Total hardness	123.89 ± 6.60	50.1 ± 9.17	500	100
Sulphate	0.002 ± 0.0011	0.004 ± 0.001	250	
Phosphate	0.06 ± 0.01	0.08 ± 0.01	5	
Nitrate	BDL	0.002 ± 0.001	50	
Total Acidity	19.17 ± 1.33	11.17 ± 0.76	200	
Total Alkalinity	78.5 ± 8.05	37.35 ± 8.14	100-500	
Chloride	16.38 ± 0.85	16.05 ± 0.57	250	100
Copper	0.03 ± 0.01	0.03 ± 0.02	1.3	1.3
Lead	BDL	0.12 ± 0.01	0.01	0.01
Manganese	0.03 ± 0.01	0.02 ± 0.01	0.1	0.05
Zinc	BDL	BDL	0.1	5.0
Cadmium	0.11 ± 0.02	0.02 ± 0.01	0.01	0.003
Nickel	BDL	0.03 ±0.01	0.07	0.02

BDL =Below detection limits.

Table 3 Total Metal Concentration (MgKg^{-1}) of the Sediments from River Jibam

Sample	Cu	Pb	Mn	Zn	Cd	Ni
Dry season	0.03± 0.01	0.01 ± 0.001	0.56 ± 0.01	3.03 ± 0.40	0.07 ± 0.02	0.05 ± 0.01
Wet season	0.12 ± 0.02	0.22 ± 0.03	1.40 ± 0.32	3.46± 0.30	0.05 ± 0.01	0.12 ± 0.03

Table 4. Concentration (MgKg^{-1}) of Sequential Fraction of Metals in sediment of RJ_D

Fraction	Cu	Pb	Mn	Zn	Cd	Ni
Exchangeable	0.03 ± 0.01	0.01 ± 0.01	0.33 ± 0.10	0.36 ± 0.12	0.09 ± 0.01	BDL
Carbonate	0.02 ± 0.01	0.01± 0.01	0.39 ± 0.20	0.64 ± 0.03	0.02 ± 0.01	BDL
Fe – Mn Oxide	0.01 ± 0.001	0.01 ± 0.01	0.67 ± 0.30	0.90 ± 0.14	0.03 ± 0.01	BDL
Organic	0.02 ± 0.01	0.01 ± 0.01	0.10 ± 0.01	0.88 ± 0.20	0.06 ± 0.02	BDL
Residual	0.03 ± 0.02	0.01± 0.01	0.43 ± 0.01	1.37± 0.40	0.08± 0.01	BDL

BDL = Below detection limits.

Table 4.1 Percent (%) of Metal Sequential Fraction of metals in sediment of RJ_D

Fraction	Cu	Pb	Mn	Zn	Cd	Ni
Exchangeable	26.07	**22.05**	16.97	8.58	**31.93**	BDL
Carbonate	15.22	17.97	20.50	15.47	6.39	BDL
Fe – Mn Oxide	7.61	20.58	**34.78**	21.73	12.05	BDL
Organic fraction	20.65	17.97	5.39	21.17	21.97	BDL
Residual	**30.45**	21.90	22.36	**33.04**	27.67	BDL

Table 5 Concentration ($MgKg^{-1}$) of sequential fraction of metals in sediment of RJ_W

Fraction	Cu	Pb	Mn	Zn	Cd	Ni
Exchangeable	0.03 ± 0.01	0.22 ± 0.10	0.22 ± 0.01	1.68 ± 0.30	0.05 ± 0.03	BDL
Carbonate	0.02± 0.01	0.18 ± 0.01	0.33 ± 0.03	1.62 ± 0.40	0.03± 0.01	BDL
Fe – Mn Oxide	0.05 ± 0.02	0.21 ± 0.01	0.06 ± 0.01	1.45± 0.20	0.04 ± 0.02	0.01 ± 0.001
Organic fraction	0.07 ± 0.03	0.18 ± 0.001	0.27 ± 0.02	4.05 ± 1.72	0.06 ± 0.02	0.03 ± 0.01
Residual	0.06 ± 0.02	0.18 ± 0.01	0.35± 0.04	4.01 ± 1.03	0.06± 0.01	0.04 ± 0.01

BDL = Below detection limits.

Table 5.1 Percent (%) of metal sequential fraction of metals in sediment of RJ_W

Fraction	Cu	Pb	Mn	Zn	Cd	Ni
Exchangeable	11.87	**22.83**	20.83	13.09	19.32	BDL
Carbonate	8.92	18.66	**32.67**	12.67	14.28	BDL
Fe – Mn Oxide	21.78	21.24	5.68	11.35	15.13	12.15
Organic fraction	**32.18**	18.62	25.98	**31.59**	**26.89**	37.5
Residual	25.25	18.66	33.59	31.30	24.37	**50**

BDL = Below detection limits.

The result for the physical and chemical analysis of water samples from river Jibam is shown in table 1 and 2. In table 1, the mean temperature for the river for the dry season (24.7^{0}C) and wet seasons (24.5^{o}C) are virtually the same but slightly lower in the wet season. pH for the river is slightly acidic in the dry season (6.61) and slightly alkaline in the wet season(7.57). All were within the WHO limits [26]. The acidic nature of the water may be attributed to organic acids from decaying vegetation and the alkaline nature to the presence of carbonates and bicarbonates ion [27]. Value for turbidity was very low (0.97 NTU) and within the WHO limits in the dry season and high in the wet season (29.4 NTU) which is above the WHO limits. Electrical conductivity for the river is higher in the dry season (150b uS/cm) and lower in the wet season (60 uS/cm). The values for total solids and suspended solids were higher in the wet season and lower in the dry season while dissolved solids was higher in the dry season with 18.3 mg/l and lower in the wet season with 17.5 mg/l. The values for total hardness, total acidity and total alkalinity were all within the WHO limits for drinking water and higher values in all cases were observed in the dry season. The concentrations of sulphates and phosphates recorded higher values in the wet season and all were within the WHO limits for drinking water. A low value for Nitrate, 0.002 mg/l, was detected in the wet season, this can be attributed to runoffs from the surrounding, while it was not detected in the dry season. The mean concentration of chloride was 16.38 mg/l in the dry season and 16.05 mg/l in the wet season. The mean concentration of Lead in the water samples for the wet season is 0.12 mg/l which is higher than the WHO limits for drinking water but it was not detected in the wet season. Nickel as well was not detected in the dry season, but 0.03 mg/l was recorded in the wet season . Zinc was not detected in both the wet and dry season. Cadmium was 0.11 mg/l in the dry season and 0.02 mg/l in the wet season which were higher than WHO limits for drinking water. Manganese is higher in the dry season with 0.03 mg/l and 0.02 mg/l in the wet season and all the values are above the WHO limits for drinking water. The correlation coefficient of -0.1286 indicates that there exists a very weak negative correlation in metal concentration of water samples between dry and wet seasons in River Jibam. The critical value of t at 5% significant level with 10 degrees of freedom is 2.228. Hence, comparing the calculated (-0.4270) value with the critical value, the null hypothesis is accepted and it is concluded that there exist no significant variation in the total metal concentration of the water samples between dry and wet seasons of River Jibam.

The result for total metal concentration of the sediments in Table 3 revealed a higher concentration of copper (0.12mg/kg), lead(0.22mg/kg), manganese(1.40mg/kg), zinc(3.46mg/kg) and nickel (0.12mg/kg) in the wet season while cadmium revealed a higher concentration in the dry season with 0.07mg/kg. However, the trace metal analysed in the sediments of the rivers in the wet and dry seasons were within the guideline for sediment quality. The correlation coefficient of 0.4857 indicates that there exists a moderate positive correlation in total metal concentration of the sediments between dry and wet seasons of River Jibam. The critical value of t at 5% significant level with 10 degrees of freedom is 2.228. Hence, comparing the calculated value (-0.3815) with the critical value, the null hypothesis is accepted and it is concluded that there exist no significant variation in the total metal concentration of the water samples between dry and wet seasons of River Jibam. Correlation and t-test analysis of total metal concentration of water and sediment was also carried out. For the dry season, the Correlation value of 0.1857 reveal a very weak positive correlation in total metal concentration between water and sediment. The critical value of t at 5% significant level with 10 degrees of freedom is 2.228. Hence, comparing the calculated value (-1.2027) with the critical value, the null hypothesis is accepted and it is concluded that there exist no significant variation in the water and sediments. For the wet season, the Correlation value of -0.1857 reveal a very weak negative correlation in total metal concentration between water and sediment. The critical value of t at 5% significant level with 10 degrees of freedom is 2.228. Hence, comparing the calculated value(-1.5924) with the critical value, the null hypothesis is accepted and it is concluded that there exist no significant variation in the water and sediments.

The speciation pattern for copper (shown in Fig 5) for River Jibam in the wet and dry season indicate the highest percentage of copper in the residual (0.03 ± 0.02 Mg/Kg) and the organic fractions (0.07 ± 0.03 Mg/Kg) in the dry and wet seasons respectively. This indicates that copper is not bioavailable in the river being investigated.The speciation pattern for lead (shown in Fig 6) in the sediments of River Jibam indicates the highest percentage of lead in the exchangeable fraction in both the dry and wet season with 0.01 ± 0.01 Mg/Kg and 0.22 ± 0.10 Mg/Kg respectively. Although, the other fractions were considerably high.This indicates that lead will be released easily to the water layers, hence more bio-available to living organism in the study area.

The speciation pattern for manganese (shown in Fig 7) in River Jibam for the dry season indicates an occurrence of the highest concentration of manganese in the Fe-Mn Oxide fraction (0.67 ± 0.30 Mg/Kg) and the least in the organic Fraction (0.10 ± 0.01 Mg/Kg). In the wet season the highest percentage of manganese occurred in the carbonate fraction (0.33 ± 0.03 Mg/Kg) and the least in the Fe- Mn Oxide (0.06 ± 0.01 Mg/Kg)

The speciation pattern for zinc (shown in Fig 8) in River Jibam indicates an occurrence of the highest percentage of zinc in the dry and wet season in the residual fraction (1.37 ± 0.40 Mg/Kg) and organic fraction (4.05 ± 1.72 Mg/Kg) respectively. This means that zinc will not be released easily into the water layers when environmental conditions change. This may suggest why zinc was below the detection limits in the water samples analysed from the river in both season. In the speciation pattern for cadmium (shown in Fig 9) in River Jibam indicates an occurrence of the highest percentage of cadmium in dry and wet seasons in the exchangeable fraction (0.09 ± 0.01 Mg/Kg) and organic fraction (0.06 ± 0.02 Mg/Kg) respectively. This study shows that the percentage of cadmium in the exchangeable fraction in River Jibam in the dry season is labile, highly toxic and the most bioavailable. In the wet season a contrary situation is obtained. The speciation pattern of nickel in the sediments of River Jibam (shown in Fig 10) reveal that nickel was not detected in any of the fractions in the dry season but in the wet season the highest percentage of Ni was obtained in the residual fraction (0.04 ± 0.01 g/Kg). This indicates that Ni is not bioavailable or cannot be mobilised. This may suggest the results obtained for Ni in the water samples from the same river**,** where it was below the detection limit Figures 5, 6, 7, 8,9 and 10 show the speciation pattern of Cu, Pb, Mn, Zn, Cd and Ni respectively in the dry and wet season of the study period presented as percentage fraction of metal species.

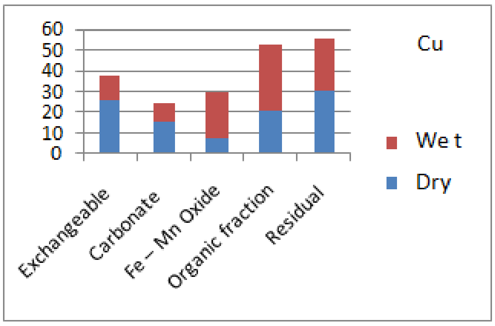

Fig 5

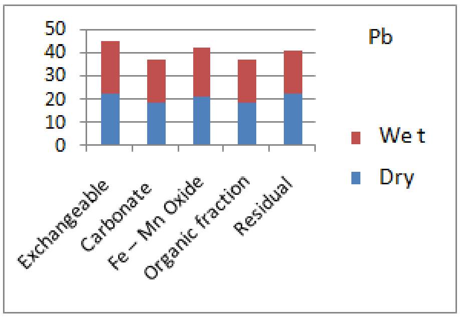

Fig 6

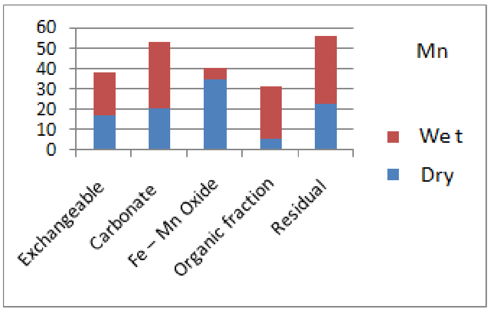

Fig 7

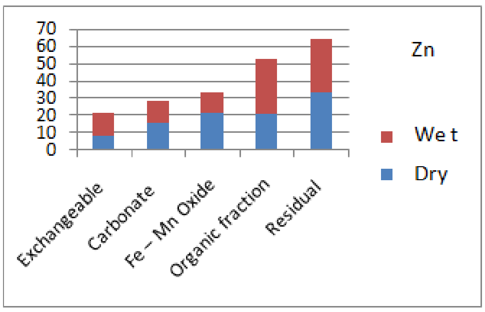

Fig 8

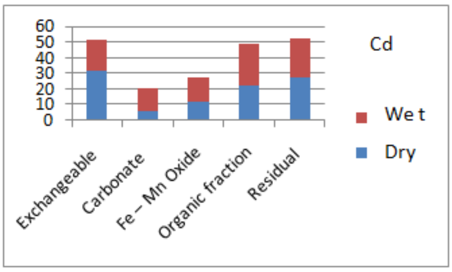

Fig 9

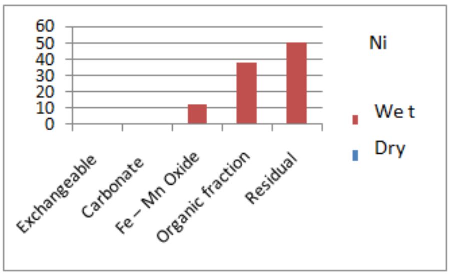

Fig 10

4. Statistical Analysis.

The results obtained for heavy metals in the water and sediments in tables 1 and 2, were subjected to statistical analysis such as correlation coefficient and t-test. The Spearman's rank correlation coefficient was employed to determine the correlation. The formula is given as $\rho = 1 - \frac{6\sum d^2}{n(n^2-1)}$, ..(1). where **d** is the difference between the ranks and **n** is the sample size. The t statistics was computed by $= \frac{\bar{x}_1 - \bar{x}_2}{s_p\sqrt{\left(\frac{1}{n_1}+\frac{1}{n_2}\right)}}$ .. (2) .where $\bar{x}_1$ and $\bar{x}_2$ represents the means of RJ_D and RJ_W respectively. Also, s_p represents the pool variance of RJ_D and RJ_W as well as n_1 and n_2 representing the sample sizes of RJ_D and RJ_W. The formula for the pool variance is given by

$$s_p = \sqrt{\left(\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2-2}\right)} \quad ....(3)$$

The data were firstly resolve or decomposed into a single value by adding and subtracting the $\pm$ value to each value of the observations and the analysis is done into two categories. That is, category A is the data obtained by adding $+$ value only, while category B is the data obtained by subtracting the $-$ value only.

IV. Conclusion

The study on river jibam showed quite a variation in the wet and dry season based on the parameters investigated. The water samples obtained in the dry season are generally of higher quality than the wet seasons. Virtually all the parameters analysed fell within the WHO and SON standard for drinking water. However, a higher level of turbidity was observed in the wet season. Cadmium and lead were slightly above the WHO limits for drinking water which may have a devastating effect on the community. The results of speciation study showed that lead was available predominantly in the exchangeable fraction in the wet and dry season and cadmium was available largely in exchangeable fraction only in the dry season, indicating anthropogenic origin. Therefore, when environmental conditions change Cadmium and lead bound to such labile phases can easily remobilize in the water system. While other elements exist mostly in fractions that are not easily mobilized or boiavailable in the river in the wet and dry season.

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Appendix

Table 6: Analysis of category A of Total metal concentration of water samples

Parameters	**RJ_D**	**RJ_W**	**Ranks for RJ_D**	**Ranks for RJ_W**	**D**	**d^2**
Copper	0.04	0.05	4.5	5	-1.5	2.25
Lead	0.0	0.13	2	6	-4	16
Manganese	0.04	0.03	4.5	2.5	2	4
Zinc	0.0	0.0	2	1	1	1
Cadmium	0.13	0.03	6	2.5	3.5	12.25
Nickel	0.0	0.04	2	4	-2	4

Table 7: Analysis of category A of Total metal concentration of sediment samples

Sample	**RJ_D**	**RJ_W**	**Ranks for RJ_D**	**Ranks for RJ_W**	**d**	**d^2**
Cu	0.04	0.14	2	2	0	0
Pb	0.011	0.25	1	4	-3	9
Mn	0.57	1.72	5	5	0	0
Zn	3.43	3.76	6	6	0	0
Cd	0.09	0.06	4	1	3	9
Ni	0.06	0.15	3	3	0	0

Table 8: Analysis of category A of total metal concentration of water and sediment samples in the dry season only.

Sample	**Water**	**Sediment**	**Ranks for water**	**Ranks for Sediment**	**d**	**d^2**
Cu × Cu	0.04	0.04	4.5	2	2.5	6.25
Pb×Pb	0.0	0.011	2	1	1	1
Mn×Mn	0.04	0.57	4.5	5	-0.5	0.25
Zn×Zn	0.0	3.43	2	6	-4	16
Cd×Cd	0.13	0.09	6	4	2	4
Ni×Ni	0.0	0.06	2	3	-1	1

Table 9: Analysis of category A of total metal concentration of water and sediment samples in the wet season only.

Sample	**Water**	**Sediment**	**Ranks for water**	**Ranks for sediment**	**d**	**d^2**
Cu × Cu	0.05	0.14	5	2	3	9
Pb×Pb	0.13	0.25	6	4	2	4
Mn×Mn	0.03	1.72	2.5	5	2.5	6.25
Zn×Zn	0.0	3.76	1	6	-5	25
Cd×Cd	0.03	0.06	2.5	1	1.5	2.25
Ni×Ni	0.04	0.15	4	3	1	1