

Table 1: Weight and relative weight for determining WQI.

Parameters	SON Standard	w_i	W_i
pH	6.5-8.5 (7.5) ^a	4	0.091
TDS mg/L	500	4	0.091
Cl mg/L	250	3	0.068
F mg/L	1.5	5	0.114
SO ₄ mg/L	100	3	0.068
NO ₃ mg/L	50	5	0.114
Fe mg/L	0.3	3	0.068
Pb mg/L	0.01	5	0.114
Cu mg/L	1	2	0.045
Cd mg/L	0.003	5	0.114
EC μ S/cm	1000	5	0.114
		$\Sigma=44$	$\Sigma=1$

during the rainy season discharges into the Ekulu river. The water of this river is used by nearby residents for washing clothing and cars, bathing, swimming, and cooking. In this study, the Onyeama area constituted a sampling point whereas 4 km downstream Onyeama mine was another sampling point identified as 'Damija'. The third sampling point which is about 1 km downstream Damija is identified as 'The Hotel' (Figure 1).

Figure 1 Map of the study area showing sampling locations, Onyeama mine (waterfall) covering a distance of about 5 km.

Sampling

Samples were collected in triplicates bi-weekly in October, 2017 and February, 2018 to cover both the wet and dry seasons. The sampling locations were selected to include the waterfall zone, Damija zone and The Gate hotel zone. Damija zone is located 2.5 km downstream the waterfall zone and 1.5 km upstream The Gate hotel zone. The water samples were collected into a 1 L HNO₃ pre-washed polyethylene containers. Preservation of the heavy metals in the water samples was achieved by acidifying the samples using 5 mL of 6M HNO₃ prior to transportation to the laboratory for analysis. The sediment and water samples were put into a sampling box filled with ice cubes for maintaining sample temperature below 4 °C and transported to the laboratory for analysis. The study area and sampling locations are as presented in (Figure 1).

Laboratory analysis

Analysis of water samples: The physic-chemistry parameters such as Electrical Conductivity (EC), pH, Total Dissolved Solids (TDS), Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), chloride, sulphate, nitrate, and phosphate were analyzed following APHA (1998) standard procedure [11]. Aliquots of 100 mL were drawn from the collected water samples and filtered using whatman filter paper. The filtrate is collected and analyzed for heavy metals (Cu, Zn, Cr, Pb, Cd) using SensAA GBC Flame Atomic absorption spectrometer.

Water quality index (WQI)

Sahu and Sikdar (2008) procedure of estimating WQI was

adopted in this study:

- Weight (w_i) assignment based on the health effects of the parameters.

Assigned weight is between 1 and 5. The parameters that are of major importance are assigned highest weight whereas those that are of minor importance are assigned low weight. Hence, cadmium, lead, nitrate and fluoride are assigned a weight of 5 each whereas copper and iron are assigned 2 and 3 respectively. See (Table 1) for detailed weights as assigned.

- Relative weight (W_i)

The relative weight (W_i) is computed as follows:

$$W_i = w_i / \sum w_i \dots\dots\dots \text{Eq. 1}$$

Where: w_i is the arbitrarily assigned weight based on the above described criterion.

- Assignment of quality rating scale

$$q_i = (C_i / S_i) \times 100 \dots\dots\dots \text{Eq. 2}$$

q_i = quality rating scale; C_i = concentration in groundwater sample of the parameters

S_i = Standard organization of Nigeria (SON) standard for each chemical parameter.

- Computation of Water quality sub-index (S_i)

The water quality sub-index is computed as follows:

$$SI = W_i \times q_i \dots\dots\dots \text{Eq. 3}$$

- Determination of water quality index (WQI)

$$WQI = \sum SI \dots\dots\dots \text{Eq. 4}$$

The weight and the relative weight of the parameters used in determining the WQI is as presented in (Table 1).

The w_i values are adapted from [12].

Water quality ranking using WQI is based on the following scheme: < 50 implies excellent water; 50-100 implies good water; 100-200 implies poor water; 200-300 implies very poor water; >300 implies water unsuitable for drinking [12].

Results and Discussions

Values of the water quality parameters

(Table 2) presents the values of the water quality parameters.

(Table 2) Concentration of the heavy metals and values of the physico-chemical parameters for the months of October, 2017 and February, 2018

The Electrical Conductivity (EC) in the month of October 2017 varied from 19.4 - 64.1 μ S/cm and increases as we move from the Onyeama section of the river to The Hotel indicating the possibility of human activities taking place between Onyeama and The Hotel releasing substances into the river that dissociate to form ions capable of conducting electricity (Table 2). The TDS and EC values around Damija and The Hotel are higher and significantly different

Table 2: presents the values of the water quality parameters.

Location	Values of Parameters for October 2017										
	pH	EC	TDS	Cl	SO ₄	NO ₃	TOC	Cr	Pb	Cu	Cd
		µS/cm	mg/L								
Onyeama	6.1	19.4	10.1	4.2	3.5	0.4	20	0.002	0.28	0.05	BDL
Damija	6.2	61.6	39.7	12.3	9.3	1.1	30	0.11	1.6	BDL	BDL
Hotel	6.5	64.1	40.8	12.6	9.9	0.9	20	0.38	0.92	0.02	0.01
Values of Parameters for February 2018											
Onyeama	5.7	15.5	8.2	3.1	2	0.35	15	0.01	0.21	0.15	0.008
Damija	6.3	13.3	7.8	2.7	1.8	0.35	25	BDL	0.14	0.014	0.017
Hotel	5.9	15.4	8.3	2.9	1.8	0.2	10	BDL	0.48	0.005	0.005

Table 3: WQI of Ekulu river.

October, 2017 (rainy season)			
Location	WQI	Rank	Major contaminants
Onyeama	372	Unsuitable for drinking	TOC and Pb
Damija	1910	Unsuitable for drinking	TOC and Pb
The Hotel	1198	Unsuitable for drinking	Pb, TOC and Cd
January 2018 (dry season)			
Onyeama	312	Unsuitable for drinking	Pb and Cd
Damija	288	Very poor	Pb and Cd
The Hotel	594	Unsuitable for drinking	Pb and Cd

from those around Onyeama during the rainy season supporting the possibility of anthropogenic input of contaminants around Damija and The Hotel. However, there is no significant difference in the EC and TDS values for all locations indicating that the relative high input of contaminants during the rainy season could be linked to run-off.

The river is mildly more acidic in the dry season than the rainy season as the pH was in the range 5.7-6.3 in the dry season but 6.2-6.5 in the rainy season (Table 2). The result also indicates that the water sample taken around Onyeama is more acidic than those taken from Damija and The Hotel and is most likely to be due to acid mine drainage around Onyeama.

The rainy season concentration of nitrate, chloride and sulphate is higher than the dry season values indicating input from agricultural activities transported by run-off and possible input from run-off draining through indiscriminate waste dumps and transporting chloride and sulphate into the river.

In comparison with the studies carried out in Nyaba and Ekulu river as reported by [13,14], the values of the physico-chemistry parameters of the present study are lower except for pH and EC values which are equivalent.

TOC is higher in wet season than dry season for all the locations and is attributable to run-off carrying minor oil spillages to the river.

The Pb concentration level of the water exceeds that of World Health Organization (WHO) maximum allowable contaminant level (MACL) of 0.01 mg/L for all seasons. The rainy season concentration of Cr in Damija and The Gate Hotel sections of the river exceeds the WHO MACL of 0.05 mg/L. During the rainy season, only the Gate Hotel is contaminated with Cd with concentration level of 0.01 mg/L which is higher than 0.003 mg/L WHO MACL for Cd. The concentration of copper for all the seasons is significantly lower

than the WHO MACL of 2 mg/L. In comparison with other rivers in Nigeria such as River Argungu, the concentration of Pb, Cu, Zn and Cd in Ekulu river is lower but Cr concentration level is higher in Ekulu river [15]. The reported concentration levels of all the studied heavy metals in the water column of the rivers of other parts of the world such as Tembi River, Iran and Odiel River, Spain are higher than those of Ekulu River [16,17].

In the study conducted in Ekulu river as reported in 2013, the river was polluted with Pb, Fe and Cu [18]. In yet another study conducted in 2015, it was reported that the Ekulu river was polluted with cadmium [19]. The findings of the present study with respect to heavy metal pollution are in agreement with those of the earlier studies mentioned above.

Water quality evaluation using WQI

The WQI of Ekulu river around the locations studied is presented in (Table 3).

The major contaminants of Ekulu river in the studied sections of the river in the month of October, 2018 were mainly hydrocarbons and lead. The Water Quality Index (WQI) for the month of October ranged from 372-1198 indicating water quality ranking of 'unsuitable for drinking' for all locations studied. This therefore demonstrates that Ekulu river within the studied sections should not be a source of drinking water unless it is treated. In the dry season, the major contaminants were cadmium and lead. This study therefore provides evidence that the Ekulu river within Onyeama and The Hotel is not fit for drinking and must be treated before consumption.

Conclusion

This study having determined the concentration of heavy metals and values of physico-chemistry parameters of Ekulu river found that

the major contaminants of Ekulu river around the studied locations viz, Onyeama, Damija and The Hotel were lead and cadmium. Acid mine drainage, indiscriminate waste dumping and agricultural run-off are potential sources of pollution with these contaminants. The water quality index for all the locations for all seasons varied in the range 288-1910 showing that the water ranked from 'very poor' to 'unsuitable for drinking'. This result indicates that the Ekulu river within the studied locations cannot serve as a source of drinking water unless it is treated before consumption. This study has therefore provided enough information to guide policy formulation and implementation by government agencies for the protection of the river and public health.

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