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ASSESSMENT OF EFFECT OF SANDMINING ACTIVITIES ON PHYSICOCHEMICAL PROPERTIES AND METAL CONCENTRATIONS OF SURFACE WATER OF WARRI RIVER, NIGER DELTA, NIGERIA

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ABSTRACT

The Warri River in Niger Delta, Nigeria is one River in which indiscriminate and commercial sand mining activities have been taking place in recent times. Thus, this study was carried out to assess the effect of sand mining activities on physicochemical properties and metal concentrations of surface water of the Warri River, Niger Delta, Nigeria. Water samples were collected from six sand mining sites along the Warri River between January and December, 2016. The physicochemical properties and heavy metal concentrations of water samples were determined following the methods of the American Public Health Association. The result showed that electrical conductivity, turbidity, total suspended solids, total solids, salinity, total hardness, biochemical oxygen demand and the heavy metals (Cd, Cr, Cu, Pb, Mn, Ni and Fe) exceeded the World Health Organization (WHO) maximum permissible values. Temperature, pH, total dissolved solids, alkalinity, sulphate, nitrate, chloride, dissolved oxygen, chemical oxygen demand, calcium, magnesium, sodium, potassium and Zn were within their respective WHO maximum permissible values. Health risk assessment indicated no adverse non-carcinogenic risk, whereas there was a potential carcinogenic risk associated with metals in the water while quality index values indicate unsuitability of the water for drinking purposes.

Keywords**:** Sandmining, Warri River, Physicochemical properties, Metals, Water quality index

INTRODUCTION

Water is a major resource on planet earth and occupies three-forth of the earth's surfaces. Approximately, 97% of the water in the earth are saline water contained in the oceans while about 3% of the water in the earth is fresh water contained in lakes, rivers and ground water from which human and animals get their water supply (Al-Ghamdi *et al*., 2014). About 70% of the 3% earth's fresh water is housed in ice, glaciers, permafrost and snow covers while the remaining 30% is ground water in deep and hard to reach aquifers (Mishra and Dubey, 2015). Only about 0.25% of the earth fresh water is surface water contained in rivers, ponds, dams, streams and lakes (El-Dessouki and Ettouney, 2002; Kalogirou, 2005; Eltawil *et al*., 2009). Rivers are the main fresh and surface water resources for man. People in coastal areas use water for many purposes, including irrigation of agricultural lands, transportation, fishing, power generation, recreation, domestic and industrial purposes (Wetzel, 2009). However, the quality of river waters is deteriorating due to the plethora of anthropogenic activities such as river sand mining, industrialization, urbanization, agricultural activities, transportation and indiscriminate waste disposal among others which affects their physicochemical properties (An *et al*., 2004; Gupta*et al*., 2011; Dimowo, 2013).

River sand mining is the practice of excavating sand from the river bed (Langer, 2003; Ashraf *et al*., 2010). River sand mining is a flourishing multi-billion-dollar business because sand and gravel constitute the second highest raw material used on earth after water (UN Comtrade, 2014). Although, sand is a paramount importance as society expands and develops, previous studies have revealed that in-stream sand mining can reduce water quality, degrade the channel bed and banks and threaten the existence of the aquatic ecosystem as well as impact the environment and socioeconomic activities of coastal dwellers (Kondolf, 2008; Ashraf *et al*., 2011; Ahmad *et al*., 2012; Shaji *et al*., 2014; Tesi *et al*., 2018). The Warri River is a major River in Niger Delta of Nigeria and is one river in which indiscriminate sand mining business has been taking place in recent times. Limited information has been accorded to the impact of sand mining activities on the overall quality of the River water and its suitability for drinking purposes. Although, there are reports on water quality of the River arising from activities other than sand mining operations. This study is a sequel to our earlier report where a detailed assessment of the socioeconomic impacts of the river sand mining was published (Tesi *et al*., 2018). Hence, this present study aimed to provide information on the physicochemical properties and metal concentrations of surface water around sand mining areas of the Warri River.

MATERIALS AND METHODS

Description of Study Area

The study area is Warri River in Niger Delta, Nigeria. Detailed descriptions of the study area have been documented elsewhere (Tesi *et al*., 2018). The river has a total length of 136 km and stretches between Latitudes $5^{0}21^{l}$ - $6^{0}00^{l}$ N and Longitudes $5^{0}24^{l}$ - $6^{0}2^{l}$ E (Aghoghovwia, 2011). The Warri River originates from Utagba-Uno town in Ndokwa West Local Government Area of Delta State, flows southwards and emptied its water into the Atlantic Ocean (Egborge, 1994). The lithological unit of the Warri River includes the Ameki formation in the upstream of the River and is made up of coarse grained sand and gravels and the Agbada formation that comprised sandy and clay soils that are carried from the upstream to the midstream and downstream of the River (Mogborukor, 2007). The area has a tropical equatorial climate with an extended wet season that reign between April and October with a break in the month of August. The mean annual rainfall is 2509mm (NiMET, 2016). A map of the study area is presented in Figure 1.

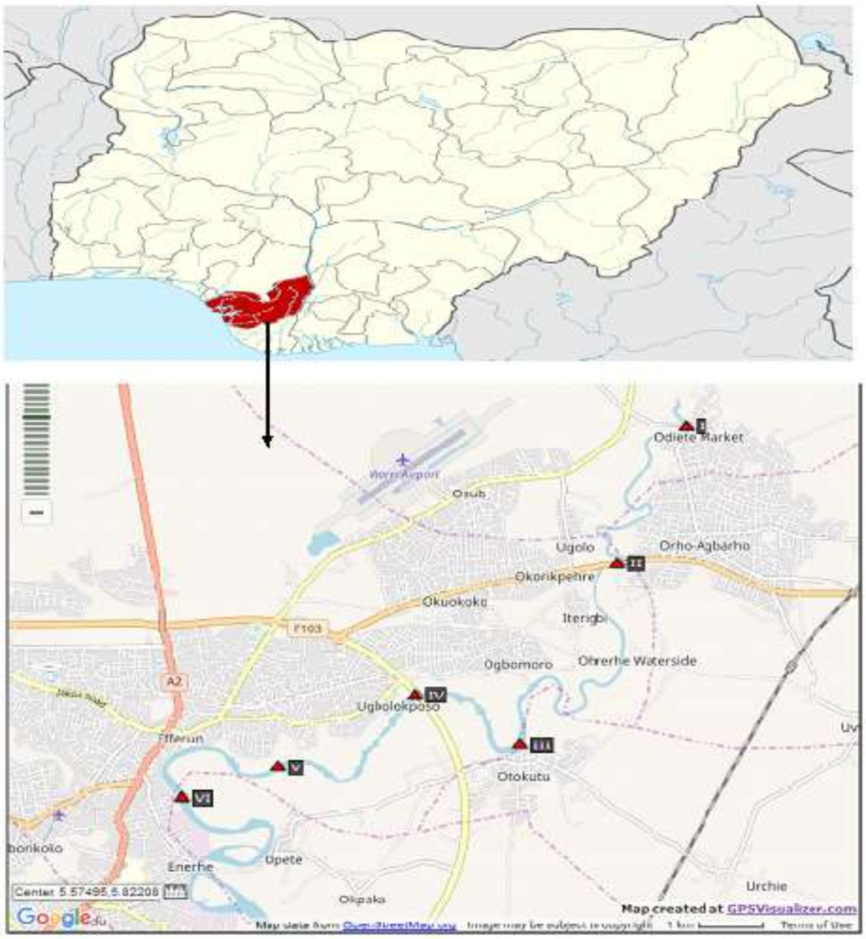

Fig. 1: Map of study area indicating sampling points

Sampling locations and sample collection

Water samples were collected from six sand mining locations along the Warri River shown above.At each sampling point, five grab water samples were collected and mixed together to form a composite. The collection of water samples was done on a monthly basis for a period of one year beginning from January to December, 2016. Thus, a total number of 72 water samples were collected. The collected samples were stored in a cooler containing ice and delivered on the same day of collection to the laboratory for analysis.

Determination of physico-chemical properties and metals concentration of water samples

The physico-chemical properties (pH, electrical conductivity, turbidity, total suspended solids (TSS), chloride, nitrate, sulphate, alkalinity, salinity, total hardness, dissolved oxygen

(DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD)) and metal levels (calcium, magnesium, sodium, potassium, cadmium, lead, chromium, copper, nickel, manganese, zinc and iron) of the water samples were determined in accordance with standard methods by APHA (2006).

Health Risk Assessment of metals in water samples

The non-carcinogenic and carcinogenic risk of metals exposures were evaluated using the two major exposure routes: ingestion and dermal contact. The non-carcinogenic risk was calculated as hazard index using equations (1) to (4) while the carcinogenic risk was calculated as total cancer risk using equations (5) to (7) adopted from USEPA (1989), USEPA (2011) and Wu *et al.* (2009).

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + \text{HQ}_{\text{dermal}} \quad (1)$$

$$\text{HQ} = \frac{CDInc}{RfD} \quad (2)$$

$$\text{CDI}_{\text{ing-nc}} = \frac{C \times \text{IngR x EF x ED}}{\text{BW x AT}_{nc}} \quad (3)$$

$$\text{CDI}_{\text{dermal-nc}} = \frac{\text{C x SA x Kp x ET x EF x EDx CF}}{\text{BW x AT}_{nc}} \quad (4)$$

$$Total\ Cancer\ Risk = ILCR_{ing} + ILCR_{inh} + ILCR_{derm} \quad (5)$$

$$\text{ILCR}_{\text{ing}} = \frac{C \times IngR \times EF \times ED \times CF \times SFO}{BW \times ATca} \quad (6)$$

$$\text{ILCR}_{\text{derm}} = \frac{C \times SA \times Kp \times ET \times EF \times ED \times CF \times SFO \times GIABS}{BW \times ATca} \quad (7)$$

where, HQ is the hazard quotient, $\text{CDI}_{\text{ing-nc}}$ and $\text{CDI}_{\text{derm-nc}}$ are chronic daily intake for ingestion, and dermal contact respectively. ILCR_{ing} and $\text{ILCR}_{\text{derm}}$ are the incremental lifetime cancer risk through ingestion and dermal contact respectively. The definitions and values of all other variables used in the risk assessment are provided in Tables 1 and 2 respectively.

Generally, HI value greater than 1 indicates that there is adverse non-carcinogenic risk of metal exposure while total cancer risk values greater than 1.0×10^{-6}indicate that there is carcinogenic risk from metals.

Table 1: Values of variables for estimation of human health risk assessment

Parameters	Unit	Definition	Child values	Adult values	References
C	mg/L	Metals concentration in water			
ABS_d	-	Dermal absorption factor for metals		0.001	USEPA, 2011
BW	kg	Average body weight	15	60	Iwegbue *et al.* (2018)
Kp	cm/h	Dermal permeability coefficient	See Table 2		USEPA (1989)
ED	Year	Exposure duration	6	30	USEPA (2011)
EF	d/yr	Exposure frequency	350	350	USEPA (2011)
ET	h/day	Exposure time	1	0.58	USEPA (1989)
CF	L/cm^3	Conversion factor	0.001		USEPA (2011)
GIABS	-	Gastrointestinal absorption	See Table 2		USEPA (2011)
IngR	Litres	Water ingestion rate	1.8	2.2	USDOE (2011)
SA	cm^2	Skin surface area	6600	18000	USEPA (1989)
ATnc	D	Averaging time for non-carcinogenic	ED x 365		USDOE (2011)
ATca	d	Averaging time for carcinogenic	LT x 365		USDOE (2011)
LT	Year	Lifetime	55 years		WHO (2018)

Table 2: Toxicological parameters of the investigated metals used for health risk assessment

Metals	RfD_{Ing}	RfD_{Derm}	CSF_{ing} (mg/kg/d)	GIABS	Kp
Cd	0.5	0.025		0.025	1.0×10^{-3}
Pb	1.4	0.42	5.0×10^{-3}	0.013	4.0×10^{-3}
Cr	3	0.075		0.04	2.0×10^{-3}
Cu	40	8		1	1.0×10^{-3}
Ni	20	0.8		1	4.0×10^{-3}
Mn	24	0.96	8.5×10^{-3}	1	1.0×10^{-3}
Zn	300	60		1	6.0×10^{-3}
Fe	700	140		1	1.0×10^{-3}
Reference	USEPA (1989)	USEPA (1989)	USDOE, 2011	USEPA, 2011	USEPA (1989)

Quality Index of the water samples

The water quality index was evaluated using the equation as defined by Cude (2001):

$$WQI = \frac{\sum QiWi}{\sum Wi}$$

but,

$$\text{Qi} = \text{Quality rating of each parameter} = \frac{Vactual - Videal}{Vstandard - Videal} \times 100$$

$$Wi = Unit\ weight = 1/Si$$

where:

V_{actual} = Actual value of the water quality parameter obtained from laboratory analysis

V_{ideal}= ideal value of this parameter in pure water (V_{ideal} = 0 except pH = 7 and DO = 14.6 mg/L)

$V_{standard}$ = Recommended WHO standard of the water quality parameter.

Qi = Quality rating of ith parameter for a total of n water quality parameters

Si =Standard permissible value for nth parameter

WQI values were categorized into five, according to Tyagi *et al*. (2013): 0-25 (Excellent water quality), 26-50 (Good water quality), 51-75 (Poor water quality), 76-100 (Very poor water quality) and >100 (Unsuitable for drinking).

Data Analysis

Data obtained for physico-chemical parameters and metals content were expressed as Mean ± SD. Data were analysed using analysis of variance (ANOVA). Values were considered statistically different at $p < 0.05$. All statistical analyses were performed using SPSS version 20 (SPSS, Inc - Chicago, Illinois, USA).

RESULTS AND DISCUSSION

Physico-chemical properties and metals concentration of water samples

The results of the physico-chemical properties of the water samples during the entire study period are shown in Table 3.

Table 3: Physico-chemical properties and heavy metals concentrations in water samples

	Sites					
Parameters	**I**	**II**	**III**	**IV**	**V**	**VI**
Temperature (°C)	26.0±2.80 (21.4-30.9)	26.3±2.47 (22.1-30.4)	29.3±3.22 (24.7-38.6)	29.1±2.91 (23.9-37.1)	26.9±2.62 (23.0-31.8)	27.0±2.74 (23.3-32.6)
pH	7.12±0.75 (5.58-8.66)	7.28±0.57 (6.61-8.45)	7.61±0.74 (6.52-8.71)	7.59±0.81 (6.67-8.55)	7.43±0.81 (5.83-8.47)	7.42±0.76 (5.97-8.36)
Turbidity (NTU)	25.9±13.1 (9.63-46.9)	26.6±13.5 (9.73-54.3)	81.8±10.4 (27.3-190)	83.4±9.22 (33.8-195)	47.0±5.45 (17.3-83.9)	44.9±4.27 (17.6-84.9)
TSS (mg/L)	9.71±1.95 (5.04-18.9)	9.95±4.76 (5.02-17.7)	53.6±5.18 (13.2-88.4)	52.2±5.75 (13.7-92.0)	20.5±1.14 (8.82-39.6)	18.8±4.02 (8.07-38.7)
TDS (mg/L)	7.35±3.17 (3.67-14.1)	7.38±3.57 (3.70-15.2)	27.7±6.16 (20.3-39.5)	27.1±4.93 (3.96-37.4)	14.5±5.94 (6.44-27.9)	14.8±5.71 (7.17-27.4)
Chloride (mg/L)	37.5±3.19 (11.4-84.2)	41.3±3.57 (11.6-89.2)	184±14.1 (60.5-436)	185±12.4 (74.5-397)	81.7±6.89 (21.0-195)	82.7±6.37 (20.3-230)
Nitrate (mg/L)	9.15±0.81 (3.63-20.5)	9.11±0.82 (3.72-18.5)	42.5±3.15 (13.4-85.4)	40.6±3.00 (13.7-80.2)	31.9±3.22 (5.01-116)	29.6±2.68 (4.68-95.4)
Sulphate (mg/L)	1.54±1.21 (0.38-3.86)	1.77±1.31 (0.38-3.99)	8.76±3.63 (3.35-13.0)	8.87±2.12 (4.82-12.8)	2.60±0.39 (0.89-8.04)	2.84±0.67 (0.9-8.13)
Alkalinity (mg/L)	7.17±2.41 (2.14-19.6)	8.15±2.51 (2.56-21.2)	47.2±4.83 (15.0-147)	49.7±5.41 (13.4-178)	16.9±1.33 (4.70-45.4)	17.3±1.42 (4.20-46.4)
Salinity (mg/L)	0.88±0.06 (0.24-1.99)	0.84±0.09 (0.17-1.52)	4.29±0.85 (0.92-11.0)	4.40±0.43 (0.63-11.4)	1.91±0.29 (0.19-6.33)	1.95±0.43 (0.15-5.12)
Total Hardness (mg/L)	74.9±9.90 (31.5-154)	68.5±13.7 (30.4-155)	253±24.2 (96.7-452)	245±29.7 (103-467)	137±19.7 (61.8-289)	201±19.5 (61.9-756)
DO (mg/L)	5.33±0.34 (2.19-8.56)	5.82±0.07 (2.38-8.34)	4.09±0.77 (2.49-7.41)	4.20±0.25 (4.11-4.63)	4.67±0.25 (4.20-5.65)	4.83±0.13 (4.16-5.70)
BOD (mg/L)	3.54±1.59 (1.37-5.92)	3.29±1.20 (1.54-5.57)	3.11±0.86 (2.39-3.87)	3.30±0.10 (2.61-4.05)	4.06±2.54 (1.96-7.82)	4.22±1.90 (2.50-6.36)
COD (mg/L)	9.26±2.05 (4.24-19.3)	10.4±3.86 (4.52-18.6)	21.5±2.11 (11.5-32.6)	24.0±4.23 (14.7-38.8)	13.8±2.86 (5.16-25.2)	13.9±2.45 (6.37-26.9)
Calcium (mg/L)	4.68±1.79 (2.22-8.46)	5.77±2.88 (2.28-10.1)	16.2±1.16 (5.51-37.8)	17.9±2.96 (6.06-38.1)	9.56±1.43 (3.21-19.9)	9.00±2.01 (3.32-19.1)
Magnesium (mg/L)	2.54±0.73 (1.43-3.45)	2.41±0.65 (1.57-3.83)	10.7±1.82 (6.37-19.5)	10.7±0.89 (6.21-18.9)	4.85±0.71 (2.21-9.50)	4.40±0.54 (1.79-9.86)
Sodium (mg/L)	7.01±2.39 (3.24-11.1)	6.73±2.20 (3.48-9.30)	20.5±4.19 (9.98-38.4)	20.6±4.05 (9.21-38.9)	12.5±1.92 (6.78-26.4)	12.2±0.85 (6.36-24.1)
Potassium (mg/L)	2.72±0.02 (0.71-8.52)	2.69±1.04 (0.94-7.60)	15.3±2.17 (3.44-26.0)	15.0±1.39 (3.57-26.4)	7.50±1.08 (0.81-15.0)	7.44±0.98 (1.35-15.6)
Cadmium (mg/L)	0.004±0.001 (0.003-0.005)	0.004±0.001 (0.003-0.005)	0.05±0.04 (0.01-0.09)	0.07±0.01 (0.05-0.08)	0.01±0.003 (0.002-0.008)	0.01±0.002 (0.003-0.009)
Lead (mg/L)	0.07±0.06 (0.003-0.15)	0.16±0.02 (0.13-0.18)	0.05±0.03 (0.02-0.07)	0.04±0.03 (0.01-0.09)	0.08±0.05 (0.03-0.15)	0.12±0.04 (0.07-0.16)
Chromium (mg/L)	0.19±0.02 (0.15-0.21)	0.25±0.08 (0.20-0.30)	0.12±0.04 (0.06-0.17)	0.13±0.06 (0.05-0.18)	0.15±0.05 (0.09-0.21)	0.17±0.09 (0.07-0.26)
Copper (mg/L)	0.28±0.07 (0.23-0.40)	0.33±0.14 (0.26-0.45)	0.25±0.13 (0.11-0.38)	0.23±0.13 (0.09-0.40)	0.20±0.16 (0.008-0.40)	0.23±0.18 (0.01-0.45)
Nickel (mg/L)	0.16±0.07 (0.05-0.51)	0.19±0.02 (0.07-0.42)	0.23±0.15 (0.05-0.40)	0.25±0.20 (0.06-0.51)	0.20±0.13 (0.05-0.36)	0.30±0.21 (0.06-0.57)
Manganese (mg/L)	0.67±0.20 (0.48-0.84)	0.82±0.04 (0.79-0.85)	0.16±0.10 (0.03-0.24)	0.17±0.10 (0.07-0.31)	0.44±0.36 (0.07-0.84)	0.52±0.40 (0.08-0.83)
Zinc (mg/L)	2.74±0.18 (0.01-6.74)	2.64±0.16 (0.03-5.97)	3.97±3.66 (0.23-9.54)	3.64±3.19 (0.27-7.89)	2.83±2.76 (0.007-6.74)	2.83±2.80 (0.007-6.94)
Iron (mg/L)	1.19±0.47 (0.001-3.20)	1.22±0.52 (0.001-3.74)	1.02±1.01 (0.04-2.48)	1.05±1.02 (0.04-2.97)	1.18±1.41 (0.002-3.18)	1.26±1.44 (0.003-3.74)

Results are expressed as Mean±SD (Range)

The mean water temperature varied slightly (26.0 to 29.3 °C). There was no significant difference ($p>0.05$) in temperature readings for all locations. Temperature is reportedly a stable ecological factor in shallow water bodies in West Africa (Longhurst, 1958). The slight variation/relative uniformity of water temperature readings may thus be attributed to the shallow nature of the Warri River and the regular tidal motion of the water, thereby ensuring complete mixing of the water (Okoye and Iteyere, 2014).The water temperature values obtained in this study are below the permissible range of 35-40 ^oC set by the World Health Organization (WHO) (WHO, 2011) and hence, the water is suitable for sustaining aquatic lives. The mean values obtained for temperature in this study are similar to those obtained by Udom and Mbajiorgu (2006) for water samples subjected to sand mining from Abak stream in Akwa-Ibom State of Nigeria.

The water pH values showed a narrow range of 7.12 to 7.61.The pH values obtained in this study are within theWHO (2011) and Standard Organization of Nigeria (SON) (SON, 2007) permissible pH range of 6.5-8.5.The immediate surrounding environment of a River can influence the average pH of the water; for instance, while Egborge (1994) reported alkalinity of the Warri River, Okoye and Iteyere (2014)recorded acidic pH values in the same Warri River but around Ubeji axis, and acidity was attributed to the salinity regime of the environment. Similarly, Aghoghovwia (2014) recorded that most parts of the Warri River were acidic, and the acidic nature was attributed to the influx of humic substances into the River via proliferation of markets around those parts of the River. This implies that sand mining activity does not influence the pH of the River water towards acidity and hence, dissolution of pH-dependent contaminants such as metals is not expected to be significant.

The mean turbidity values of the water samples studied ranged from 25.9 to 83.4 NTU. The turbidity of the water samples was higher than the 5 NTU set by WHO (2011). The generally high turbidity may be due to the sand mining operations, which involves the dispersion of suspended particles. High turbidity decreases the ability of water to transmit light. Primary productivity in the river may be reduced because of high turbidity (Krishnamoorthi *et al*., 2011). For Total suspended solids (TSS), the values ranged from 9.71 to 53.6 mg/L and exceeds the maximum permissible value (5.0 mg/L) for drinking water set by WHO (2011). A significant difference ($p<0.05$) in TSS level was observed across the sampled sites. However, the River water is not considered as wastewater since it has TSS values less than 100 mg/L (TSS values greater than 100 mg/L but less than 220 mg/L is classified as medium waste water (Akan *et al.,* 2008).Sand mining activities reportedly increase turbidity and TSS in River water (Ako *et al.,* 2014). Hence, the observed variation could be attributed to the fact that sand mining operations are concentrated more at points III and IV.

The mean total dissolved solids (TDS) values of the water samples studied ranged from 7.35 mg/L at sampling point I to 27.7 mg/L at sampling point III. Like TSS, a similar trend was observed. However,the TDS of the water samples are lower than the maximum permissible limit of 500 mg/L set by WHO (2011) and SON (2007). The mean values obtained for TDS in this study were similar to those reported by Udom and Mbajiorgu (2006), Seiyaboh *et al*. (2013) and Okorafor *et al*. (2013) but were lower than those reported by Peck and Rohasliney (2013). The chloride concentration (ranging from 37.5 – 185 mg/L), nitrate concentration (ranging from 9.11 – 42.5 mg/L), sulphate concentration (ranging from 1.54 – 8.87 mg/L) and alkalinity (ranging from 7.17 to 49.7mg/L) were all below their respective WHO (2011) limits of 200mg/L, 50mg/L, 200mg/L and 50mg/L, respectively.However, salinity (ranging from 0.84 – 4.40 mg/L) and total hardness (ranging from 68.5 - 253 mg/L) exceeded their limits of 0.5-1.0 mg/L and 150 mg/L.

The DO levels of the water samples in this study ranged from 4.09 to 5.82 mg/L. The maximum value of DO was observed at sampling point II while the minimum value was observed at sampling point III. The low DO values obtained in this study may be attributable to high organic matter content and the low flow of water. Higher flowing waters have higher DO levels because of the water movement at the air-water interface (Radwan *et al*., 2003; Peck and Rohasliney, 2013). While high organic matter in water limits primary production and the senescence of phytoplankton increases microbial respiration that leads to the depletion of dissolved oxygen (Prasanna and Ranjan, 2010; Mandal *et al*., 2011). For BOD, the mean values ranged from 3.11 mg/L to 4.22 mg/L. Vowels and Connel (1980) and Mara (1983) classified aquatic pollution with respect to BOD as follows: unpolluted (BOD < 1.0 mg/L), moderately polluted (BOD ≥ 2 ≤ 9 mg/L) and heavily polluted (BOD > 10 mg/L), while the maximum permissible limits set by WHO (2011) is3.0 mg/L. Based on these classifications, all sampling points can be classified as being moderately polluted and were also higher than the WHO limit. The consequences of high BOD are same for low DO and hence, aquatic lives will be under serious threat in this River.

The mean values of COD of the water samples ranged from 9.26 to 24.0 mg/L. The maximum permissible value of COD set by WHO (2011) is 100 mg/L. The COD values obtained in this study were below the maximum permissible COD value while COD values were higher than their corresponding BOD values. This may be attributable to the fact that some organic substances which are not oxidized biologically can be oxidized chemically as COD measures all the oxidizable organics while BOD measures the oxygen available for biological activities (Okorafor *et al*., 2013). Moreover, the higher COD values in comparison to BOD values could be as a result of high organic matter of total suspended solids and total solids from the sand mining activities in the Rivers. The COD values obtained in this study were higher than those reported by Okorafor *et al*. (2013).

Metal concentrations in water samples

Geographical and geological differences as well as varying activities around Rivers can affect the amount of metals present in them (Olatunji and Osibanjo, 2012). Furthermore, the availability and toxicity of many metals in their aquatic environment can be altered depending on the pH of the water body (Ogunfowokan *et al*., 2005). Thus, the concentrations of the studied metals in surface water of the Warri River may be a function of the prevailing pH and seasonal variations.

The mean concentrations of Cd in the water samples in this study ranged from 0.004 to 0.07 mg/L. A significant difference ($p<0.05$) was observed across the studied sites. The significant variation in Cd concentrations could be attributed to differences in rural/urban effluents along the River course at the various sampling points (Okoye and Iteyere, 2014). The concentrations of Cd observed in this study were greater than the permissible values of 0.001 mg/L set by WHO (2011).

The concentration of Pb in the water samples ranged from 0.04 0.16 mg/L. There was a significant difference ($p<0.05$) across the sampled locations. The relatively high Pb concentration at point VI could be attributed to high automobile emissions from vehicular exhaust along the ever busy East West road. The mean concentrations of Pb obtained in this study were above the permissible value of 0.01mg/L set by SON (2007) and WHO (2011). This implies potential significant health risks associated with consumption of this water at all the various sampled locations. The concentrations of Pb recorded in this study were lower than those reported by Okorafor *et al*. (2013) but were in agreement with others in literatures for different River systems (Egereonu *et al*., 2005; Agbaire and Obi, 2009; Hong *et al*., 2014).

The mean concentrations of Cr in these water samples ranged from 0.12 to 0.25 mg/L. The highest and lowest concentrations were observed at sampling points II and III respectively. The concentrations of Cr observed at all sampling points were higher than the WHO (2011) and SON (2007) permissible value of 0.05 mg/L. Similar concentrations were reported by Hong *et al*. (2014) while lower concentrations were reported by Kaizer and Osakwe (2010).

The mean concentrations of Cr, Cu, Ni, Mn and Fe in the water samples ranged from 0.12 to 0.25 mg/L, 0.20 to 0.33 mg/L, 0.16 to 0.30mg/L, 0.16 and 0.82 mg/L and 1.05 to 1.26 mg/L, respectively. These concentrations were all greater than their respective limits (0.05 mg/L for Cr, Cu, Ni and Mn, and 0.03 mg/L for Fe) set by WHO (2011). Variation in concentrations of these metals can be largely attributed to urbanisation of the surrounding River as well as the degree of sand mining operation at the different sampled points.The presence of Mn in water in excess of 0.2 mg/L makes water distasteful to drinking but no specific toxic effect (Nwachukwu *et al*., 1989).

The mean concentrations of Zn in the water samples ranged from 2.64 to 3.97 mg/L in all sites. The concentrations of Zn obtained were below the standard values of 5.0mg/L and 3.0 mg/L set by WHO (2011) and SON (2007) respectively, but, sampling points III and IV had Zn values higher than the 3.0 mg/L set by SON. Higher concentrations of Zn in water from different Rivers have also be reported in literatures (Kaizer and Osakwe, 2010; Olatunji and Osibanjo, 2012).

Health Risk of metals in water samples

The non-carcinogenic and carcinogenic health risk associated with the exposure of humans to metals in the sandmining areas of the Warri River are presented in Table 4. The HQ_{ing} and HQ_{derm} for children were greater than those of adults in all the sites while the contribution from the ingestion pathway (HQ_{ing}) was higher than that of the dermal (HQ_{derm}) exposure pathways. The HQ values of the individual metals for the two exposure routes were less than 1.

The hazard index (HI) values for children in this study were higher than those of adults. However, the HI values for both adults and children exposure were below 1 indicating that there is no adverse non-carcinogenic risk associated with exposure to metals in the water of the sand mining areas. The contribution of metals to the total hazard index followed the order Cr > Pb > Cd > Cd > Mn > Ni > Zn > Cu > Cu > Fe. The values obtained for hazard index in our study were similar to those obtained by Li and Zhang (2010) for water from upper Han River, China, Muhammad *et al*. (2011) for surface and groundwater of Kohistan region, northern Pakistan, Asare-Donkor *et al.* (2016) for water of Bosomtwe Crater Lake in Ghana, Masok *et al*. (2017) for water from Richard Bay in South Africa and Qu *et al*. (2018) for water from Wen-Rui Tang River, China.

The total cancer risk was calculated for Cr and Pb only because the value of cancer slope for the other metals could not be assessed. The incremental lifetime cancer risk via ingestion and dermal contact routes for children were greater than that of adult. This may be due to smaller body weight of children and smaller skin surface area (Tesi *et al*., 2016; Iwegbue *et al*., 2018).

Table 4: Hazard index and Total cancer risk of metals in water of sand mining areas of Warri River

	ADULT			CHILD			ADULT			CHILD		
	HQIng	HQDerm	HI	HQIneg	HQDerm	HI	ILCRIng	ILCRDerm	Total Cancer Risk	ILCRIng	ILCRDerm	Total Cancer Risk
Cd	1.04E-02	9.88E-04	**1.14E-02**	3.41E-02	2.50E-03	**3.66E-02**						
Pb	1.31E-02	8.26E-04	**1.39E-02**	4.27E-02	2.09E-03	**4.48E-02**	8.55E-05	2.25E-02	2.26E-02	5.09E-04	5.99E-02	6.04E-02
Cr	1.18E-02	4.49E-03	**1.63E-02**	3.87E-02	1.14E-02	**5.01E-02**	7.52E-03	4.82E-04	8.00E-03	4.47E-02	1.29E-03	4.60E-02
Cu	1.34E-03	3.17E-05	**1.37E-03**	4.37E-03	1.34E-05	**4.39E-03**						
Ni	2.34E-03	1.11E-03	**3.45E-03**	7.65E-03	2.81E-03	**1.05E-02**						
Mn	4.07E-03	4.83E-04	**4.56E-03**	1.33E-02	1.22E-03	**1.46E-02**						
Zn	2.19E-03	1.15E-04	**2.30E-03**	7.15E-03	2.92E-04	**7.45E-03**						
Fe	3.48E-04	8.25E-06	**3.56E-04**	1.14E-03	1.25E-04	**1.26E-03**						
Total	**4.56E-02**	**8.06E-03**	**5.36E-02**	**1.49E-01**	**2.04E-02**	**1.70E-01**	**7.60E-03**	**2.30E-02**	**3.06E-02**	**4.52E-02**	**6.12E-02**	**1.06E-01**

The total cancer risk of metals in the water samples of the study area exceeded the target risk of 1 × 10^{-6}signifying a high potential carcinogenic risk to humans from exposure to metals in the water of the study area. The total cancer risk values obtained in this study were similar to those reported for water of Bosomtwe Crater Lake in Ghana (Asare-Donkor *et al*., 2016).

Quality Index of Water Samples

The water quality index (WQI) is a unique rating for depicting the composite influence of the determined water quality parameters and communicates water quality information to the public on the overall quality status of water in a single term (Tyagi *et al*., 2013).The WQI values obtained in this study (not shown) ranged from 401 to 5967. Based on the WQI categorization earlier defined, the WQI values of the water samples obtained in this study indicates that water from Warri River around the different sand mining areas is unsuitable for drinking purposes, since the WQI values all exceeded100.

CONCLUSION

This study was carried out to assess the physicochemical properties of surface water around sand mining areas of Warri River, Niger Delta, Nigeria.The result of the study showed that electrical conductivity, turbidity, total suspended solids, total solids, salinity, total hardness, biological oxygen demand (BOD) and the metals (Cd, Cr, Cu, Pb, Mn, Ni and Fe) were above their World Health Organization (WHO) maximum permissible value while temperature, pH, total dissolved solids, alkalinity, sulphate, nitrate, chloride, dissolved oxygen (DO), chemical oxygen demand (COD), calcium, magnesium, sodium, potassium and Zn were within or below their respective World Health Organization (WHO) maximum permissible value.The result of the water quality index indicated that the River water in the sand mining area was unsuitable for drinking.

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