IJFAC

Indonesian Journal of
Fundamental and Applied Chemistry

Article http://ijfac.unsri.ac.id

Chemometric Assessment of Orashi River after Confluence with Oguta Lake

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Abstract

This study was carried out to evaluate the surficial water and sediment of Orashi River after confluence with Oguta. A total of 50 sub-samples were collected for the two media and was homogenized to form 10 composite samples (5 each). Water and sediment samples were analyzed for heavy metals concentrations and physico-chemical parameters. Data obtained was interpreted using ten chemometric models and standards of the Federal Ministry of Environment as touchstone values. Approximately 100 % of water samples were contaminated as opposed to 40 % of sediment samples. Both water and sediments showed that Cd was the highest contaminant with contamination factors of 38 and 1.52 respectively. Water revealed pollution load index higher than sediment probably due to its dissolution ability to metals. Geo accumulation index was observed to have highest value for Cd (45) at point A while Fe (> 4) at all points and same time the highest negative value. All points exhibited very high ecological risk (RI; 1112.7–1473.9) for water while sediments at those points showed low (RI < 150). The water quality index (WQI) ranged from 1633.33–2275.57 with a minimum deviation of 1910 % from WQI (100) adjudged to be unsuitable for consumption. The exchangeable sodium percentage (ESP) for all sampling sites ranged from 0.17-0.25 % suggesting good water for irrigation purposes. There was low sodium absorption ratio (SAR) and cation ratio of structural stability (CROSS) for the river water showing that it is good for irrigation. The sediment quality index was all less than 1 indicating no pollution of sediment. Transfer factors followed the order As>Cd>Ag>Cr>Fe>Cu>Mn>Co>Ni. In conclusion, the water was polluted but good for irrigation use. However, continuous use could lead to health problems due to bioaccumulation of metals while sediments were generally not polluted and of good quality.

Article info

Received 27 June 2019
Received in revised 25 July 2019
Accepted 26 July 2019
Available online 10 October 2019

Keywords: Crude oil, Heavy metal, Pollution, Toxicity, Water, Environment

INTRODUCTION

The need for assessing water quality is necessary; as water after the air we breathe is the next important thing for human survival [1]. In theory, the earth is abundantly blessed with water covering up to 70 % of the earth crust. But in practice most of the water is useless for direct human use. Only about 2.5% is freshwater which continues to decline in both quantity and quality [1,2]. This decline is due to continuous, rapid and unorganized industrialization, leading to increased waste generation with its attendant pollution of rivers and endangering water animals [3,4]. Of all pollutant of concern, heavy metal such as cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), iron (Fe), arsenic (As) and mercury (Hg) are the most important, perhaps due to their tendency or ability to bio accumulate in living tissues and destroys the health of it host [5].

Nigeria is indeed blessed with inland water bodies stretching about 283,293.47 hectares (ha), but

DOI: 10.24845/ijfac.v4.i3.91

this blessing has been turned to a curse by humans with about 198,305.43 hectares (ha) degraded due to pollution. River Orashi is one of such endangered inland water bodies in Nigeria, situated in the Niger Delta region of the country. The region is a wetland, with a population estimate of 20 million people belonging to more than 40 different ethnic groups. Floodplain of Niger Delta region is about 7.5% of Nigeria's total land mass [6]. The region is recognized for its richness in crude oil and their relative health and biodiversity has become a source of concern. The reason is due to history of crude oil spillage and precarious dumping activities around the river [7]. Waste dumpsites are the major sources of heavy metals pollution in the river through surface run-off. Earlier studies reveals that both the surface water and the sediments are under anthropogenic stress and mildly polluted [7,8]. However, no study has focused on the confluence point of the river with Oguta Lake.

The neighboring Oguta Lake is in Oguta Local Government Area, an area which experience petroleum-industry related activities due to the presence of some oil companies such as Shell Petroleum Development Company (SPDC) and Nigeria Agip Oil Company (NAOC). Since 1960, the area has experienced over 4000 oil spillage according to the estimates of the U.S. Department of Energy [9,10], caused by leaking pipelines from vandals, illegal tapping of the wells and from artisanal refining under very primitive conditions [11]. Literature reveals that effluents from petroleum industry discharged in marine environment contain high concentrations of heavy metals, which can be problematic for aquatic fauna and flora [12-14]. The discharged oil are rapidly distributed and remobilized over a large area by influence of rising tides and floods enhanced by rain. Therefore, problems originated from Oguta lake may affect not only the lake but neighboring rivers and environment.

Orashi river is a vital tributary of the Niger Delta and serve as freshwater source for people living around the area [7]. The aim of this present work was to use chemometric method to assess the surface water and surface sediment of river Orashi for contamination, pollution, consumption and irrigation purposes after confluence with Oguta lake. Chemometrics can simply be defined as using mathematical or statistical equations/methods/models to interpret/process data collected through a chemical system or process [1,15]. This study can be considered the first attempt to evaluate this region of Orashi River after confluence with Oguta lake by using different chemometric models. The models are effective tools for analyzing, interpreting large environmental data and also give proper estimation of accumulation or pollution by heavy metals. This study will provide handful information of the current status of the confluence point and be useful also for policy makers and environmentalist. Given the importance of Orashi river for household uses, drinking and irrigation. The importance of the current work cannot be overemphasized.

MATERIALS AND METHODS

Study Area

River Orashi (aka River Ulasi) is located in Ahoda West Local Government Area of Rivers State, Nigeria. Geographically, the river lies between latitudes 50º 45″ and 60º 35″ N and longitudes 40º 50″and 50º 15″ E. However, the region covered in the study is the region classified as midstream after it confluence with the nearby Oguta lake in Oguta LGA of Imo State displayed in Figure 1. Geologically the entire area is characterized by a vast flood plain built up by accumulation of sedimentary deposits washed down into the Niger and Benue Rivers [16]. The length of the river is more than 7 km. The area has a tropical humid hot climate with two major seasons, rainy season (between March and October) and the dry season (between November and March) [7,8].

Methods

Sample collection, preservation and preparation

In March 2018, a total of 50 sub-samples (25 surface water; 25 surface sediment) were collected for the study. The 25 sub-samples each were pooled and homogenized to form 5 samples each for water and sediment marked A to E (i.e. 5 sub-samples per point). The sub-samples were collected following a "W" shaped design. The grab sampling technique (sampling was conducted in a way to avoid collecting surface scum) was used for collecting water samples at the depth of collection was about 0.3 m. Sediment samples were collected using a self-made sediment core sampler and the depth of collection was top 5 cm. Surface water was collected in 500 mL high-grade polyethylene bottles and sediment in black polyethylene bags. The sampling materials used were previously soaked and rinsed in 10% HNO_3 overnight. The bottles were capped tightly and stored at 4 ˚C to prevent evaporation [17,18] and transported to the Old Chemistry laboratory, Imo State University for analysis. On reaching the lab, sediment samples were air-dried, grinded to pass a 200 mesh-sieve and kept for further analysis. All sampling and preservation methods strictly followed standard protocol as described by American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF) 1999 [19].

Water and sediment quality parameters

All sample analysis was carried out following standard protocol [19,20]. The pH and temperature were measured using Jenway 3510 pH meter [1] and soil gardener's thermometer (England) used only for sediment temperature. The phosphorus content was determined as phosphate by the vanadium phosphomolybdate (Vanadate) colorimetric method measured at 420nm according to AWWA, WEF, APHA [20]. Sulphate was determined using turbidimetric method according to method 4500 of AWWA, WEF, APHA [20]. Nitrate was analyzed using colorimetric method using the Nitrate Nitrogen Comparator [19,20]. Argentometric method was used in chloride determination according to EPA method [21]. Total organic matter (TOM) was determined according to the loss on ignition method [22] while total organic carbon (TOC) was quantified using the dry techniques according EPA [23].

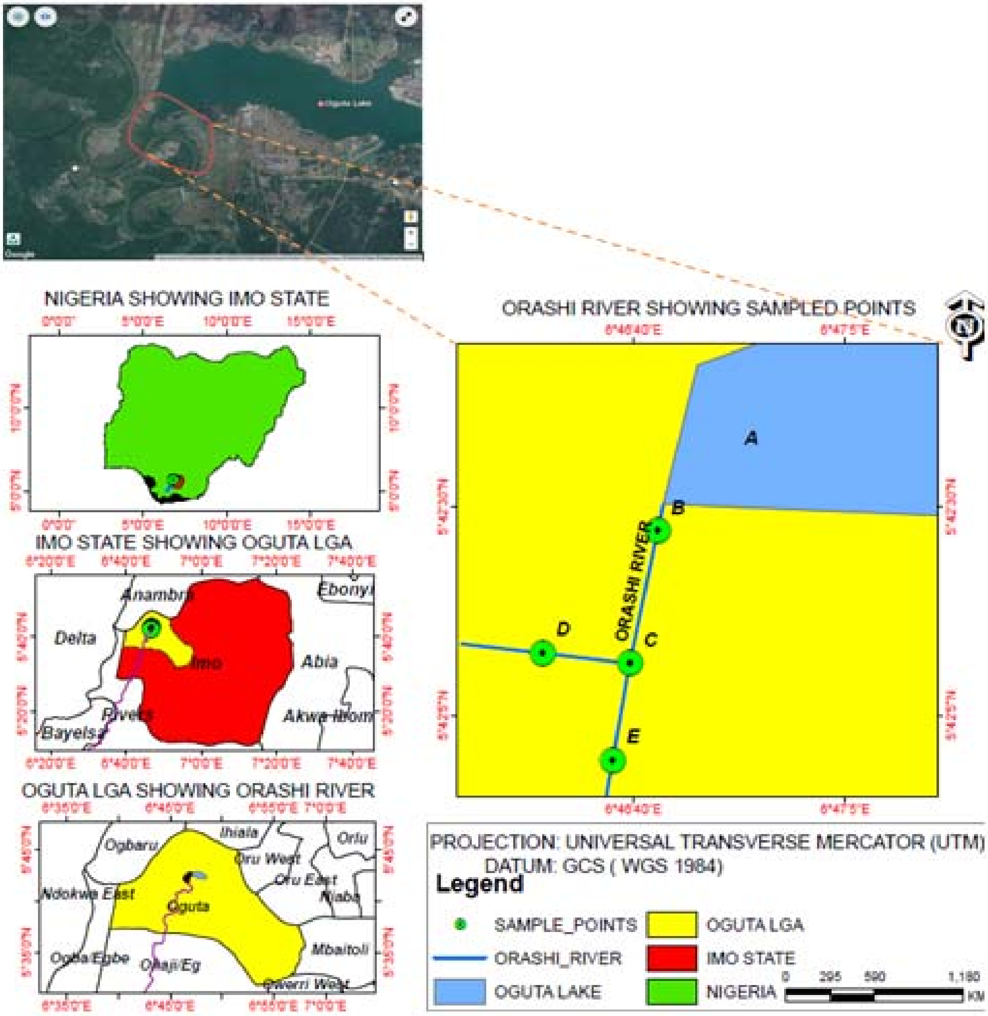

Figure 1. Map showing study area and sampling points

Sample digestion

All chemicals used for digestion in the study were of analytical grade and obtained from Finlab, Owerri, Nigeria. De-ionized water was used in various water quality protocols followed in the study. For heavy metal estimation, the aqua-regia wet digestion was employed. Aqua-regia was prepared by mixing concentrated hydrochloric acid (HCl) with concentrated nitric acid (HNO_3) in ratio of 3 to 1 and allowed to mix properly for 5 hours. 10 ml of well-mixed water samples and 10 g of sediment samples were taken in two different acid-washed beakers and 30 ml of aqua-regia was introduced into each. The mixture was reduced to 10–20 ml by heating at 90°C on a hot plate. The reduced mixture was allowed to cool and made to a final volume of 50 ml by addition of de-ionized water, followed by filtration using

Whatman no. 42 filter paper [17,18]. The filtrate was used for heavy metal determination by using Atomic Absorption Spectrophotometer.

Table 1. Optimal Instrumental parameters for AAS determination of the metals

Metal symbols	Wavelength (nm)	Spectral Band Width (nm)	Flame gases	Time of measurement (secs)	Atomization flow rate (L/min)
Ca	422.7	0.7	Air-Acetylene	4	1.2
Mg	285.2	0.7	Air-Acetylene	4	1.1
Na	589.0	0.2	Air-Acetylene	4	1.2
Co	240.7	0.2	Air-Acetylene	4	0.9
Pb	283.3	0.7	Air-Acetylene	4	0.9
Cu	324.8	0.7	Air-Acetylene	4	0.9
Ni	232.0	0.2	Nitrous Oxide-Acetylene	4	0.9
As	193.7	0.7	Air-Acetylene	4	0.9
Fe	248.3	0.2	Air-Acetylene	4	0.9
Mn	279.5	0.2	Air-Acetylene	4	0.9
Zn	213.9	0.7	Air-Acetylene	4	0.9
Ag	328.8	0.7	Air-Acetylene	4	0.9
Cr	357.9	0.7	Air-Acetylene	4	0.9
Hg	253.7	0.7	Air-Acetylene	4	0.9
Cd	228.8	0.7	Air-Acetylene	4	0.9

Heavy metal determination

The digested filtrates were used for the total metal quantification using Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 400). The characteristic wavelengths of metals determined were first set using the hollow cathode lamp, then digested filtrates samples was aspirated directly into the flame (except for Hg which required cold-vapor). To ensure accuracy of data, calibration of the equipment was done for each element using a standard sample prepared as a control with every set of samples. Concentration was in mg/l (ppm) which was converted to mg/kg by dividing with the volume of sample aspirated. The instrumental parameters for particular metals that were analyzed is presented in table 1:

Statistical analysis

The statistical analysis were done using Microsoft excel 2007. Correlation analysis was used to establish relationship between physicochemical parameters while test statistics was used to test for differences between means both at 5 % level of significance.

Chemometric assessment of surface water and sediment

In the interpretation of geochemical data, choice of touchstone values plays a significant contribution. The touchstone/background value, which serves as a reference baseline in this study, was taken from the Federal Ministry of Environment standard. The degree of contamination from heavy metals was evaluated by determining the contamination factor (CF), pollution load index (PLI), potential ecological risk (RI) and geo accumulation index (Igeo); consumption-wise was evaluated using the water quality index (WQI), irrigation purposes was evaluated using exchangeable sodium percentage (ESP), sodium absorption ratio (SAR) and Cation Ratio of Structural Stability (CROSS) while sediment quality index (SQI) was used to assess overall sediment quality.

RESULT AND DISCUSSION

Physicochemical assessment of water and sediment

The characterization results for the surface water and surface sediment is presented in table 2. The table is presenting some descriptive statistics such as the range, mean and standard deviation for easy interpretation and comparison with standard of Federal Ministry of Environment for water and sediment. For water, temperature showed mean of 29.20±0.54 °C which was within the standard range of 20-30 °C, pH was 6.70±0.37 also within recommended limit of 6.50-8.50. Major cations such as Na, K, Ca and Mg showed mean of 1.41±0.27, 0.87±0.32, 2.23±1.32 and 3.56±2.53 mg/kg respectively. Ca and Mg were below the threshold limit of 250 and 100 mg/kg recommended for river water. Among the major anions such as NO_3^- (21.88±3.26 mg/kg), PO_4^{2-} (2.44±0.86 mg/kg), SO_4^{2-}

(10±3.53 mg/kg), only mean chloride (291.52±44.55 mg/kg) exceeded the set limit of 250 mg/kg. Although, chloride naturally exists in river water, but high concentrations like this, is definitely from anthropogenic or human-caused, factors such as road salt and sewage contamination. For mean concentration of heavy metals only the following metals; Cu (1.74±0.29 mg/kg); As (1.34±0.24 mg/kg); Ag (0.30±0.02 mg/kg); Cr (0.46±0.22 mg/kg) and Cd (0.38±0.04 mg/kg), exceeded the permissible limit set by federal ministry of environment. The high concentration of these metals is associated with petroleum related pollution. In sediment, parameters whose mean value exceeded their respective standards or touchstone values from Federal Ministry of Environment include pH (7.07±0.32), phosphate (6.08±5.44 mg/kg), K (159±122.09 mg/kg), Mg (3.94±1.37 mg/kg), Cd (0.18±0.02 mg/kg), Cu (3.38±0.37 mg/kg) and Fe (0.07±0.02 mg/kg). Lead (Pb) was not detected in both the surface water and surface sediment. Comparable results have been reported for surface water and sediment from other parts of the river downstream [7,8].

Table 2. The results for the physical and chemical analysis of surface water and surface sediment

Parameter	FMEnv Standard	A	B	C	D	E	Range	Mean	SDV
Water									
Temp.^{0}C	20.00-30.00	29.10^{a}	28.60^{b}	29.10^{a}	29.80^{c}	29.90^{c}	28.60-29.90	29.20	0.54
pH	6.50-8.50	6.40^{a}	5.60^{b}	5.60^{b}	5.60^{b}	6.10^{c}	5.60-6.40	6.70	0.37
Na (mg/kg)	NA	1.33^{a}	1.67^{b}	1.37^{c}	1.30^{d}	1.37^{c}	1.30-1.67	1.41	0.27
K (mg/kg)	NA	0.82^{a}	1.89^{b}	0.18^{c}	1.29^{d}	0.19^{c}	0.18-1.89	0.87	0.32
Ca (mg/kg)	250.00	2.52^{a}	1.68^{b}	5.05^{c}	1.68^{b}	2.52^{a}	1.68-2.52	2.69	1.38
Mg (mg/kg)	100.00	2.67^{a}	4.45^{b}	1.19^{c}	1.95^{d}	1.36^{e}	1.19-4.45	2.23	1.32
Cl- (mg/kg)	250.00	360.78^{a}	267.83^{b}	262.37^{b}	255.08^{c}	311.56^{d}	255.08-360.78	291.52	44.55
NO$_3$- (mg/kg)	50.00	18.90^{a}	20.40^{b}	26.20^{c}	19.40^{a}	24.50^{c}	18.90-26.20	21.88	3.26
PO$_4^{2-}$ (mg/kg)	5.00	3.80^{a}	2.60^{b}	2.40^{b}	1.60^{c}	1.80^{c}	1.60-3.80	2.44	0.86
SO$_4^{2-}$ (mg/kg)	200-400	15.00^{a}	5.00^{b}	10.00^{c}	10.00^{c}	10.00^{c}	5.00-15.00	10.00	3.53
Pb (mg/kg)	0.05	ND	ND	ND	ND	ND	ND	ND	ND
Cu (mg/kg)	0.10	1.28^{a}	1.68^{a}	1.72^{a}	2.00^{b}	2.01^{b}	1.28-2.01	1.74	0.29
Ni (mg/kg)	0.05	ND	0.18	ND	ND	ND	ND-0.18	0.04	0.07
As (mg/kg)	0.20	1.77^{a}	1.34^{b}	1.26^{c}	1.21^{c}	1.14^{d}	1.14-1.77	1.34	0.24
Fe(mg/kg)	1.00	0.16^{a}	0.12^{b}	0.08^{c}	0.04^{d}	0.20^{e}	0.04-0.20	0.12	0.06
Mn (mg/kg)	0.20	0.20^{a}	0.20^{a}	0.10^{a}	ND	0.20^{a}	ND-0.20	0.18	0.08
Zn (mg/kg)	3.00	0.46^{a}	0.74^{b}	0.74^{b}	0.76^{b}	0.78^{b}	0.46-0.78	0.58	0.24
Ag (mg/kg)	0.1	0.30^{a}	0.29^{a}	0.28^{a}	0.30^{a}	0.32^{a}	0.28-0.32	0.30	0.02
Cr (mg/kg)	0.05	0.76^{a}	0.34^{b}	0.03^{c}	0.27^{d}	0.28^{d}	0.03-0.76	0.46	0.22
Hg (mg/kg)	0.10	ND	ND	ND	ND	ND	ND	ND	ND
Cd (mg/kg)	0.01	0.43^{a}	0.38^{b}	0.32^{c}	0.39^{b}	0.38^{b}	0.32-0.43	0.38	0.04
Co (mg/kg)	0.05	ND	0.05^{a}	0.02^{b}	ND	0.02^{b}	ND-0.05	0.02	0.02
Sediment									
pH	6.71	6.81^{a}	7.55^{b}	7.28^{c}	6.87^{a}	6.85^{a}	6.81-7.55	7.07	0.32
NO$_3^-$ (mg/kg)	26.10	11.70^{a}	16.40^{b}	15.78^{c}	12.40^{d}	15.52^{c}	11.70-16.40	14.36	2.15
PO$_4^{2-}$(mg/kg)	3.80	3.40^{a}	0.50^{b}	4.20^{c}	14.70^{d}	7.60^{e}	0.5-14.70	6.08	5.44
SO$_4^{2-}$(mg/kg)	30.00	10.00^{a}	ND	10.00^{a}	ND	ND	ND-10.00	4.00	5.47
Cd (mg/kg)	0.12	0.17^{a}	0.19^{a}	0.16^{a}	0.20^{b}	0.19^{a}	0.16-0.2	0.18	0.02
TOC %	16.49	15.80^{a}	13.80^{b}	16.18^{c}	17.25^{d}	14.29^{e}	13.80-17.25	15.46	1.41
Cl$^-$ (mg/kg)	751.80	642.30^{a}	409.95^{b}	638.22^{a}	522.63^{c}	583.40^{d}	409.95-642.30	599.30	96.63
TOM %	15.5	8.13^{a}	1.37^{b}	14.26^{c}	4.62^{d}	8.36^{e}	1.37-14.26	7.34	4.81
Pb (mg/kg)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cu (mg/kg)	2.70	3.78^{a}	2.92^{b}	3.12^{c}	3.70^{a}	3.38^{d}	2.92-3.78	3.38	0.37
Ni (mg/kg)	0.19	0.12^{a}	0.20^{b}	0.18^{b}	0.08^{c}	0.09^{c}	0.08-0.20	0.13	0.05
Cr (mg/kg)	0.47	0.22^{a}	0.51^{b}	0.32^{c}	0.28^{d}	0.30^{c}	0.22-0.51	0.33	0.11
Ag (mg/kg)	0.16	0.18^{a}	0.14^{b}	0.13^{b}	0.15^{b}	0.16^{b}	0.13-0.18	0.15	0.02
Mn (mg/kg)	0.30	ND	0.30^{a}	0.20^{b}	0.70^{c}	0.40^{d}	ND-0.70	0.29	0.27
Fe (mg/kg)	0.06	0.07^{a}	0.09^{a}	0.08^{a}	0.04^{b}	0.09^{a}	0.04-0.09	0.07	0.02
K (mg/kg)	85.00	95.00^{a}	370.00^{b}	130.00^{c}	60.00^{d}	140.00^{e}	60-370.00	159.00	122.09
Ca (mg/kg)	19.34	17.66^{a}	8.41^{b}	11.40^{c}	15.99^{d}	13.35^{e}	8.41-17.66	13.36	3.67
Mg (mg/kg)	2.96	1.78^{a}	4.15^{b}	5.60^{c}	4.15^{b}	4.01^{d}	1.78-5.60	3.94	1.37
As (mg/kg)	1.14	0.99^{a}	0.51^{b}	0.62^{c}	0.28^{d}	0.31^{e}	0.28-0.99	0.54	0.29
Co (mg/kg)	0.07	0.13^{a}	ND	0.02^{b}	0.05^{c}	0.04^{c}	ND-0.13	0.05	0.05

NA=Not available; ND=Not detected; SDV=Standard deviation; FMEnv=Federal Ministry of Environment
Values having the same superscripts in rows are not statistically different ($p<0.05$).
Values having different superscripts in rows are statistically different ($p>0.05$).

Correlation analysis

Using correlation analyses in environmental analytical studies have been well documented by many researcher [1,24-26]. The model furnishes important information regarding relationships between multiple parameters in a sample matrix. Thus enabling understanding on how physical and geochemical factors such as pH, water/rock interaction, topography, metals filing, etc. affect chemical components in a matrix. Heavy metals relationship in sample matrix is usually complex. Correlation analysis can help reveal information concerning the pollution and/or contamination sources of metals. When correlations is high between parameter in a sample, it may suggest similar contamination or pollution source(s) e.g. petroleum-related industrial activities, dumping of waste along the river channel in the area. A high and significant positive correlation ($r > 0.5$) was observed among some of the metals, anions and physical parameters. In the surface water, temperature correlated strongly with some metals such as Cu ($r = 0.66$) and Ag ($r = 0.71$). pH showed strong association with most anions such as Cl^- ($r = 0.99$); PO_4^{2-} ($r = 0.60$); SO_4^{2-} ($r = 0.76$) and heavy metals such as As ($r = 0.65$); Fe ($r = 0.77$); Mn ($r = 0.59$); Ag ($r = 0.57$); Cr ($r = 0.79$) and Cd ($r = 0.68$). Many studies have shown that pH is an important factor that controls the behavior of ions in environmental matrix [1,27-29]. Between metals, the highest correlations were found between Cu and Zn ($r = 0.91$); Ni and Co ($r = 0.87$); As and Cr ($r = 0.86$); As and Cd ($r = 0.64$); Fe and Mn ($r = 0.88$); Fe and Ag ($r = 0.64$); Cd and Cr ($r = 0.93$). In the surface sediment, strong positive correlation was recorded for pH and some metals such as Fe ($r = 0.77$); K ($r = 0.87$) and Mg (0.63). TOM had high correlations with NO_3^- ($r = 0.82$); PO_4^{2-} ($r = 0.84$); Cl^- ($r = 0.92$) and As ($r = 0.64$) while TOC and PO_4^{2-} had strong association ($r = 0.77$). Between metals in sediment, the highest correlations were found between Cd and Cd ($r = 0.60$); Cu and Co ($r = 0.54$); Ni and Cr ($r = 0.79$); Ni and Fe ($r = 0.76$); Ni and K ($r = 0.60$); Fe and K ($r = 0.77$); Cr and K ($r = 0.66$); Ca and As ($r = 0.60$); As and Co ($r = 0.62$). The strong positive correlations among metals in surface water and surface sediment suggest that they are probably released from a similar origin. Some of the relationship exhibited by the metals has been observed [30]. However between the two media (i.e surface sediment and surface water) reveals very low correlation ($r = 0.004$; $y = 0.022x + 0.709$), suggesting that the general contamination source of the water may not be totally responsible for the sediment contamination and vice-versa, even though the relationship was positive.

Contamination factor and pollution load index

Contamination factors (Cf) and pollution load index (PLI) were quantitatively estimated according to the mathematical formulae (1) and (2). These models were originally proposed by Forstner and Calmano in 1993 [31] and Thomilson and coworkers in 1980 [32]. Contamination factor reveals the level of contamination by individual metals in a sample. It is computed simply by dividing the measured value by their background or target values from reference table. The background/target value used for computing Cf for water and sediment are obtained from the Federal Ministry of Environment presented in Tables 1. Cf was computed for metals in the surface water and surface sediment.

$$Cf = \frac{Actual\ measurement\ of\ metal\ in\ samples}{Target\ values\ from\ refrence\ table} \quad (1)$$

$$PLI = (Cf_1 X\ Cf_2 X\ Cf_3 \ldots\ldots Cf_n)^{1/n} \quad (2)$$

Where Cf= contamination factor and n = number of heavy metals used in computing (n=9).

The significance of intervals of contamination factor has been described. When Cf < 1 reveals low contamination, when Cf is $1 \leq 3$ reveals moderate contamination, when Cf is $3 \leq 6$ reveals considerable contamination, and when Cf ≥ 6 reveals very high contamination [1]. Approximately 100 % of the samples were contaminated by the tested heavy metals for surface water while 40% of the sediment samples were contaminated. The computed contamination factor is presented in Figure 2. Generally, the surface water was more contaminated when compared to the sediments. Only Fe exhibited low contamination in the water while other metals exhibited moderate to very high contamination. The order of mean metal contamination in water was Cd (38) > Cu (17.28) > Cr /As (6.72) > Ag (2.98) > Ni (0.72) > Mn (0.70) > Co (0.36) > Fe (0.12) > Pb (0). In the sediment, low contamination was exhibited by Ag, As, Co, Cr, and Ni while moderate contamination was exhibited Cd, Cu, Mn, and Fe respectively. The order of mean metal contamination in sediments was Cd (1.52) > Cu (1.25) > Fe (1.23) > Mn (1.07) > Ag (0.92) > Cr (0.88) > Ni (0.70) > Co (0.67) > As (0.48) > Pb (0). Pb was not detected in the two media (water and sediment).

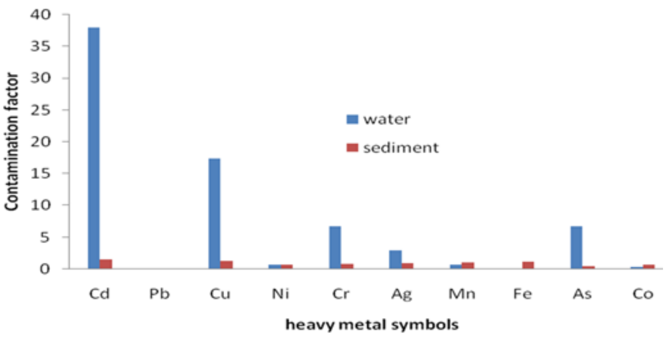

Figure 2. Mean contamination factors for heavy metals in surface water and surface sediment

Pollution Load Index (PLI) is a useful tool in estimating the metal pollution load and exposes the intensity of metal pollution in a sample. When the PLI is greater than a unit, it means that the sample is highly loaded with metals and thus polluted. However, when the PLI is less than a unit, it is said to be "no pollution". The computed PLI for different water and sediment samples is compared in Figure 3. According to the PLI, the surface water is highly loaded with heavy metals and thus polluted. However, for sediment samples C, D and E are unpolluted while A and B were slightly polluted.

Geoaccumulation Index (Igeo)

Muller in 1981 [33] developed Igeo (Geo accumulation Index) and ever since many analytical environmental researchers have adopted it and find it really useful for assessing toxic metals contamination in environmental sample [25,34].

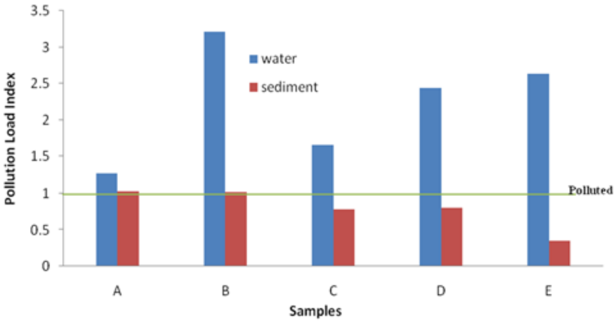

Figure 3. Heavy metal Pollution load index in samples

Igeo furnishes information regarding metal accumulation in the natural ecosystem due to anthropogenic influences. Increasing anthropogenic activities will cause increasing geo accumulation of these metals in the ecosystem [25]. The Igeo was estimated mathematically expressed in equation (3):

$$\text{Igeo} = \log_2 (0.67 \times C_f) \qquad (3)$$

The 0.67 present in equation 3 is the matrix correction factor that normalizes lithogenic effects.

The Igeo is associated with a qualitative scale of pollution intensity, five classes of pollution were described: unpolluted (Igeo ≤ 0); moderately polluted ($0 <$ mean Igeo < 1); considerable polluted ($1 <$ Igeo < 3); strongly polluted ($3 <$ mean Igeo < 4); extremely polluted (Igeo ≥ 5) [25]. Following this classification;

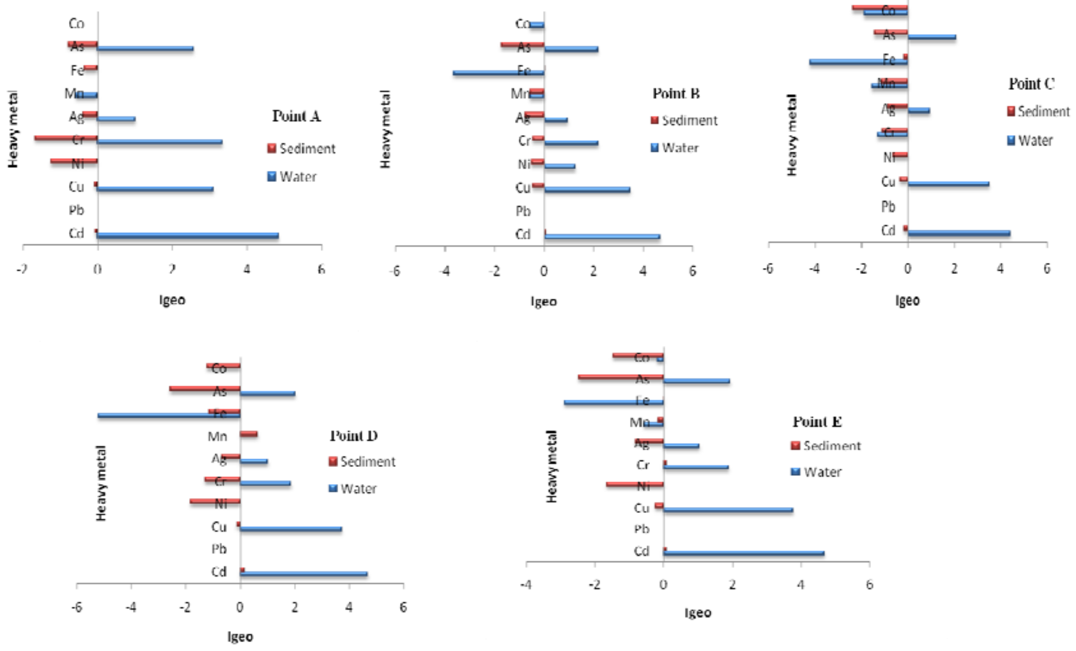

Figure 4a-4e. Geo accumulation index for heavy metals in the two mediate different points samples collected along the midstream of River Orashi after confluence with Oguta lake, can thus be categorized: surficial water was unpolluted with Mn, Fe, and Co; moderately polluted with Ni, and Ag; considerable polluted with Cr and As; strongly polluted with Cu to extremely polluted with Cd. However, surficial sediment was unpolluted with Cu, Ni, Cr, Ag, Mn, Fe, As, Co but moderately polluted with Cd. Some studies conducted on some rivers have implicated high load of Cd [34-37] and literature reveals that high load of Cd is common in soils and groundwater of the tropics [1,25,38].

Point-wise distribution of Igeo is compared in Figures 4a-4e. Comparing the surface water and sediment, the surface water was polluted at varying degrees as opposed to the surface sediment. The order of pollution for water was: Point A: Cd > Cu > Ag > As; Point B: Cd > Cu > Ni > Cr > Ag > As; Point C: Cd > Cu > Ag > As; Point D: Cd > Cu > Cr > Ag > As; Point E: Cd > Cu > Cr > Ag > As. In conclusion, based on the Igeo classification, the magnitude of heavy metal pollution of the water of Orashi River decreased in the order of Cd > Cu > As > Cr > Ni > Ag > Co > Mn > Fe while sediment decreased in the order of Cd > Mn > Cu > Fe > Ag > Cr > Co > Ni > As (mean of Figures 4a-4e).

Potential Ecological Impact Assessment

Hakanson in 1980 [39] developed the Potential Ecological Risk Index (RI) for aquatic environment pollution control. Hakanson defined RI as “a risk index which provides a fast and simple quantitative value on the potential ecological risk of a given contamination situation in a given lake or fresh water system”. RI has also been widely used by environmental analytical researchers whether in area of biological toxicology or geochemistry. Ecological risks caused by heavy metals can be evaluated comprehensively by the model. The calculating method of RI is expressed in mathematical equation (4):

$$RI = \sum T_r \times C_f \quad (4)$$

where, Cf is the single metal contamination factor (calculated using equation (1), T_r is the metal toxic response factor. According to Hakanson [39], T_r gives information about the potential transport avenues of toxic substances to man, and the threat to the aquatic ecological system. T_r values for the metals were Cr: 2; Cu = Pb = Co : 5; Ni: 6: As: 10; Cd: 30; Hg: 40; Mn: 1; metals whose values were not found (Fe and Ag) were excluded from the calculation.

The RI values may be classified as follows: from RI < 150—low ecological risk for the waterbody to RI > 600—very high ecological risk for the waterbody [34]. RI values for the surficial water and sediment is compared in Figure 5. All points (100 %) for water samples exhibited very high ecological risk from heavy metal pollution with RI values ranging from 1112.7 to 1473.9 (Figure 5). These very high risks at all sampling sites for water are mainly due to the high cadmium load in the river. In contrast, the sediments were generally lower than RI = 150, suggesting the sites for surface sediment exhibited low ecological risk from heavy metal pollution. Low RI was reported for surface sediment in Yangee River, China [34].

Consumption assessment of surface water

The tendency of consuming the river water was assessed using the water quality index (WQI). WQI

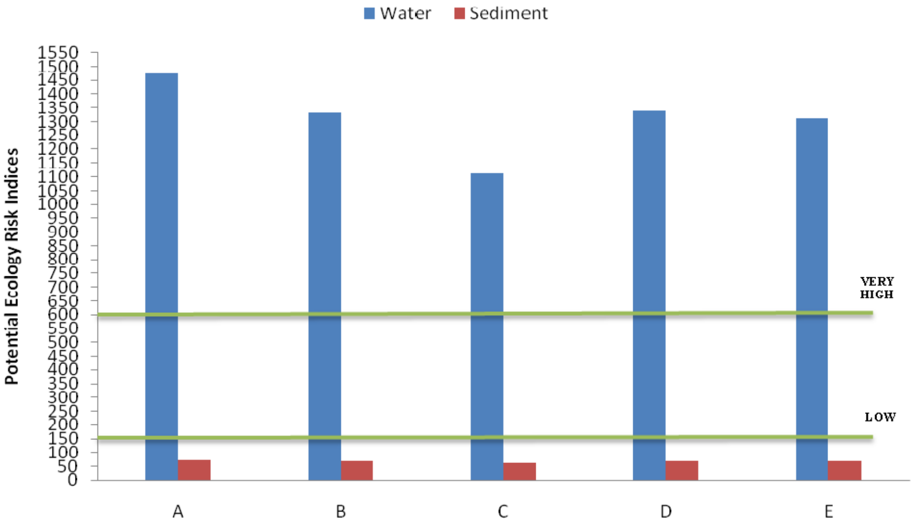

Figure 5. Potential ecological risk indices (RI) of heavy metals in surface water and sediments

was estimated according equation (5).

$$WQI = \frac{\sum_{i=1}^{n} q_i.W_i}{\sum_{i=1} W_i} \qquad (5)$$

Where W_i; weightage factor for individual quality indices and q_i; quality rating for the individual quality indices in the sample. The calculation for weightage factor and quality rating was described by Enyoh [1]. Of the 22 quality parameters analyzed, we used only 19 for computing WQI. Parameters not used were the ones for which the standard was not available. The computed WQI for surficial water from the different sampling sites is presented in Figure 6. For WQI classification, when WQI value is greater than 300, the water is unsuitable for drinking. The sampling sites (A to E) revealed WQI values ranging from 1633.33 to 2275.57, which on average is approximately 1910% deviated from good water quality (WQI = 100). Therefore, the surface water of Orashi river after confluence with Oguta lake is extremely polluted and cannot be used for consumption purposes.

Suitability of surface water for Irrigation purposes

Three major irrigation models were used for assessing the suitability of the river for irrigation purposes. The models include exchangeable sodium percentage (ESP), sodium absorption ratio (SAR) and cation ratio of structural stability (CROSS). These models largely depend on the sodium concentration of the river and also major cationic concentrations.

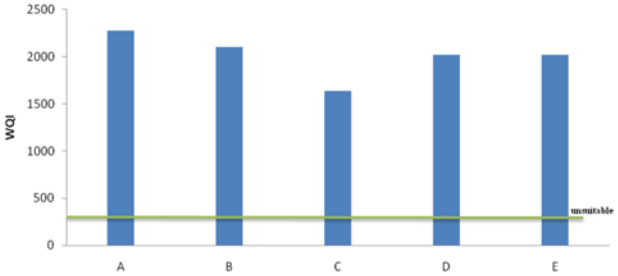

Figure 6. Water quality index for surface water

Exchangeable sodium percentage (ESP)

ESP was computed using equation (6) as the ratio of sodium to the cation exchange capacity (CEC) of the water.

$$ESP = \frac{Na^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} x\ 100 \qquad (6)$$

The computed ESP is presented in Figure 7. The % Na for the entire sampling sites ranged from 0.17 % to 0.25 %, suggesting good water for irrigation. However, a threshold of 60 % was recommended [40]. High sodium content in irrigation water will cause sodium effect on applied soil and can be hazardous [41].

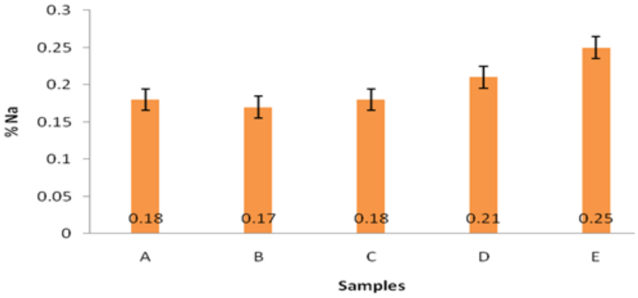

Figure 7. Percent of sodium for sampling sites

Sodium Adsorption Ratio (SAR) and Cations Ratio of Structural Stability (CROSS)

SAR and CROSS were estimated using the mathematical Equations (7) and (8). The two models basically furnish similar information except that concept of SAR addresses only the effects of sodium on the stability of soil aggregates. Meanwhile, potential negative effects of high potassium (K) and manganese (Mg) concentrations are ignored by the SAR, which is taken care of in CROSS model. The CROSS is considered a more updated SAR model. CROSS was introduced by Rengasamy and Marchuk in 2011 [42].

$$SAR = \frac{Na^+}{\sqrt{\frac{(Ca^{2+}Mg^{2+})}{2}}} \qquad (7)$$

$$CROSS = \frac{Na^+ + 0.56\ K^+}{\sqrt{\frac{(Ca^{2+} + 0.6\ Mg^{2+})}{2}}} \qquad (8)$$

There are no general standard limit set for SAR and CROSS. However, a report on SAR for Manawatu District Council (MDC) recommends that CROSS should be kept below 13 to avoid structural problems developing [43]. Therefore, the low SAR (1.1 to 1.38) and CROSS ranging from 1.23 to 2.62, suggesting that river Orashi after confluence with Oguta lake is good for irrigation purposes (Figures 8 and 9).

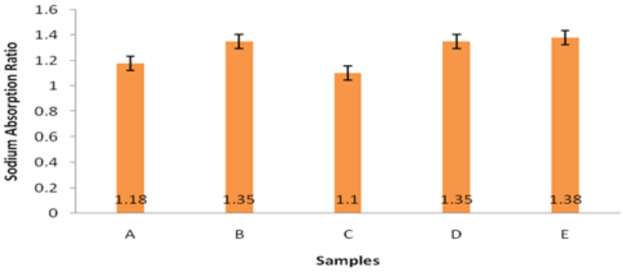

Figure 8. Computed SAR for various sampling site

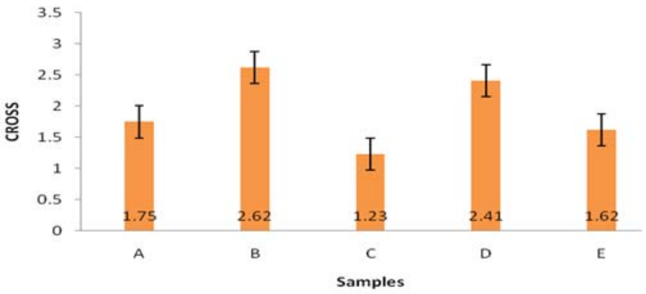

Figure 9. Computed CROSS for various sampling site

Sediment Quality Assessment

The sediment quality was assessed using the sediment quality index. The index was originally used for soil by Islam [44] and adopted for sediment assessment in the current study. The model is an inductive additive approach based on normalization, summation, and average of selected sediment quality indicator properties put into a single integrator. Mathematically, it expressed in equation (9).

$$Sediment\ Quality_{index} = \sum(CC_{max}{}^{-1})n^{-1} \qquad (9)$$

where C is the value of any particular sediment property, C_{max} is highest value of that particular sediment property and n is the total number of sediment properties used in the calculation (n=19). Lead was not included in computing the SQI because it was not detected in the entire samples collected. SQ_{index} is associated with qualitative scale and may be classified as thus: Excellent sediment quality when $0 < SQi < 0.5$; Good sediment quality when $0.5 \leq SQi < 1$ and Poor sediment quality $SQi \geq 1$. The computed SQi is compared in figure 10. Based on the classification the surface sediments are of good quality and thus not polluted. This could be due to dissolution abilities of water for heavy metals compared to sediment.

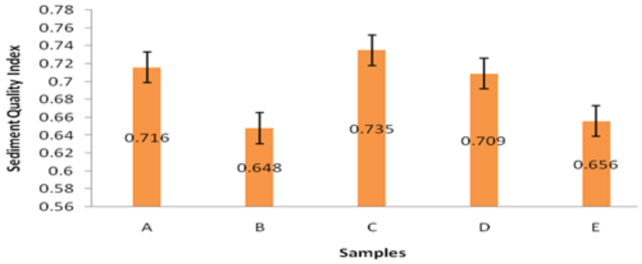

Figure 10. Computed sediment quality index

Water to Sediment transfer factor

The water to sediment transfer factor for heavy metal was calculated using equation (10). The transfer factor explains the potentiality of heavy metals being absorbed by the surface sediment from the surface water.

$$W - S_{tf} = \frac{C_m in\ water}{C_m\ in\ sediment} \qquad (10)$$

Interpreting the computed transfer factor (Figure 11) in percentage, 34 % to 59 % of Cu was transferred from the surface water to the surface sediment. Nickel detected in the sediment at points A, C, D and E was probably not from the surface water, meanwhile a transfer of 15 % was computed at point B. Arsenic (As) transfer factor ranged from 179 % at point A to 432 % at point D which was the most transferred metal. Fe was 100 % transferred at point C and D while 228 %, 133 % and 222 % was computed for points A, B, and E respectively.

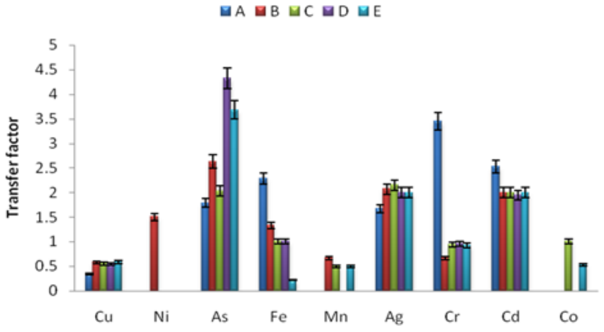

Figure 11. Water to sediment transfer factor for heavy metals.

Manganese ranged from 50 % at C and E to 67 % at B while there was no transfer at points A and D respectively suggesting that the recorded concentrations in the sediment was not from the surface water. 100 % and 53 % cobalt (Co) was transferred at points C and E respectively. Other points where no transfer was computed for Co, but was detected in either of the medium suggests that the Co source for those points were probably dissimilar. Cd transferred 195 % to 253 % while Cr transferred 67 % to as high as 345 % from surface water to the sediment. Silver (Ag) transfer ranged from 167 % to 207 % for all points. The mean trend of absorption of the heavy metals on the sediment reveals As (2.89) and Ni (0.3) to be the highest and lowest transferred metal recorded for the area. However, the decreasing order of transfer factor was As > Cd > Ag > Cr > Fe > Cu > Mn > Co > Ni.

CONCLUSION

The study has successfully characterized the surficial water and sediment of river Orashi immediately after it confluence with Oguta lake using different chemometric models. Information from models is viewed as simplified concepts of environmental issues. Thereby making for easy understanding of these environmental issues by policy makers, this way decisions on environmental issues are quickly arrived at. Present study has revealed that the surface water is highly contaminated/polluted with very high ecological risk index causing high deterioration of its aquatic ecosystem. Due to the relatively high concentrations of the metals, the river water seems not to be suitable for drinking purposes as revealed by the high water quality index (> 1000). However, the surface sediment was of good quality with low ecological risk index and geo accumulation index. Although, the river is highly degraded, it is particularly good for agricultural activities as irrigation water revealed by low % ESP, SAR and CROSS. Profiles of accumulation and correlation analysis of the metals revealed strong correlations between the metals and also showed that the metals were generally of anthropogenic origin with possible multi-element contamination which could double the effect of the toxic metals if ingested. The contamination was majorly from petroleum related activities and fumes from speed-boat use. pH was within the standard range and showed strong association with most anions and heavy metals such as As, Fe, Mn, Ag, Cr and Cd while with As and Fe in the sediment.

Following the current pollution status of this point of river Orashi, the following recommendation was deduced to protect the river from further degradation.

- Waste discharged into the river must be treated to meet the standard of Federal Ministry of Environment.
- Existing laws such as the National Environmental Regulations which prohibits persons from indiscriminate dumping of wastes in undesignated place set in 2009 by National Environmental Standards and Regulations Enforcement Agency (NESREA) should be implemented or enforced to control the presence of toxic substances in the river.
- Monitoring toxins levels and extensive analysis of river water and sediment quality should be carried out at regular intervals (could be seasonal) to reveal the pollution status and health of the aquatic ecosystem and will inform on the mitigation measures to be taken
- Regular examination of aquatic animal such as fish should be analyzed for heavy metal bioconcentration as data obtained will expose possible health threat to human through fish consumption.
- Inhabitant and users who frequent the river should be enlightened about polluted state of the river and the role they will play in its remediation.

As one of the major occupations of the locals is farming, surface water from this point could be collected and used for irrigation purposes.

ACKNOWLEDGMENT

Authors acknowledge Group Research in Analytical Chemistry, Environment and Climate Change (GRACE&CC) for the financial support throughout the current research work.

Conflict of interest

The authors declare no conflict of interest regarding the publication of this manuscript.

REFERENCES

[1] E.C.Ebere, A.W. Verla, N.J. Egejuru, 2018. “pH variations and chemometric assessment of borehole water in Orji, Owerri Imo State, Nigeria.”*Journal of Environmental Analytical Chemistry*,vol. 5(2), pp. 1-9.

[2] P.U. Okorie.2017. “The Challenges of Declining Freshwater Resources.”In Proc. *The World Environment Day Conference*, Imo state University Owerri, Nigeria.

[3] O.A. Olorode, E.A. Bamigbola, O.M. Ogba. 2015. “Comparative Studies of some River Waters in Port Harcourt based on Their Physico - Chemical and Microbiological analysis, Niger Delta Region of Nigeria”. *International Journal of Basic and Applied Science*, vol. 3(3), pp. 29 - 37.

[4] O.A. Davies and C.C. Tawari. 2010. “Season and Tide Effects on Sediment Characteristics of Trans-Okpoka Creek, Upper Bonny Estuary Nigeria.”*Agriculture and Biology Journal of North America*,vol. 1(2), pp. 89-96.

[5] A.W. Verla, E.N. Verla, C. MedoAjero, K. ChiomaLele, N.O. Stellamarris, C.E. Ebere. 2019. “Biomonitoring of Heavy Metals in Blood and Urine of African Children from Owerri Metropolis.”*Eastern Nigeria. Journal of Chemical Health Risks*,vol. 9(1), pp. 11-26.

[6] T.C.N. Angaye and C.E. Mieyepa.2015. “Assessment of elemental and microbial quality of Lake Efi in bayelsa state, Central Niger Delta, Nigeria.”*Journal of Environmental Treatment Techniques*,vol. 3(3), pp. 71 - 75.

[7] I. Enetimi. C.N.S. Tariwari, C.N Angaye, B.C. Okogbue.2016. “Physicochemical Quality Assessment of River Orashi in Eastern Niger Delta of Nigeria.”*Journal of Environmental Treatment Techniques*,vol. 4(4), pp. 143-148.

[8] E.I. Seiyaboh, W.E. Alagha and T.C.N. Angaye. 2016. “Sedimentary Assessment of Basic River in the Niger Delta: A Case Study of Orashi River in the Eastern Niger Delta of Nigeria.”*Greener Journal of Geology and Earth Sciences*,vol. 4(3), pp. 051-055.

[9] IUCN Niger – Delta Panel, 2013. “Sustainable Remediation and Rehabilitation of Biodiversity and Habitats of Oil Spill Sites in the Niger Delta. Main Report including recommendations for the future.” A report by the independent IUCN - Niger Delta Panel (IUCN-NDP) to the Shell Petroleum Development Company of Nigeria (SPDC). Gland, Switzerland:IUCN, pp 75.

[10] W. Elekwachi, O.N. Hycienth, F.O. Johnmark and C.J. Onyishi. 2009. “Oil Spill Incidents and Wetlands Loss in Niger Delta: Implication for Sustainable Development Goals.”*International Journal of Environment and Pollution Research*, vol. 7(1), pp.1-20.

[11] S.A. Odoemelam, 2005. “Bioaccumulation of trace elements in fish from Oguta Lake in Nigeria.” *Journal of Chemical Society of Nigeria*,vol. 30(1), pp. 18-20.

[12] F.A. Walter, R.I. Kingsly and W.Y. Allan. 2005. “Heavy metal concentrations and burden in the bivalves (Anadara (Senilia) senilis, Grassostrea tulipa and Perna perna) from lagoons in Ghana: Model to describe mechanism of accumulation/excretion.” *African Journal of Biotechnology*, vol. 2(9), pp. 280-287.

[13] A.A. Nwabueze, E.O. Nwabueze, and C.N. Okonkwo. 2011. “Levels of Petroleum Hydrocarbons and some Heavy Metals in Tissues of Tympanotonus fuscatusperiwinkles from Warri river of Niger Delta Area of Nigeria.”*Journal of Applied Sciences and Environmental Management*,vol. 15(1), pp. 75-78.

[14] S. Veerasingam, R. Venkatachalapathy, P. Raja, S. Sudhakar, V. Rajeswari, R. Mohamed Asanulla, R. Mohan, and P. Sutharsan. 2011. “Petroleum Hydrocarbon Concentrations in Ten Commercial Fish Species along Tamilnadu Coast, Bay of Bengal, India.” *Environmental Science and Pollution Research*,vol. 18(4),pp. 687–93.

[15] International Chemometrics Society, 2006. Definitions.

[16] E.N. Ezekiel, A.I. Hart, and J.F.N. Abowei, 2011. “The Physical and Chemical Condition of Sombreiro River, Niger Delta, Nigeria.”*Research Journal of Environmental and Earth Sciences*, vol. 3(4), pp. 327-340.

[17] M. Sehgal, A. Garg, R. Suresh, andP. Dagar. 2012. “Heavy metal contamination in the Delhi segment of Yamuna basin.”*Environmental and Monitoring Assessment*,vol. 184(2), pp. 1181–1196.

[18] V.K. Singh, K.P. Singh, andD. Mohan. 2005. “Status of heavy metals in water and bed sediments of River Gomti-a tributary of the Ganga River.” *India Environmental Monitoring Assessment*, vol. 105, pp. 43–67.

[19] Standard Methods for the Examination of Water and Wastewater (1999). American Public Health Association, *American Water Works Association*, Water Environment Federation,pp. 1-541.

[20] American Public Health Association (APHA) 1998. *Standard methods for the evaluation of water and waste waters*. 20th Ed. Wahington DC. American Public health.

[21] L.H. Keith. 1996. “*Compilation of EPA’s Sampling and Analysis Methods.*” 2nd ed. Lewis Publ./CRC Press, Boca Raton, Fla.

[22] C.E. Ebere, E.A. Ihionu, A.W. Verla, andN.P. Ebosie. 2017. “Physicochemical Properties of Palm Oil and Soil from Ihube Community, Okigwe, Imo State, Nigeria.”*International Letters of Natural Science*, vol. 62, pp 35-49.

[23] Brian A. Schumacher.2002. *Methods for the Determination of Total Organic Carbon (Toc) In Soils and Sediments. Ecological Risk Assessment Support Center*, Office of Research and Development, US. Environmental Protection Agency. pp. 1-25.

[24] A.A. Odewande, andA.F. Abimbola.2008. “Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria.”*Environmental Geochemistry and Health*, vol. 30, pp. 243–254.

[25] E.N. Verla, A.W. Verla, and C.E. Ebere.2017. “Pollution Assessment Models Of Soils In Portharcourt City, Rivers State, Nigeria.”*World News of Natural Sciences* (WNOFNS), vol. 12, pp. 1-23.

[26] A.A. Ansari, I.B. Singh, andH.J. Tobschall. 1999. “Status of anthropogenically induced metal pollution in the Kanpur-Unnao industrial region of the Ganga Plain, India.”*Environmental Geology*, vol. 38, pp. 25–33.

[27] Y.D. Jing, Z.L. He, andX.E. Yang.2007.“Effects of pH, organic acids, and competitive cations on mercury desorption in soils.”*Chemosphere*, vol. 69(10), pp. 1662–1669.

[28] B.A. Butler. 2009.“Effect of pH, ionic strength, dissolved organic carbon, time, and particle size on metals release from mine drainage impacted

streambed sediments."*Water Research*, vol. 43(5), pp. 1392–1402.

[29] J. Pérez-Esteban, C. Escolástico, A. Moliner, andA. Masaguer, 2013."Chemical speciation and mobilization of copper and zinc in naturally contaminated mine soils with citric and tartaric acids", *Chemosphere*, vol. 90(2), pp. 276–283.

[30] G. Darko, M. Dodd, M.A. Nkansah, Y. Aduse-Poku, E. Ansah, D.D. Wemegah and L.S. Borquaye. 2017."Distribution and ecological risks of toxic metals in the topsoils in the Kumasi metropolis, Ghana."*Cogent Environmental Science*,vol. 3, pp. 1-15.

[31] U.W. Forstner,W. Calmano. 1993. "Sediment quality objectives and criteria development in Germany."*Water Science Technology*, vol. 28, pp. 307-316.

[32] D.L. Thomilson, J.G. Wilson, C.R. Harris, D.W. Jeffrey. 1980. "Problem in the assessment of heavy metals levels in estuaries and the formation of a pollution index."*Helgoland Marine Research*, vol. 33, pp. 566-575

[33] G. Muller. 1981. "Die schwermetallbelstung der sedimente des neckars und seiner nebenflusse: Eine estandsaufnahme."*ChemikerZeitung*, vol. 105, pp. 157-164.

[34] J. Li. 2014. "Risk Assessment of Heavy Metals in Surface Sediments from the Yanghe River, China."*International Journal of Environment Research and Public Health*, vol. 11, pp. 12441-

[35] A.W. Verla, E.N. Verla, C.E. Amaobi, C.E. Ebere. 2018. "Water Pollution Scenario at River Uramurukwa Flowing Through Owerri Metropolis, Imo State, Nigeria."*International Journal of Applied Scientific Research* (IJASR), vol. 3(3), pp. 40-46.

[36] S.M. Sakan, D.S. Dordevic, D.D. Manojlovic,P.S. Predrag. 2009. "Assessment of heavy metal pollutants accumulation in the Tisza River sediments." *Journal of Environmental Management*,vol. 90, pp. 3382–3390.

[37] J. Shafi, Z.S. Mirza, N. Kosour and M. Zafarullah. 2018."Assessment of Water Quality and Heavy Metals Contamination of River Ravi in Pakistan." *Pakistan Journal of Analytical and Environmental Chemistry*,vol. 19(2), pp. 169–180

[38] C.E. Duru, I.P. Okoro, and C.E. Ebere. 2017. "Quality Assessment of Borehole Water within Orji Mechanic Village Using Pollution and Contamination Models."*International Journal of Chemistry, Material and Environmental Research* (IJCMER), vol. 4(3), pp. 123-130.

[39] L. Hakanson. 1980. "An ecological risk index for aquatic pollution control, a sedimentological approach."*Water Research*, vol. 14, pp. 975-1001.

[40] Hydrology Project Training Module. 1999. "Major Ions in Water." Training module # WQ – 28, pp 1-41.

[41] G. Fipps. 2017. "Irrigation Water Quality Standards and Salinity Management."*Texan A&M Agrilife Extension service*, pp 1-17.

[42] P. Rengasamy, A. Marchuk.2011. "Cation ratio of soil structural stability (CROSS)". *Soil Research*, vol. 49(3), pp. 280-285.

[43] R. Lieffering. 2013. "Feilding Wastewater Treatment Plant Upgrade – Sodium and Potassium Irrigation Risk Assessment."*SAR Report For Manawatu District Council (MDC) Final*, pp 1-9.

[44] I. Rafiq. 2000. "*Evaluation of Soil Quality. Soil, water and bioenergy resources*." Ohio State University, South Centers. Assessed 31/03/2019.