

An Assessment of the Trace Metal Contents of Owan River, Edo State, Nigeria

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ABSTRACT

The trace metal contents of surface water and sediment of Owan River, Edo State, Nigeria were investigated from January to June 2013. Three stations were studied from upstream to downstream using standard methods. The concentration of the heavy metals analyzed in the water differed insignificantly ($p > 0.05$) across the stations. At average, the rank of heavy metal concentrations in the surface water was $Fe > Zn > Mn > Cu > Ni > Cr > Cd > V > Pb$ and their ranges across the stations were Fe (0.210-1.250 mg/l); Mn (0.010-0.150 mg/l); Zn (0.010-0.320 mg/l); Cu (0.010-0.090 mg/l); Cr (0.00-0.020 mg/l); Cd (0.00-0.020 mg/l), Pb (0.00-0.020 mg/l), Ni (0.00-0.020 mg/l) and V (0.00-0.020 mg/l). The concentrations of all the heavy metals analyzed in the sediment differed significantly ($p < 0.05$) across the stations. The rank of the heavy metal concentrations in the sediment was $Fe > Zn > Mn > Cu > Cd > Cr > Pb > Ni > V$ and their ranges across the stations were Fe (211.0-811.90 mg/kg); Mn (9.01-32.30 mg/kg); Zn (9.98-56.80 mg/kg); Cu (5.80-22.30 mg/kg); Cr (0.12-8.08 mg/kg); Cd (1.14-7.16 mg/kg); Pb (1.10-8.11 mg/kg); Ni (0.64-7.24 mg/kg) and V (0.53-6.43 mg/kg). The mean concentrations of Fe and Cd in all sampled stations were higher than NIS standard for drinking water. The concentrations of THC in water and sediments differed significantly ($p < 0.05$) across the stations and ranged from 0.00-0.150 mg/l and 4.67-20.40 mg/kg respectively. Assessment of accumulation pattern of heavy metals in water and sediments using relative accumulation indices (RAI) revealed that the highest and lowest concentrations of heavy metal occurred in stations 1 and 3 respectively. Water Quality Index (WQI) showed that the quality of the water at all the stations was not suitable for drinking.

Keywords: Heavy metals, THC, Owan River, Relative Accumulation Indices (RAI), Water Quality Index (WQI)

1.0 INTRODUCTION

Various human activities on have resulted in unprecedented accumulation of trace/heavy metals in the various matrixes of the ecosystem. Aquatic ecosystem which has been envisaged by many as a universal receptacle (Ezenwa, 2013), is not an exception to this menace. It has accumulated a great concentration of heavy metal for many years. Past studies on aquatic ecosystem (Edema and Egborge, 1999; Omoigberale and Ogbeibu, 2005; Puyate *et al.*, 2007; Omoigberale and Ogbeibu, 2010; Omoigberale and Eweka, 2010; Wogu and Okaka, 2011; Ezenwa, 2013) have revealed high concentrations of heavy metal especially in the water, sediment and biota samples collected at points of intense human activities. This unlawful and unsustainable activities of human is not just detrimental to aquatic organisms or those organisms found at lower trophic level, human beings and other animals at higher trophic level are at great risk because of the processes such as bioavailability, bioamplification and bioaccumulation of these substances (Monica *et al.*, 2009). According to Egborge (1994), heavy metals which are not biodegradable can easily be assimilated and bioaccumulated in the protoplasm of aquatic organisms.

Over the last century, intensified emission of various heavy metals had resulted from human activities such as fossil fuel combustion, agrochemical applications, metallurgical industrial activities and industrial wastes generation (Fitzgerald and Clarkson, 1991; Mason *et al.*, 1994). These activities undoubtedly have altered the natural recycling capability of these elements both in terrestrial and aquatic ecosystem. In aquatic ecosystem, heavy metals exist in colloidal, particulate and dissolved forms (Adepoju-Bello *et al.*, 2009). The occurrence of lead, arsenic, mercury, cadmium, chromium, and nickel in aquatic ecosystem can endanger public health when incorporated into the food chain, or released into overlying waters which serve as drinking water supplies. Heavy metals such as cadmium, nickel, vanadium and lead have been identified to exhibit strong positive correlation with total hydrocarbon - THC (Ogbeibu, 2011). Water quality index (WQI) is a means to recapitulate large amounts of water quality data into simple terms (excellent, good, poor) for reporting to management and the public in a consistent manner (Ashwani, and Anish, 2009). It evaluates the overall quality of water using an established standard and further predicts if water quality poses a potential threat to various uses including habitat for aquatic life, irrigation water for agriculture and livestock, recreation and aesthetics, and drinking water supplies

The aims of this study were to quantify and estimate the spatial variations in the concentrations of selected heavy metals (iron, manganese, zinc, copper, chromium, cadmium, lead, nickel and vanadium) and total hydrocarbons (THC) in water and sediment samples collected from designated stations at Owan River. It further assessed the suitability of the surface water of the river for domestic purposes using water quality index (WQI).

2.0 MATERIALS AND METHODS

2.1 Study Area

The study was conducted along certain stretch of Owan River in Ovia North-East Local Government Area, Edo State (Lat. 6°16'0" N; 6°45'24" N and Long. 5 ° 43' 54"; E5 ° 46' 30" E). The river runs through Okpokhumi, Sabongidda and empties into the River Osse. The region is notable for its intensive cocoa farming and plantain plantation. A vast number of these farms are located along the river bank. These farms are also heavily treated with Agrochemicals to protect and boost the crops yield. A sub-station of the Cocoa Research Institute of Nigeria, where researches to improve cocoa production is carried out is sited near the River. The study area has experienced deforestation over the years and it is assumed to be due to increase in the population size of the settlement around the river. Owan River is the major source of water for domestic purpose within the community; the river serves as a source of water for drinking, cooking, washing, bathing, processing of agro products and swimming. Other human activities include construction and maintenance of

canoe and boats, and transportation. Three sampling stations were chosen almost equidistant apart along the river course (Stations were 1km apart). These stations were established based on ecological settings, vegetation and human activities in the area.

2.2 Sample collection

Monthly sampling of the designated stations along the stretch of Owan River was carried out from January to June, 2013. The water samples were collected in acid washed polyethylene bottles. The water samples were acidified with 2 ml of concentrated nitric acid and placed in ice box in order to keep the required species of cations in soluble form, and slow down or stops biological changes. The acid pre-treatment ensured that heavy metals did not get adsorbed to the surface of the container during transportation and storage.

The sediment samples were collected by scooping with light dredge (0.30cm deep) from the points where the water samples were taken, at different sampling stations. The sediment samples were stored in polyethylene bags and labeled properly. Immediately after, the samples were taken to the laboratory for analysis.

The water and sediment samples were analyzed for selected heavy metals concentrations using standard methods (APHA, 1998; Radajevic and Bashkin, 1999; Onyeonwu 2000). Heavy or trace metals were determined after digestion using Unicam 929 Atomic Absorption Spectrometry. Total hydrocarbon content of the sediment was determined using method adopted from American Standard tests and method (ASTM, 1996).

2.3 Relative accumulation indices (RAI)

Relative accumulation indices was calculated using the method describe by Samir and Ibrahim, (2008).

$$\text{Relative accumulation indices (RAI)} = \frac{\text{Concentration of Heavy Metal in Sediment}}{\text{Concentrations of Heavy Metal in Water}}$$

2.4 Water Quality Index

Water quality index (WQI) was calculated using the Weighted Arithmetic Index method as described by (Cude, 2001).

$$Q_i = \{[(V_{\text{actual}} - V_{\text{ideal}}) / (V_{\text{standard}} - V_{\text{ideal}})] * 100\}$$

- Q_i = Quality rating of ith parameter for a total of n water quality parameters
- V_{actual} = Actual value of the water quality parameter obtained from laboratory analysis
- V_{ideal} = Ideal value of that water quality parameter can be obtained from the standard Tables. V_{ideal} for pH = 7 and for other parameters it is equalling to zero, but for DO $V_{\text{ideal}} = 14.6 \text{ mg/L}$
- V_{standard} = Nigerian Industrial Standard – NIS (2007). Nigerian Standard for Drinking Water Quality

Then, after calculating the quality rating scale (Q_i), the Relative (unit) weight (W_i) was calculated by a value inversely proportional to the recommended standard (S_i) for the corresponding parameter using the following expression;

- $W_i = 1 / S_i$

Where,

- W_i = Relative (unit) weight for nth parameter
- S_i = Standard permissible value for nth parameter
- 1 = Proportionality constant.

Finally, the overall WQI was calculated by aggregating the quality rating with the unit weight linearly by using the following equation:

- $WQI = \frac{\sum W_i Q_i}{\sum W_i}$

Where,

- Q_i = Quality rating
- W_i = Relative weight

Table 1: Grades Water Quality Index (WQI) and status of water quality (Ramakrishniah *et al.*, 2009)

Water Quality Index Levels	Description
< 50	Excellent
50 – 100	Good
100 – 200	Poor
200 – 300	Very poor (bad) water
> 300	Unsuitable (unfit)for drinking

Data Analysis: Results were presented as mean \pm standard deviation. One way analysis of Variance (ANOVA) with Duncan Multiple Range (DMR) post hoc and Pearson's correlation analysis were used for the statistical analyses of results obtained at 95% confidence level using the computer application SPSS 16.0 and Microsoft Excel - 2007 for window.

3.0 RESULTS

The trace metal contents of water and sediment of the studied river are presented in Tables 2 and 3, respectively. The concentrations of total hydrocarbon in water samples obtained at station 1 were significantly higher ($p < 0.05$) than those recorded at stations 2 and 3. The rank of the average heavy metal concentrations were ranked as followed $Fe > Zn > Mn > Cu > Ni > Cr > Cd > V > Pb$. The highest concentration of the individual parameters was recorded at station 1, the lowest concentration varied between stations 2 and 3. The range of the heavy metals in the water occurred as follows: Fe (0.210-1.250 mg/l); Mn (0.010-0.150 mg/l); Zn (0.010-0.320 mg/l); Cu (0.010-0.090 mg/l); Cr (0.000-0.020 mg/l); Cd (0.000-0.020 mg/l), Pb (0.000-0.020 mg/l), Ni (0.000-0.020 mg/l), V (0.000-0.020 mg/l) and THC (0.000-0.150 mg/l). The concentrations of the individual heavy metals showed no significant difference ($p > 0.05$) across the stations when the values were subjected to one way ANOVA. The coefficient of variation (C.V.) indicated that the highest and lowest variations among the parameters were recorded in the Pb and THC respectively.

Table 3 shows the variations in concentrations heavy metals and total hydrocarbon in sediment samples obtained across the stations. The rank of the heavy metal concentrations in the sediments showed thus: $Fe > Zn > Mn > Cu > Cd > Cr > Pb > Ni > V$. The range of the heavy metals and THC in the sediments occurred as follows: Fe (211.00-811.90 mg/kg); Mn (9.01-32.30 mg/kg); Zn (9.98-56.80 mg/kg); Cu (5.80-22.30 mg/kg); Cr (0.12-8.08 mg/kg); Cd (1.14-7.16 mg/kg); Pb (1.10-8.11 mg/kg); Ni (0.64-7.24 mg/kg); V (0.53-6.43 mg/kg); THC (4.67-20.40 mg/kg). The concentrations of the individual parameters varied significantly ($p < 0.05$) across the stations and Duncan multiple range test revealed that the concentrations of all the parameters were significantly higher ($p < 0.05$) station 1 than stations 2 and 3. The coefficient of variation (C.V.) or relative variability of the heavy metals in the sediment was in the order $Fe = Mn < Zn < Cu < Cd < Cr < Ni < Pb < V$.

3.1 Relative Accumulation Indices (RAI)

The calculated relative accumulation indices showed that Fe was accumulated in sediment at high concentration levels across the stations. Among the heavy metals analysed Ni was the least accumulated at stations 1 and 2 while at station 3, Cr was the least accumulated. As total heavy metals, the accumulation in sediment relative to water was estimated to be 4263.04, 3325.60 and 2960.05 times in stations 1, 2 and 3 respectively.

3.2 Water Quality Index

Table 5 shows the summary of the computation for the WQI. The WQI values at stations 1, 2 and 3 were 248.83, 100.80 and 173.73 respectively. Across the stations, cadmium, lead and nickel made the most contribution towards the computed values of WQI.

4.0 DISCUSSION

The water quality of a river at any point reflects several major influences, including the lithology of the basin, atmospheric inputs, climatic conditions and anthropogenic inputs (Bricker and Jones, 1995; Shrestha and Kazama, 2007). In this study, sediments accumulated more of heavy metals than the water. Sediment has been known to be the major depository of metals holding more than 99% of total amount of a metal present in the aquatic system (Demirak *et al.*, 2009, Ozturk *et al.*, 2009; Aderinola *et al.*, 2009). According to Edward *et al.*, (2013) this phenomenon of higher concentration of metals in the sediment than in surface water may also be connected with the fact that pollutants discharged into the aquatic environment does not remain in aqueous phase but instead are adsorbed onto the sediments. Across the stations, the highest concentrations of each of the parameters analysed both in the water and sediment were recorded at station 1. This was possibly as a result of activities witnessed at this station and its proximity to the road among all stations. Other activities witnessed at this station include boat and canoe construction, point of loading of passengers and goods, also the villagers do their washing at this point. All these activities in combined with run-off from the hinterland contributed to high concentration of heavy metals and total hydrocarbon witnessed at this station.

The rank of heavy metals concentration in water was Fe>Zn>Mn>Cu>Ni>Cr>Cd>V>Pb while in the sediment, the order was Fe>Zn>Mn>Cu>Cd>Cr>Pb>Ni>V. The dominance of Fe over other heavy metals in aquatic ecosystem had been reported by Chukwujindu *et al.*, (2007); Puyate *et al.*, (2007); Oribhabor and Ogbeibu (2009); Wogu and Okaka (2011). Spatially, the concentrations of all parameters analyzed in the water except THC showed no significant difference despite the high values of coefficient of variation recorded. Thus the intra-station variations across the stations were similar. Within the sediment components, the intra-station variations were dissimilar across the stations hence the state of significant difference recorded in all the parameters analyzed. Across the stations whether within the water column or bottom sediment, the lowest and highest concentrations of the analysed parameters were obtained at stations 3 and 1 respectively. The reduction in the concentrations of the individual parameters downstream of the study station can be attributed to the affinity the sediment exhibit towards adsorption and immobilization of the metal. Furthermore, the auto-purification capacity of the ecosystem plays a role especially towards degradation of THC.

The concentrations of Fe, Mn and Ni recorded in the water were below the values recorded by Wogu and Okaka (2011) in Warri River while the concentrations of Zn, Cu, Cr and Cd especially at station 1 were slightly higher. The concentration of Fe, Zn and Mn recorded in this study were similar to values documented by Enuneku *et al.*, (2013) in different stretch of the Owan river. The concentrations of the

heavy metals order than Zn, Mn and V recorded in the bottom sediment in the course of this study were higher compared to the values obtained by Puyate *et al.*, (2007) at Orogodo River. The concentration of total hydrocarbon (THC) obtained in the water samples among the stations were similar to the values obtained by Oribhabor and Ogbeibu (2009) at Niger Delta mangrove creek. Furthermore, the concentrations of total hydrocarbon analyzed in the sediment samples were lower when compared to the values obtained by Ezekiel *et al.*, (2011) at Sombreiro River. These differences in concentration of heavy metals and total hydrocarbon either in the water or sediment samples analyzed in this study when compared to other studies may be attributed to factors such as lithology of the basin, atmospheric inputs, climatic conditions and anthropogenic inputs.

Atuma and Egborge (1986) and Edema (1993) associated the high concentrations of heavy metals in the aquatic ecosystems with effluents from industries, refuse and sewage. Slightly high concentration of cadmium in the sediment which was observed across all the stations can be linked to lithology of the basin aside the anthropogenic activities which further alleviated the concentration at especially station 1. Aligning with the concept by Oribhabor and Ogbeibu (2009) that THC at concentration < 1 in water as unpolluted, then this system was unpolluted by THC as at the time samples were collected. But on the contrary, since the average concentrations of THC in the water were above the value of 0.05mg/l stipulated by FMEnv – the water was contaminated by THC. Ezekiel *et al.* (2011) attributed the occurrence of THC to anthropogenic activities like transportation and oil spill.

The heavy total metal accumulation in the sediment spatially was in the order station 1 > station 2 > station 3. Thus the source of the heavy metal intrusion within the sampled stretch of Owan River was at station 1 or upstream of it. Water quality Index recorded a pattern that was slight different from RAI; unlike RAI the lowest value of WQI was recorded at station 2. WQI at all the stations was established from the average concentrations of all the heavy metals analyzed in water samples.

5.0 Conclusion

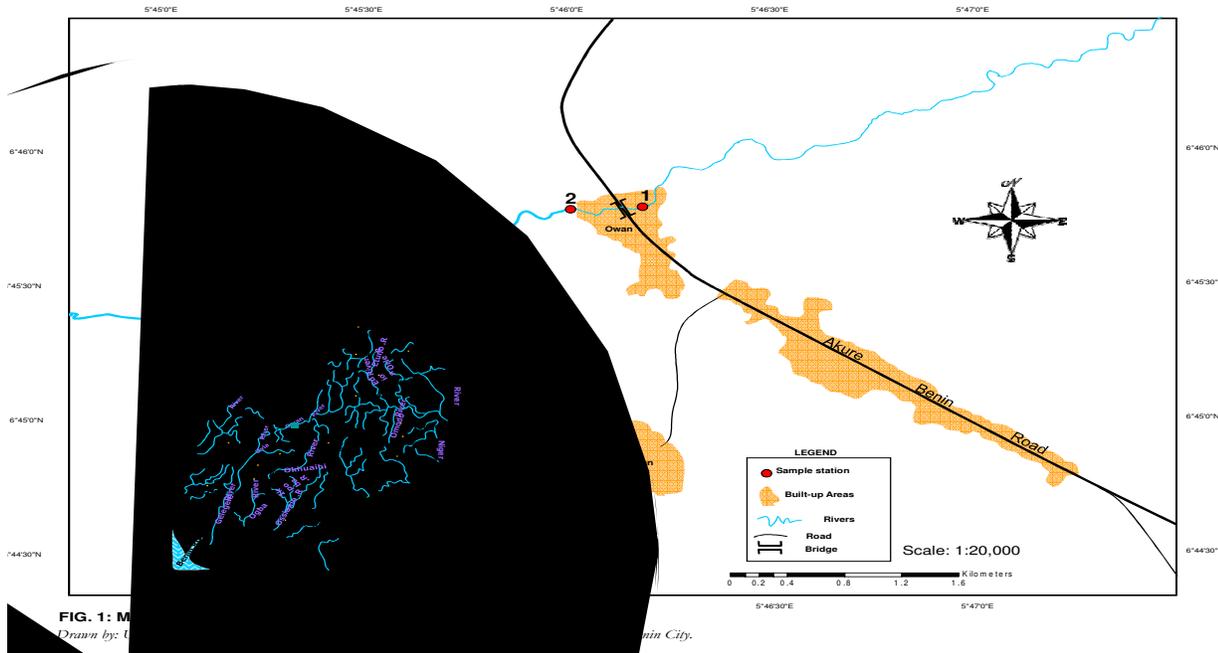
The water quality rating clearly showed that, the status of the water at all stations were not suitable for drinking as the WQI values at these stations were greater than the benchmark of 100.

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Fig

1: Map of the Study Area

Table 2: Summary of the Heavy Metals and Total Hydrocarbon Concentrations in Water Samples obtained from the Three Stations Designated at Owan River

Parameters	Station 1	Station 2	Station 3	C.V.	p-Value	NIS (2007)
	$\bar{x} \pm SD$ (Min-Max)	$\bar{x} \pm SD$ (Min-Max)	$\bar{x} \pm SD$ (Min-Max)			
Iron	0.810 ± 0.125	0.413 ± 0.106	0.523 ± 0.119	0.549	p > 0.05	0.300
	0.500-1.250	0.210-0.810	0.280-1.020			
Manganese	0.047 ± 0.021	0.031 ± 0.012	0.034 ± 0.015	1.053	p > 0.05	0.200
	0.010-0.150	0.010-0.090	0.010-0.110			
Zinc	0.164 ± 0.043	0.095 ± 0.022	0.083 ± 0.037	0.773	p > 0.05	3.00
	0.070-0.320	0.050-0.180	0.010-0.200			
Copper	0.052 ± 0.011	0.034 ± 0.008	0.025 ± 0.006	0.635	p > 0.05	1.000
	0.030-0.090	0.020-0.060	0.010-0.050			
Chromium	0.011 ± 0.003	0.006 ± 0.002	0.008 ± 0.002	0.621	p > 0.05	0.05
	0.000-0.020	0.000-0.010	0.000-0.010			
Cadmium	0.010 ± 0.003	0.004 ± 0.002	0.007 ± 0.005	0.890	p > 0.05	0.003
	0.000-0.020	0.000-0.010	0.000-0.020			
Lead	0.008 ± 0.004	0.003 ± 0.002	0.005 ± 0.002	1.242	p > 0.05	0.01
	0.000-0.020	0.000-0.010	0.000-0.010			
Nickel	0.015 ± 0.005	0.005 ± 0.002	0.009 ± 0.003	0.999	p > 0.05	0.02
	0.000-0.040	0.000-0.010	0.000-0.020			
Vanadium	0.009 ± 0.003	0.005 ± 0.001	0.006 ± 0.003	0.955	p > 0.05	N/A
	0.000-0.020	0.000-0.010	0.000-0.020			
Total Hydrocarbon	0.108 ± 0.010 ^A	0.068 ± 0.007 ^B	0.053 ± 0.015 ^B	0.458	p < 0.05	N/A
	0.080-0.150	0.050-0.090	0.000-0.110			

Note: All the parameters were measured in mg/l; p < 0.05 – Significant difference; p > 0.05 – No significant difference. Similar superscript row-wise - No significant difference.

Table 3: Summary of the Heavy Metals and Total Hydrocarbon Concentrations in Sediment Samples obtained from the Three Stations Designated at Owan River

Parameters	Station 1	Station 2	Station 3	C.V.	p-Value
	$\bar{x}\pm SD$	$\bar{x}\pm SD$	$\bar{x}\pm SD$		
Iron	689.70±40.01 ^A	348.20±38.89 ^B	336.30±51.64 ^B	0.429	p<0.01
	521.40-811.90	254.80-481.30	211.00-564.20		
Manganese	27.57±1.61 ^A	14.22±1.83 ^B	12.55±1.10 ^B	0.429	p<0.01
	21.60-32.30	8.29-19.80	9.01-15.90		
Zinc	46.87±3.15 ^A	24.53±3.98 ^B	24.90±4.95 ^B	0.445	p<0.01
	36.9-56.80	12.30-38.50	9.98-40.20		
Copper	15.79±1.91 ^A	7.94±0.82 ^B	8.01±1.05 ^B	0.462	p<0.01
	9.33-22.30	5.80-10.40	6.16-12.70		
Chromium	4.93±0.84 ^A	1.57±0.24 ^B	1.32±0.299 ^B	0.803	p<0.01
	1.82-8.08	0.92-2.46	0.12-2.30		
Cadmium	5.40±0.53 ^A	1.62±0.20 ^B	2.07±0.39 ^B	0.628	p<0.01
	3.23-7.16	1.14-2.50	1.53-2.48		
Lead	4.95±1.01 ^A	1.39±0.16 ^B	1.59±0.23 ^B	0.826	p<0.01
	1.27-8.11	1.07-2.10	1.10-2.49		
Nickel	3.83±1.00 ^A	1.11±0.13 ^B	2.10±0.60 ^B	0.820	p<0.05
	1.05-7.24	0.64-1.52	0.72-4.88		
Vanadium	3.32±0.90 ^A	0.90±0.90 ^B	1.62±0.39 ^B	0.860	p<0.05
	0.82-6.48	0.53-1.30	0.60-3.32		
Total Hydrocarbon	13.80±1.92 ^A	8.15±0.57 ^B	6.91±0.86 ^B	0.440	p<0.01
	7.60-20.40	6.28-10.20	4.67-9.60		

Note: All the parameters were measured in mg/kg; p<0.01 – Highly significant difference; p<0.05 – Significant difference.

Table 4: Relative Accumulation Indices of Heavy Metals in Sediment of the Owan River

Stations	River Components	Fe	Mn	Zn	Cu	Cr	Cd	Pb	Ni	V	Total
1	Sediment (mg/kg)	689.57	27.57	46.87	15.79	4.93	5.40	4.95	3.83	3.32	
	Water (mg/l)	0.81	0.05	0.16	0.05	0.01	0.01	0.01	0.01	0.01	
	RAI (x times)	847.83	586.52	286.35	305.61	455.38	522.74	645.43	257.98	355.18	4263.04
2	Sediment (mg/kg)	348.20	14.22	24.53	7.94	1.57	1.62	1.39	1.11	0.90	
	Water (mg/l)	0.41	0.03	0.10	0.03	0.01	0.00	0.00	0.01	0.00	
	RAI (x times)	842.42	458.55	257.34	235.84	253.78	388.80	418.00	214.19	256.67	3325.60
3	Sediment (mg/kg)	336.30	12.55	24.90	8.01	1.32	2.07	1.59	2.10	1.62	
	Water (mg/l)	0.52	0.03	0.08	0.02	0.01	0.01	0.00	0.01	0.01	
	RAI (x times)	642.61	374.68	298.16	326.94	171.74	281.59	352.96	241.92	269.44	2960.05

Table 5: Summary of the Water Quality Index (WQI)

Parameters	WiQi		
	Station 1	Station 2	Station 3
Iron	903.70	459.26	581.48
Manganese	117.50	77.50	83.75
Zinc	1.82	1.06	0.93
Copper	5.17	3.37	2.45
Chromium	433.33	246.67	306.67
Cadmium	114814.81	46296.30	81481.48
Lead	7666.67	3333.33	4500.00
Nickel	3708.33	1291.67	2166.67
WQI	248.83	100.80	173.73