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Environmental pollution loads on surface water chemistry and potentially ecological risks of inland aquatic ecosystem in South-Eastern State, Nigeria

E. A. Ubuoh¹, F. U. Nwogu^{1*}, C. C. Ofoegbu¹ and P. C. Chikezie²

Abstract

The study assessed water chemistry of Nworie inland aquatic ecosystem in South eastern, Nigeria from January, 2020 to December 2022. Water samples were taken from the upper, middle, and lower river at 200 m interval. Data collected were subjected to multivariate analyses. Results of physicochemical tracers indicated mean CaCO_3 , Ca^{2+} & Chemical Oxygen Demand (COD) to be 172.8 mg/l, 103.1 mg/l, 16.50 mg/l respectively above the World Health Organisation (WHO) critical limits, while turbidity (NTU), dissolved oxygen (DO) mg l^{-1} , chloride (Cl^-) mg/l, Magnesium (Mg) mg/l, Sodium (Na) mg/l, sulphate (SO_4^{2+}) mg/l, nitrate (NO_3^-) mg/l, potassium (K) mg/l and phosphate (PO_4^{3-}) were below the limits. Heavy metals (mg/l) showed mean values viz: Cd^{2+} (0.053), Cr^{2+} (0.049), Fe^{2+} (0.443), Ni^{2+} (0.024), and Pb (0.787) which were all above some critical global limits, except for Cu^{2+} and Zn^{2+} and in decreasing abundance: $\text{Pb}^{2+} \geq \text{Fe}^{2+} \geq \text{Cu}^{2+} \geq \text{Zn}^{2+} \geq \text{Cd}^{2+} \geq \text{Cr}^{2+} \geq \text{Ni}^{2+}$. Physicochemical tracers and elements in water correlated in both positive and negative directions. Principal component analysis (PCA) showed significant loads of PC_3 ; CaCO_3 , NO_3 , COD, DO, Ca, PO_4 , Cu, Fe, Zn, PC_2 ; moderate loads of SO_4 , Cl, & Na originating from complex human activities. Contamination factor (C_f), recorded high for cadmium while pollution load & ecological risk recorded low in decreasing order: $\text{Cr}^{2+} \geq \text{Zn}^{2+} \geq \text{Ni}^{2+} \geq \text{Cd}^{2+} \geq \text{Pb}^{2+} \geq \text{Cu}^{2+} \geq \text{Fe}^{2+}$ with contamination degree in order of: Lower River (LR) \geq Upper River (UR) \geq Middle River (MR) and low risk index. Continuous monitoring of human activities along the whole River is important to mitigate any aquatic ecosystem damage for water quality sustainability.

Keywords Aquatic ecosystem, Ecosystem risk, Multivariate approaches, Water chemistry

Introduction

Water quality deterioration, lack of access to safe and clean water are among the serious environmental problems challenging many countries of the world today. Water quality deterioration, lack of access to safe and

clean water are among the serious environmental problems challenging many countries of the world today. For instance, globally, not less than 4 billion people lack access to safe drinking water, or water that is perceived as unsafe to drink without point-of-use treatment systems (Biswas and Tortajada 2019). It is estimated worldwide that in every eight persons, one is at high risk of biochemical oxygen demand caused water pollution; one in six is at high risk from nitrogen caused pollution, and one in four from phosphorous pollution (International Food Policy Research Institute & Veolia, 2015). In the whole South Asian region with a population of more than 1.7 billion people, it is highly difficult to come across a

*Correspondence:

F. U. Nwogu
fredianuchenna@gmail.com

¹ Department of Environmental Management and Toxicology, Michael Okpara University of Agriculture, Umuahia, Umudike, Abia, Nigeria

² Department of Biochemistry, College of Natural Sciences, Michael Okpara University of Agriculture, Umudike, Abia, Nigeria

city, or town or even village with majority of people who confidently think the tap water safe to drink without fear of health ailments. In developed countries such as France and United States, only but few people are drinking directly from the tap because of issues of quality and sociocultural conditions. (Biswas et al. 2018).

The reason for this problem cannot be untied from the ever-increasing population increase, industrialization and urbanization (Wang and Choi 2019). As a result of the persistent water quality challenge, the United Nations in its July 2016 assembly deemed it pertinent to declare human access to consumption fit clean and safe water, a fundamental human right (UN, 2016). This declaration was a conscious effort at ensuring that nations realize and take very seriously the issues of provision of safe drinking water for their citizenry, especially with various research reports globally indicating increased ecological risk and pollution load in rivers. For instance Zhuang et al. (2021) reported increased metal(oid) pollution load and ecological risk in Danjiang river in China, Zhi-hua et al. (2021) also reported surface water pollution from BOD, COD, heavy metals and antibiotics in yellow river China. Kumar et al. (2023) recently reported surface water pollution load by heavy metals and ecological risk in Gomti river in India. Large quantities of wastes have been reported to be discharged into river regimes (Badr et al. 2013; Amany et al. 2019), alongside complex anthropogenic activities that go on, and more predominantly practiced in Sub-Saharan Africa, South eastern, Nigeria. Accordingly, among the anthropogenic activities/sources are the issues of untreated industrial effluents, inappropriately disposed municipal wastes, as well as agricultural runoff which subsequently contribute to the pollution of aquatic ecosystems and deterioration of water quality (UN, 2016; Hasan et al. 2019; Uddin and Jeong 2021; Ubuoh et al. 2022a).

River regimes are essential, vulnerable and notable for their fresh outlook, as well as its ecosystem services to man which includes water resources provision for domestic, industrial, agricultural, as well as the sustenance of man and aquatic life (Farah et al. 2002). These rivers are also notable for its function as an alternative water sources for consumption purposes such as drinking, domestic, and irrigation purposes (Iwegbue, 2012; Daso- Osibanjo 2018). However, developing countries such as Uganda, Kenya, Cameroon and developed countries such as Canada, Russia and United States with largest and extensive surface water bodies respectively (www.google.com/developed and developing countries with largest surface water) are usually vulnerable to pollution. Pollution of water bodies occurs when its acceptability for consumption and its quality is compromised by humans anthropogenic activities (Umeham 2000;

Oloyede et al. 2003; Amadi et al., 2003; Ekaise and Anyasi 2005; Akaninwor and Egwim 2006). Within the past decade, reports have shown that among the leading causes of river and water quality deterioration are the excessive discharge of a combination of myriads of organic and inorganic hazardous chemicals emanating from industrial, agricultural and domestic sources (Arafat Rahman et al. 2021). It is opined that river regimes are constantly heavily imparted with pollutants arising from incessant sewage and industrial waste disposal with myriad of manmade induced operations that subsequently alter a combination of physical, chemical and microbiological qualities (Koshy and Nayar 1999). Water resources have been reported worldwide to come under serious threats from human pollution viz technological inventions and inadequate agricultural drainage system into surrounding surface waters (Jin et al. 2020a; Jin et al. 2020b; Ubuoh et al. 2022b).

According to Whitehead et al. (2018); Hasan et al. (2019), Arafat Rahman et al. (2021), several industrial units are mostly sited along river side and bank or other water bodies in consideration of proximity to waste and effluent disposal. These industrial point sources may with the absence of strict regulation and monitoring by environmental regulatory bodies, directly or indirectly discharge untreated effluents into the surrounding rivers, causing their pollution. This practice becomes an unavoidable evil for some of the industrial units who lack efficient effluent treatment plants (Oluwole et al., 2018). These solid wastes from the municipalities and effluents from industrial operations have been reported to adversely impact the quality of river sources for decades past (Islam et al. 2013; Islam et al., 2018; Hasan et al. 2019; Uddin and Jeong 2021). This is owing to the fact that most of these industrial wastes are heavily laden with heavy metals.

The presence of transition metals within the ecosystem in such a toxic amount is a significant concern with deleterious risk to all living creatures; man, animal and plants inclusive (Liu et al. 2019; Neckel et al. 2021; Silva et al. 2021). A substantial concentration of heavy metals in sediments and water ecosystem have notable ecological impacts ranging from reduction of soil fertility and agricultural productive potential (Raklami et al. 2021) to their environmental behaviour in terms of their transfer, fate, persistence and associated health risks to consumers in the food pyramid. Thus, the effect of heavy metals is hugely dependent on their environmental behavior, their specific chemical structure as well as their binding state. These factors are key in influencing their bioavailability, mobility, and toxicity to organisms and aquatic ecosystem (Akçay et al. 2003; Wildi et al. 2004; Wang and Tessier 2009). These river systems are eventually

laden with severe pollutants and its corresponding challenging environmental implication and subsequent biological and hydrological risk potentials (Whitehead et al. 2018; Uddin and Jeong 2021), together with toxic chemicals in untreated industrial wastewater which cannot be removed (Kant, 2012; BIWTA, 2019),

Nworie river micro-watershed In South eastern Imo state is one of the most polluted inland rivers in Nigeria, where human activities such as indiscriminate dumping of wastes, bathing, sand mining, fishing, washing, farming and other activities are predominant (Akubugwo and Duru 2011; Ahiarakwem and Onyekuru 2011). Some of these activities may have led to the pollution of the river regimes with heavy metals and alteration of its physico-chemical characteristics (Okoye et al. 2011; Yadar and Kumar 2011; Ubuoh et al. 2017a, b; Ubuoh et al. 2022a). Need worry is the fact that there is shortage or limited data pertaining the potential environmental pollution loads and ecological risk on Nworie Inland aquatic ecosystem, despite its ecosystem services to the dwellers

within the settlement, who primarily depend on the river for domestic/human utilization. Hence, it is imperative to regularly investigate the physicochemical characteristics and the heavy metal pollution load of Nworie Inland river micro-watershed, as well as the associated pollution sources and ecological risks using combination of pollution and ecological risk index factors such as pollution load, associated ecological risk and ecological risk factor, contamination factor, degree of contamination and geo-accumulation index, for water sustainability and survival of man and his environment.

Methodology

Study area

Nworie surface water micro-watershed is in Owerri of Imo state Southeastern geopolitical zone of Nigeria (Fig. 1). Imo state is situated on latitude 4°45'N, 7°15'N and longitude 6°50'E, 7°25'E. Imo state covers a total land area of about 5100 sq.km (Okorie et al. 2012), with a human density ranging within 230–1400 humans per

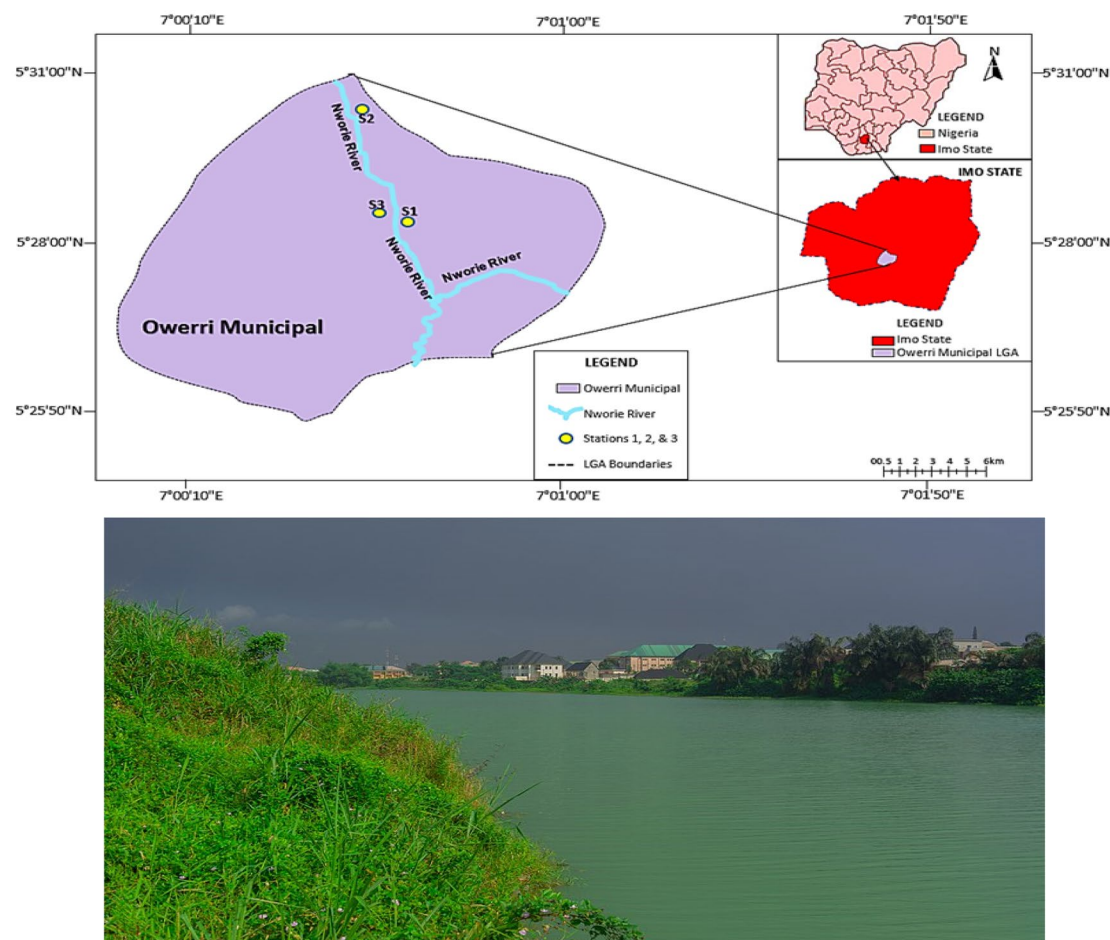


Fig.1 Digital and real time (350×220 pixels) map of Nworie river showing the relief and catchment areas in the study locations

Table 1 Surface water sampling points and coordinates

Locations	Co-ordinates Of the study locations	Human activities
Egbeada = UR	N 05° 29' 10.9", E 007° 01' 43.5"	Mining and excavation of sand, waste dumping, farming, metal scraps etc
Amakohia = MR	N 05° 30' 56.6", E 007° 00' 59.2"	Mechanic workshop, waste dumping, farming and road construction etc
Umezuruike Hospital = LR	N 05° 29' 16.1", E 007° 01' 30.0"	Effluent discharges from hospital, washing of cars, bathing etc

square kilometer. According to National Bureau of Statistics, the entire populace in Imo state hovers around 329,563 (NPC 2006). Nworie River is heavily influenced with human activities such as: farming, harvesting food washing, and cassava fermentation, cloth washing, swimming, and bathing, fishing, defecation, and animal washing, timbering, sand excavation and gravel exploration, washing of vehicles, industrial discharge of sewage, waste discharge, drinking water and transportation (Agudozie et al. 2019; Ubuoh et al. 2022a, b).

Sampling and preparation of inland water samples

Nworie inland water was sampled for laboratory analyses to evaluate the chemistry and the concentration amount (Table 1).

A total of 72 samples comprising of 24 samples from each of the 3 locations (Table 1) and collected over a period of 2 years (January, 2020 to December, 2022) on a monthly bases and the bulk mean used for laboratory analyses. The samples were fetched from the above locations at the Egbeada (i.e. upper river course), Amakohia (i.e. middle river course) and Umezuruike hospital (i.e. lower river course) courses of the river respectively, using properly labelled 1 L plastic bottles. The bottles were cleaned and washed with chromic acid. During the collection, water was sampled at surface level by bending over the sampling bottles against the top most water current and allowing the water passage unperturbed into the bottle mouth until the bottle is filled up. The fetched samples were filtered with a Whatman filter alongside a 45 micro-meter fibre glass. 3.3 ml of HNO₃ was added at the field to the water samples to a pH of 1.5 and shaken to mix and was allowed to stand for atleast 16 h prior to analyses so as to allow potentially adsorbed metals to redissolve and to serve as a form of preservation. The samples were painstakingly handled so as to avoid sample contamination and was kept under a temperature 4 °C before being taken to the laboratory for total recoverable (inorganically and organically bound dissolved and suspended) metal analysis (Tables. 2 and 3).

Determination and laboratory analyses

for physicochemical and heavy metal parameters

Water samples collected were analysed for Physicochemical properties viz: pH, turbidity (NTU) hardness

Table 2 Descriptive table for ecological risk factor (Er)

Classes	Indications
$Eri \leq 40$	low potential ecological risk
$40 \leq Eri < 80$	moderate potential ecological risk
$80 \leq Eri < 160$	considerable potential ecological risk
$160 \leq Eri < 320$	high potential ecological risk
$Eri \geq 320$	very high ecological risk

(Hakanson, 1980)

Table 3 Descriptive table for ecological risk index (Ir)

Classes	Indications
$Ir < 150$,	low ecological risk
$150 \leq Ir < 300$	moderate ecological risk
$300 \leq Ir < 600$	considerable ecological risk
$Ir > 600$	very high ecological risk

(Hakason, 1980)

expressed as CaCO₃ (mg l⁻¹), chemical oxygen demand (COD) mg l⁻¹, dissolved oxygen (DO) mg l⁻¹, chloride (Cl⁻) mg/l, Magnesium (Mg) mg l⁻¹, Sodium (Na) mg l⁻¹, sulphate (SO₄²⁻) mg l⁻¹, Calcium (Ca²⁺) mg/l, nitrate (NO₃⁻) mg/l, potassium (K) mg/l and phosphate (PO₄³⁻) mg/l. An immersed insitu readings of water samples for hydrogen ion concentrations was taken with the use of Multi-meter pH device in line with the procedure adopted by Dirisu et al. (2016). The Absorptiometric Method was applied in the determination of the turbidity and calibrated using the 1000 NTU, 100 NTU and 10 NTU. Hardness (mg/l-CaCO₃) was analysed by EDTA-titrant and the calculation was hinged on the derivative by Lind (1979) and APHA (1995). Water hardness (CaCO₃) was estimated by Eq. (3) of Todd (1980) formula. The COD and DO were determined according to the methods used by Edet et al. (2020). The concentration of the following water parameters like Cl⁻, Ca²⁺, Mg²⁺, K⁺, Na⁺, NO₃⁻, SO₄²⁻ and PO₄³⁻ were determined using the Altman Analytik (Unicam939/959 model) spectrometer. In addition, certain preservative procedures such as

Chemical addition, refrigeration, freezing and pH control were used accordingly (EPA 2009).

Furthermore, determination of heavy metals from water samples culled from the Nworie Inland River was also carried out. 100 mls of the surface water samples were determined by placing a measuring cylinder in a digestion vessel (which is a beaker fitted with a watch glass that can support open vessel reflux action) with exactly 10 mLs of HCL and 3.3 ml of HNO₃ added into the digestion vessel containing the water sample bringing the proportion of HNO₃ to HCL to 1:3 and subjected to a hot plate to provide heat. The water was heat slowly for close to 25 min to attain a temperature of 85 °C so as to ensure that the water did not attain boiling point to avoid total digestion and ensure partial digestion. More proportionate concentrations of 3HCL and 1HNO₃ were further added to the evaporated digest of 20 mls volume and the beaker digest was covered with the fitted watch glass and further heated until the solution appeared clear and light. The resultant digest was then filtered and filtrate was made up to 100 mls after being kept to lose heat for 24 h kept for analysis of elements of concern. (Radojevic and Bashkin 1999; Ojekunle et al. 2016). The heavy metals for extraction such as: Chromium (Cr²⁺), Iron (Fe²⁺), Copper (Cu²⁺), Lead (Pb²⁺), Nickel (Ni²⁺), Cadmium (Cd²⁺), and Zinc (Zn²⁺), were all extracted with 0.1 mol of HCL solution according to the method described by Osiname and Kang (1973), APHA (1998). Analytik Jena Atomic Absorption Spectrophotometer (AAS) model no: Nova AA 800 was employed to evaluate the metals at adequate wavelength (Radojevic and Bashkin 1999; Bhatti et al. 2016; Ojekunle et al. 2016).

Quality control and assurance (QC/QA)

The use of Analytical Research-grade (AR) chemicals (Merck and Sigma-Aldrich, Germany) were ensured all through this study with no further purification or modification to them as the chemicals are in their pure form (99.9%). The chemicals used are primarily nitric acid and hydrochloric acid. About 1.15 M of dilute nitric acid (HNO₃) was initially used to clean the glass-ware before being washed with distilled water. All reagents and calibrations were made with Milli-Q water standards before analysis. All analyses were run in three replicates, and all stock solutions as well as references were stored at 4 °C prior to use. All quality assurance procedures were followed; including rigorous washing and cleansing procedures and blank levels of equipment monitoring etc.

Statistical analysis

The variation in water quality data set was analysed with the use of multiple variance statistics. A number of statistical analytical methods such as Analysis of variance

(ANOVA) to establish the degree of variation between and within the bulk means for the physicochemical tracers as well as the heavy metals respectively, while Duncan Multiple analysis was used to separate the bulk means and establish significant differences within and between the means for the physicochemical tracers and heavy metals respectively. Pearson correlation analysis was used to establish the closeness or relationship within and between physicochemical characteristics of Nworie river courses while Principle component analysis (PCA) was used to show the relationship existing among the major ions, identify the sources of the ions as well as the validity of the elements of concern. In addition, ecological risk measuring tools (Tables 2 and 3) were also deployed in a bid to generate a reliable result on the influence of human activities on the river chemistry, as well as the risk associated therein. Analysis was performed with the use of GenStat Release 9.2. Conclusion was drawn at $P \leq 0.05$ level of significance. Afterwards, a comparison of the results obtained from the field with the permissible environmental standards for heavy metals and physicochemical parameters for water was made in order to establish if there are exceedances.

Aquatic ecosystem risk assessment (AERA) techniques

Pollution load index (PLI)

The Pollution load index of each river location was evaluated with reference to Tomlinson et al. (1980):

$$PLI = \sqrt[n]{cf_1 \times cf_2 \times cf_3 \times \dots \times cf_n} \quad (1)$$

From the Eq. (1), n represents additive metals value in water, CF represents contamination factor. CF_n represents concentration of the metals in water/baseline values of the metal. Pollution Load Index is a very reliable tool that helps to evaluate heavy metal pollution level. Accordingly, a PLI number that is greater than one (>1) indicates “polluted” while PLI number that is less than one (<1) points to “no pollution” (Chakravarty and Patgiri 2009; Ubuoh et al. 2019; Ubuoh et al. 2021, 2022a, b).

Contamination factor and degree of contamination

Both contamination factor (C_f^i) and degree of contamination (Cd) can be used in estimating water contamination

$$C_f^i = \frac{C_s^i}{C_n^i}, \quad C = \sum_i^m C \quad (2)$$

where C_s^i is metal content I, C_n^i is the national criteria of metal I, reference number, or background level. Classes and indicators are as follows: C_f less than one (<1) indicates low contamination, $1 < C_f < 3$ indicates moderate contamination, $3 < C_f < 6$ indicates considerably contaminated and $6 < C_f$ shows very high contamination

Table 4 Mean \pm SD of the physicochemical characteristics of Nworie Inland river

Stations	pH	Turb	CaCO ₃	COD	DO	Cl	Ca	Mg	K	Na	SO ₄	NO ₃	PO ₄
Upper River (UR)	6.157 \pm 0.361 ^a	0.139 \pm 0.010 ^{ab}	168.3 \pm 12.583 ^b	5.800 \pm 0.263 ^b	0.137 \pm 0.012 ^b	48.03 \pm 11.12 ^a	63.10 \pm 12.43 ^b	10.81 \pm 1.255 ^b	2.333 \pm 0.611 ^{ab}	1.450 \pm 0.180 ^{ab}	1.167 \pm 0.144 ^b	0.360 \pm 0.151 ^c	0.500 \pm 0.087 ^a
Middle River (MR)	6.553 \pm 0.314 ^a	0.113 \pm 0.013 ^c	123.3 \pm 10.408 ^c	3.91 \pm 0.142 ^b	0.106 \pm 0.015 ^b	36.82/766 ^{bc}	73.8 \pm 7.718 ^{ab}	17.23 \pm 2.767 ^a	1.333 \pm 0.153 ^a	1.032 \pm 0.143 ^c	1.827 \pm 0.150 ^a	1.040 \pm 0.225 ^a	0.360 \pm 0.078 ^b
Lower River (LR)	5.827 \pm 0.283 ^c	0.169 \pm 0.036 ^a	226.7 \pm 20.817 ^a	39.79 \pm 4.415 ^a	0.836 \pm 0.173 ^a	31.74 \pm 3.353 ^c	172.4 \pm 7.501 ^a	18.70 \pm 1.566 ^a	3.333 \pm 1.832 ^c	1.650 \pm 0.325 ^a	1.660 \pm 0.121 ^a	0.627 \pm 0.352 ^{ab}	0.265 \pm 0.077 ^c
Mean	6.179	0.140	172.8	16.50	0.359	38.86	103.1	15.58	2.333	1.374	1.551	0.675	0.375
%Cv	5.2	16.1	8.8	15.8	28.0	1717	9.2	12.7	25.8	16.8	9.0	38.0	21.5
Se	0.321	0.023	15.28	2.601	0.101	690	9.49	1.973	0.603	0.231	0.139	0.257	0.081
WHO STD	6.5–8.5	1.00	50	4	> 4	400	75	50	10	200	200	50	5

Values with superscripts a, b, c shows statistical significance; different Superscript letters are interpreted as significantly different while similar superscript letters are interpreted as not significantly different

(Hakanson 1980). Classification of degree of contamination according to Hakanson (1980) as regards classes and indicators are as follows: $Cd < 8$ means low contamination level, $8 \leq cd < 16$ depicts moderate contamination level, $16 \leq cd < 32$ shows considerable contamination level and $32 \leq cd$ depicts Very high contamination level. (Tables 2 and 3)

Potential aquatic ecosystem risk assessment (PAERA)

Ecosystem risk factor (E_r^i) Ecosystem risk factor (E_r^i) is used to quantify expressly, contaminants with potential ecological risk. It was expressed by Hakanson (1980) as:

$$E_r^i = T_r^i C_f^i, \left(C_f^i = \frac{C_0^i}{C_n^i} \right) \quad (3)$$

where E_r^i is lone potential ecosystem risk factor, T_r^i is a factor that represents the toxicity response of a particular metal, C_n^i is the contamination factor, C_0^i is the concentration of metals in the environmental medium and C_n^i is a reference value for metals.

Ecological risk index (Ir)

$$I_r = \sum_i^n E_r^i = \sum_i^n T_r^i C_f^i = \sum_i^n T_r^i C_0^i / C_n^i \quad (4)$$

Results and discussion

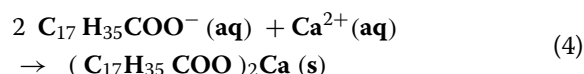
The physicochemical properties of Nworie Inland River

From Table 4, pH in the river ranged from 5.827 to 6.553, with the Lower River (LR) recording highest acidity that is significantly different from Upper River (UR) and middle River (MR) at $P \geq 0.05$, with the mean pH value of 6.179. The mean pH of the present study is slightly acidic than the pH in the reports of Ayode and Nathaniel (2018), Madina et al. (2016) and Oluyemi et al. (2010a, b), who reported pH of 6.95–7.88 in tropical man-made lake of south-western Nigeria, 6.6–7.8 in Dalanj area and 7.69 in Ife North L.G.A in Osun State, Nigeria where pH values ranged from 7.45 to 8.4 (WHO 2011; Ayers and Westcot 1994). The acidity observed in the lower course river could be from the medical waste discharge at the location (Ubuoh et al. 2017a, b; Ubuoh et al. 2021). The near neutral acidity observed in the middle (6.553) river is suggested to be due to the washing down of organic residues into the water (Jain and Agarwal 2012; Ubuoh et al. 2021). Similar ranges were reported for same river (5.70–7.20) by Ekhatior et al. (2011) and elsewhere within Edo State (Imoobe and Koye 2011; Anyanwu 2012). WHO, (2007) stated that low pH levels is capable of

facilitating corrosive characteristics, leading to drinking water contamination with adverse effect on its taste and appearance.

Turbidity ranged from 0.139 to 0.169 NTU. MR had the lowest value (0.139) while LR (0.169) had the highest value at $P \leq 0.05$ significant difference, with a mean of 0.140 NTU lower than the WHO limit of 1.00 NTU (WHO 2011). The mean turbidity of this study is at variant with result of Ayobahan et al. (2014) in Benin River, Nartey et al. (2012) in Accra and Chima et al. (2009) in Asata- Enugu whose findings were 4.33–6.11, 6.4–16.3 and 32.0–43.4 NTU respectively. The turbidity levels in the middle and lower rivers may be attributed to the presence of household municipal wastes and medical wastes dumped in the river (Ubuoh et al., 2012; Ubuoh et al. 2021).

Hardness as CaCO_3 recorded 226.7 mgL^{-1} in the LR, while the lowest value of 123.3 mgL^{-1} was observed in MR and were statistically different at $P \geq 0.05$ across the courses of the river, with a mean of 172.8 mg/l above the WHO standard of 100.0 mgL^{-1} (WHO 2011). Water hardness leads to rapid exhaustion of washing soap, and chiefly influenced by the presence of calcium and magnesium salts (Ca^{2+} and Mg^{2+}) (DWAf 1993). The value of the mean hardness in the present study exceeds that of the findings of Duru and Nwannekwu (2012) whose values were between 18.6 and 36.01 mg/l . Adeosun et al. (2016) reported a lower value of 7.0–50.4 in FUTA. The studies of Miyake et al. (2005), Arnedo-Penal et al. (2007) and Perkin et al. (2016) have correlated domestic hard water with increased eczema in children. Rivers with high value of hardness cannot lather with soap due to calcium stearate, with the chemical reaction according to Wikipedia (2022):



From the LR, the Chemical Oxygen Demand (COD) recorded the highest value of 39.79 mgL^{-1} , MR recorded the lowest value of 3.91 mgL^{-1} while UR recorded 5.800 mg/l with a mean of 16.50 mg/l below the 40 mg/l WHO/FME Standard (2003), and above the allowable (4 mg/L) limit of chemical oxygen demand for human drinking purpose in accordance with the set permissible limit of DoE (1997), WHO (2017a, 2017b), and DPHE (2019). The mean result of COD in this study is less than the observations of Ayobahan et al. (2016) who had reported values range of COD (19.14–115.16 mgL^{-1}) in Benin River, due to human activities within the catchments.

Dissolved oxygen (DO) ranged from 0.106 mgL^{-1} in the MR to 0.836 mgL^{-1} in the LR, having the mean value

of 0.359 mg/l below the >4.0 WHO/FME STANDARD (2003), and \leq the findings of Duru and Nwanekwu (2012) who reported DO content of 1.21–3.6 mg/L in a river and DO in River Tyśmienica ranging between 6.2 and 8.5 mg/L (Grzywna and Sender, 2021). Significant variations in COD and DO were observed at the three courses at $P \leq 0.05$. The low DO could be attributed to nearness to human activity such as, bathing, washing of cars, as well as farming within the area (Adeosun et al. 2016). In addition, low DO is also tied to dumping of solid wastes, sewage discharge and high level of defecation in the river bank (Ubuoh, 2010). The observed mean value of DO in this study was $<$ mean dissolved oxygen range (4.35–4.82 mg/l) of the Siluko River, southern Nigeria (Obboh and Agbala 2017), $<$ (4.5–6.4 mg/l) in Eleme River Chikere (Okpokwasili, 2001) $<$ (3.18–3.27 mg/l) in Eruvbi stream (Imoobe and Koye 2011) and $<$ (1.84–5.22 mg/l) lower zone of Ikpoba river (Ogbeibu and Edutie 2002). This could be as a result of discharge of increased levels of biodegradable and non-biodegradable matters into the river by the increased activities of humans (Obboh and Agbala 2017).

The highest chloride content (48.03 mgL⁻¹) was in upper river, while the lower river was having the lowest (31.74 mgL⁻¹), with the mean value of 38.86 mg/l, all varying statistically at $P \leq 0.05$. The mean of the chloride was not upto the 400 mg/l (WHO/FME Standard (mg/L) 2003). The findings were related to that of Agudozie et al. (2019) who reported 15–30 mgL⁻¹ in surface water of Nworie River. Accordingly, the mean value of Chloride in the present study is higher than 1.70 ± 0.279 , 4.68 ± 0.300 , 2.20 ± 0.78 , 4.79 ± 0.222 obtained in Otamiri River, Imo State, Nigeria (Adebayo et al. 2016), less than the observations of Oluyemi et al. (2010a, b), and Ogwo et al. (2014) who observed high values of chloride to be from 82–92 to 3.64–184.04 mg/L⁻¹ in rivers.

Calcium ranged from 63.10 to 172.40 mgL⁻¹, and varied significantly at $P \leq 0.05$, with a mean of 103.1 mg/l greater than the 75.00 mgL⁻¹ WHO permissible limit (WHO 2011). This finding is greater than the value of Ca obtained by Ayobahan et al. (2014) and Duru and Nwanekwu, (2012), who reported 0.10–1.49 mg/L⁻¹ and 0.73–2.64 mgL⁻¹. Again, Agudozie et al. (2019) reported a value of 5.1–7.57 mg/L from the same river. High level of calcium is capable of causing permanent hardness of the water and can impair its taste, resulting in gastrointestinal irritation (Agudozie et al. 2019).

Magnesium ranged from 10.81 to 18.70 mg/L, which were statistically the same across the sampling point at $P \leq 0.05$. The mean of the magnesium being 15.58 mg/l was lower than the 50.00 mg/L WHO limit in water (WHO 2011). The finding of Mg in this study is inconsistent with the findings of Duru and Nwanekwu (2012), and

Agudozie et al. (2019) who recorded Mg content in rivers to range from 0.01 to 0.31 and 0.176–0.268 mg/L respectively. Potassium concentration at the upper, middle and lower course river were 2.333, 1.333 and 3.333 mgL⁻¹, respectively, and varied significantly at $P \leq 0.05$. The mean value of the potassium concentration of the water was lower than the WHO limit (10 mgL⁻¹) (WHO, 2011). In addition, the result of potassium of the study is in contrast with Agudozie et al. (2019) and Ayobohan et al. (2014), who recorded 3.87–5.53 and 2.94–49.95 mgL⁻¹ in Nworie and Benin River respectively.

The sodium concentration in the lower river recorded the greatest number of 1.650, and lowest (1.023 mg/L) observed in middle river that varied differently at $P \leq 0.05$. In this study, the mean (1.374 mg/l) was below the finding of Agudozie et al. (2019), who reported 22.2–26.0 mg/L of Na in a river, and below the 200.0 mgL⁻¹ of WHO permissible limit in water (WHO 2011).

Sulphate ranged from 1.167 to 1.827 mgL⁻¹, with UR having the lowest value and MR recording highest value, with a mean of 1.551 mgL⁻¹ and varied significantly at $P \leq 0.05$. This observation is disagreement with the reports of Ogwo et al. (2014) who noted 12.85–15.85 mg/L of sulphate in a river, and the mean value of sulphate less than the 200 mg/L WHO limit in water (WHO 2011).

Nitrate in the middle river recorded the highest nitrate concentration of 1.040 mg/L, while the lowest concentration of nitrate (0.360 mgL⁻¹), was observed in the upper river, with a mean of 0.675 mg/L, below the 50.00 mg/L WHO limit (WHO 2011). This is within the findings of Duru and Nwanekwu (2012) and Ayobahan et al. (2016) who observed 0.10–0.40 and 0.93–1.18 mg/l of nitrate in rivers respectively.

Accordingly, the contents of sulphate, nitrates and chloride were low and similar values have been observed elsewhere in Edo State (Ogbeibu and Anagboso 2004; Imoobe and Koye 2011; Ekhator et al. 2011; Anyanwu 2012). According to Beauchamp (1953), African Inland waters are generally deficient in sulphate, because of their low amounts in the non-sedimentary rocks within drainage areas.

Phosphate values lies between 0.265 and 0.500 mgL⁻¹, with the upper, middle and lower course of the river recording 0.500, 0.360 and 0.265 mg/L respectively, and a mean of 0.375 mgL⁻¹. The mean value of Phosphate is lesser than 0.71–0.85 mg/l range of Phosphate in Ase, <0.34 – 0.41 mg/l in Agbarho, >0.10 – 0.13 mg/l in Ethiopie, <0.49 – 0.53 mg/l in Ekakpamre, and <0.71 – 0.90 mg/l in Afesere Rivers respectively (Kaizer and Osakwe 2010). The mean value of phosphate observed was above the 0.05 mg/L WHO limit in water (WHO 2011). An increased phosphate level is an indication of

pollution through eutrophication (Ubuoh et al. 2022a), usually facilitated by an increase in nutrient content of water (Sobczyński and Joniak 2013; Kowalik et al. 2014a, b; Neverova-Dziopak and Preisner 2015). The increase in phosphate amount is associated with indiscriminate waste disposal, agricultural drainage into rivers, application of pesticides and fertilizers with their corresponding capacities to pollute surface water (Mirzaei et al. 2016; Sun et al. 2016a, b; Grzywna and Bronowicka-Mielniczuk 2020).

Correlation matrix of physicochemical tracers

Table 5 shows a Pearson correlation matrix of closeness or relationship within and between physicochemical characteristics of Nworie river courses. Parameters showing r between (0.7) and 0.9 are taken to have a strong correlation, while parameters showing r between 0.5 and 0.7, are taken to be a moderately correlated (Helena et al. 2000). Again, when r is closer or nearer to +1 or −1, it tells that there is perfect linear relationship existing between the two parameters (Saliu et al., 2020).

From Table 5, correlation coefficient (r) ranged from − 0.09 (negatively correlated) to +1 (strongly correlated). There were significant association among the physicochemical parameters of Nworie river. Most of the physicochemical parameters strongly correlated with each other (Table 5). Negative and positive correlations existed between the contaminants of pH and Turbidity as can be seen with r value between parameters in the brackets (− 0.51), Cl (− 0.63), Mg (0.73), Na (− 0.70), SO_2^{4-} (0.95), NO_3 (1.00) and PO_3^{4-} (− 0.55) respectively. Turbidity are positively correlated with CaCO_3 (1.00), COD (0.91), DO

(0.90), Ca (0.84), K (1.00), Na (0.97), at 0.01 significance level, and Turbidity/ NO_3 ($r = -0.57$) at the 0.05 level of significance. Total hardness (CaCO_3) positively coexisted with COD (0.92), DO (0.92), Ca (0.86), K (1.00), Na (0.96) respectively at 0.01 level of significance, and negatively coexisted with NO_3 (− 0.54) at 0.05 level of significance. COD is positively coexisted with DO (1.00), leading to organic pollution of water due to wastes dumped in water (Ubuoh et al. 2022a), negate Cl (− 0.71), Ca (0.99), Mg (0.61), K (0.89), Na (0.78), and negate PO_3^{4-} (− 0.78) respectively. DO negatively coexisted with Cl (− 0.71), and positive with Ca (0.99), Mg (0.61), K (0.88), Na (0.77), and negate PO_3^{4-} (− 0.78) respectively. Cl negatively correlated with Ca ($r = -0.80$), Mg ($r = -0.99$), SO_2^{4-} ($r = -0.85$), and positively coexisted with PO_3^{4-} ($r = 0.99$) respectively. Ca positively correlated with Mg ($r = 0.71$), K ($r = 0.82$), Na ($r = 0.69$) and negate PO_3^{4-} ($r = -0.86$). Mg positively coexisted with SO_2^{4-} , NO_3 ($r = 0.91$; 0.68), and negate with PO_3^{4-} ($r = -0.97$) respectively. K positively associated with Na ($r = 0.98$) and negatively correlated with NO_3 ($r = -0.60$), Na negatively associated with NO_3 ($r = -0.75$). Ultimately, SO_2^{4-} positively associated with NO_2 ($r = 0.92$) resulting to acidity in water (Ubuoh et al. 2021), and negatively associated PO_3^{4-} ($r = -0.79$) respectively.

Heavy metal level in Nworie Inland River

The cadmium (Cd) concentration in Nworie River at the course streams ranges from 0.031 to 0.089 mgL^{-1} , with the MR having the lowest value and LR having the highest value, with a mean of 0.053 mgL^{-1} . (Table 6, Fig. 3). The mean values of Cd concentration in the water was

Table 5 Correlation Matrix of physicochemical characteristics of Nworie Inland Surface Water

Variable	pH	Turb	CaCO_3	COD	DO	Cl	Ca	Mg	K	Na	SO_2^{4-}	NO_3	PO_3^{4-}
pH	1												
Turb	− 0.51 ^a	1											
CaCO_3	− 0.48	1.00	1										
COD	− 0.10	0.91 ^b	0.92 ^b	1									
DO	− 0.09	0.90 ^b	0.92 ^b	1.00	1								
Cl	− 0.63 ^a	− 0.34	− 0.37	− 0.71 ^b	− 0.71 ^b	1							
Ca	0.04	0.84 ^b	0.86 ^b	0.99 ^b	0.99 ^b	− 0.80 ^b	1						
Mg	0.73 ^b	0.22	0.25	0.61 ^a	0.61 ^a	− 0.99 ^b	0.71 ^b	1					
K	− 0.54 ^a	1.00 ^b	1.00	0.89 ^b	0.88 ^b	− 0.30	0.82 ^b	0.18	1				
Na	− 0.70 ^b	0.97 ^b	0.96 ^b	0.78 ^b	0.77 ^b	− 0.11	0.69 ^a	− 0.02	0.98 ^b	1			
SO_2^{4-}	0.95 ^b	− 0.20	− 0.17	0.23	0.24	− 0.85 ^b	0.36	0.91 ^b	− 0.24	− 0.43	1		
NO_3	1.00 ^b	− 0.57 ^a	− 0.54 ^a	− 0.17	− 0.16	− 0.58 ^a	− 0.03	0.68 ^a	− 0.60 ^a	− 0.75 ^b	0.92 ^b	1	
PO_3^{4-}	− 0.55 ^a	− 0.44	− 0.47	− 0.78 ^b	− 0.78 ^b	0.99 ^b	− 0.86 ^b	− 0.97 ^b	− 0.40	− 0.21	− 0.79 ^b	− 0.49	1

^a means significant correlation at 0.05 level (2-tailed), while

^b means significant correlation at 0.01 level (2-tailed)

Table 6 Comparison of Heavy metals concentration of Nworie surface water to global regulatory standards limits

Station	Cd (mgL ⁻¹)	Cr (mgL ⁻¹)	Cu (mgL ⁻¹)	Fe (mgL ⁻¹)	Ni (mgL ⁻¹)	Pb (mgL ⁻¹)	Zn (mgL ⁻¹)
Upper River (UR)	0.078 ± 0.011 ^b	0.014 ± 0.006 ^b	0.020 ± 0.004 ^b	0.152 ± 0.00 ^b	0.037 ± 0.006 ^a	0.995 ± 0.179 ^a	0.024 ± 0.006 ^b
Middle River (MR)	0.062 ± 0.002 ^b	0.019 ± 0.015 ^b	0.078 ± 0.021 ^b	0.232 ± 0.064 ^b	0.033 ± 0.013 ^a	0.925 ± 0.099 ^a	0.024 ± 0.015 ^b
Lower River (LR)	0.178 ± 0.63 ^a	0.115 ± 0.074 ^a	0.805 ± 0.167 ^a	0.947 ± 0.153 ^a	0.003 ± 0.001 ^b	0.443 ± 0.073 ^b	0.129 ± 0.025 ^a
Mean	0.106	0.049	0.301	0.443	0.024	0.787	0.059
%Cv	12.7	86.7	37.1	21.5	33.5	16.0	31.2
Se	0.007	0.043	0.112	0.096	0.008	0.126	0.018
WHO LIMIT	0.003	0.10	1.00	0.03	0.02	0.01	3.0
SON	0.003	0.050	1.00	0.300	0.020	0.010	3.000
WPCL	0.003	0.020	1.00	0.450	0.020	0.010	4.250
EPA	0.010	0.050	1.00	0.500	0.020	0.050	5.000
EC	5.000	50.00	–	–	20.00	10.00	–

WHO, 2003/2011; SON 2007; WPCL 2004; EPA 2002; EC, 1998

WHO World Health Organization, SON Standard Organisation of Nigeria, WPCL Water Pollution Control Legislation, EPA Environmental Protection Agency (US), EC European Commission

above the 0.003 mgL⁻¹WHO limit in water (WHO, 2008), due to heterogeneous dumpsites (Ubuoh et al. 2017a, b; Ubuoh et al. 2021). The result of Cd in the present study is at variant with the observations of Edori et al. (2019) who recorded very low Cd in Elelenwo River in Rivers State, Nigeria. Accordingly, Edori and Iyama (2020a, b), reported 0.0–0.0008 ± 0.00 mg/L in Edagberi Creek, Engenni, Rivers State. Ogwo et al. (2014) reported 0–0.011 mg/L of cadmium in Igwi stream. High content of Cd in rivers can cause toxicity that is inimical to human health and threat to growth and development of environmental flora and fauna (Bennet-Chambers et al. 1999; Olmedo et al. 2013). cumulative Cd poisoning is capable of damaging the human kidney, liver, testes and prostate (Adelekan and Alawode 2011; Abdullahi et al. 2020). Excess Cd in the body can also result to loss of bone and muscle calcification atrophy, circulation problems, anaemia, and high blood pressure (Kabata-Pendias and Pendias 1993; Ubuoh et al. 2019). Associated diseases with Cd intake at high content are hematology and kidney dysfunction, cardiac and vascular neurology, procreative disorder, damage to hepatocytes and other important body parts (Tirkey et al. 2012).

The chromium (Cr) concentration values at the upper, middle and lower river were 0.014, 0.019 and 0.115 mgL⁻¹, respectively, and varied significantly at $P \leq 0.05$. Cr values recorded in Nworie river when compared with reports from related environments, showed higher values of Cr when compared to levels recorded in few rivers in the Niger Delta, Nigeria (Marcus and Edori 2016; Nwineewii et al. 2019; Ekpote et al. 2019; Edori and Iyama 2020a, b). The result of Cd in this study is in tandem with the observations of Ogwo et al. (2014) who recorded chromium values ranging from 0.011 to

0.013 mg/Lin the river. The mean value of the chromium (0.049 mg/L) was less than Cr 0.096 mg/ L, in river, Taiwan (Lin et al. 2017), and lower than the 0.1 mgL⁻¹ WHO limit in water (WHO 2008).

Copper (Cu) ranged from 0.020 to 0.805 mgL⁻¹ and the values at the upper, middle and lower river were 0.020, 0.078 and 0.805 mgL⁻¹ respectively. These findings were similar to 0.18–0.14 of copper in water as reported by Oluyemi et al. (2010a, b). The mean values of Cu in the present study: 0.301 mg/l is lower than the 1.000 mgL⁻¹ WHO limit in water (WHO, 2008), and less than Cu in the Houjing River water (Lin et al. 2017), Buriganga River (Bhuiyan et al. 2015), and Hindon River (Suthar et al. 2009), greater than the concentrations of Cu reported in Bomu and Oginigba Rivers located in Rivers State, Nigeria (Marcus and Edori 2016), and Asonye et al. (2007), who recorded no traces of Cu in the water sample sources examined.

Iron (Fe) ranged from 0.152 to 0.947 mg/L, with LR greater than UR and MR (which are statistically the same at $P \geq 0.05$) with a mean of 0.443 mg/L above the 0.03mgL⁻¹ (WHO 2008). The mean value is in contrast with the findings of Ayobahan et al., (2014) whose values were 0.52–2.62 mg/L of iron. The mean Fe of 0.443 in this study is greater than Iron (Fe) values (0.028–0.075 mg/L) in the Edagberi Creek (Edori and Iyama 2020a, b). Authors like Asonye et al. (2007), Haxhibeqiri et al. (2015) and Nwineewii et al. (2019) reported lower values of Fe in river than the present study. Although Iron (Fe) is invaluable in natural biochemical processes in humans (Edori and Iyama 2020a, b), it is known to have a toxicological effect on human tissues and organ when in excessive amounts (Abbaspour et al. 2014). The presence of iron in form of Fe³⁺ oxide in H₂O could damage the

gills of fishes, reduce the oxygen intake amount (Ogaga et al. 2018), and distort the normal respirational pattern of fishes in the river (Edori and Iyama 2020a, b). More so, excessive iron levels could result to organ failure in humans such as liver cancer, heart diseases, diabetes, liver cirrhosis, as well as infertility issues etc. (Kumar et al. 2017). In addition, higher amount of Fe in water leads to decoloration in water, water taste and odour, as well as cloth stains and corrosion of water pipe lines (Behera et al. 2012; Kumar et al. 2017). The symptoms of iron poisoning in water are fatigue, weakness, joint pain and abdominal pain (Jong-joo et al. 2019). The sources of iron pollution in the river are suspected to come from refuse dumps, runoff from metal scrape and medical wastes dumpsites.

Nickel statistically varied at $P \leq 0.05$ among the river courses, and ranging from 0.003 to 0.037 mg/L with a mean of 0.024 mg/L slightly above the 0.02 mg/L WHO permissible limit of potable water (WHO 2011), and less than Ni concentrations that ranged from 17 to 455 mg/L on surface water chemistry of Werii catchment, Tigray, Ethiopia (Haftu and Estifanos 2020). Nickel comes from discharges of industrial and municipal wastes into the river (Ubuoh et al. 2010, 2021; Zaigham et al. 2012; EFSA 2015). High dose of Nickel in drinking water has been reported to cause liver, lung and kidney diseases in animals like dogs, mice and rats, affecting their stomach and blood (Ishimatsu et al. 1995), as well as reducing their immune system, and inhibiting their reproduction and development (Chashschin et al. 1994; ATSDR 2005).

Lead (Pb) can find its way into the environment through either natural or anthropogenic sources, but chiefly from human induced sources (Adebanjo and Adedeji 2019). Some of the human induced sources of lead include batteries, particle emission inhibition equipment, dyes and coating paints, elastic tools, amalgams, polyvinyl chloride conduits, fossil fuels, cable concealments and insecticides etc. (Bytyç et al. 2018). Lead (Pb) levels in this study fell within 0.443–0.995 mg/L with LR less than UR and a mean value of 0.787 mg/L, greater than 0.02–0.19 of lead reported by Ayobahan et al. (2014), greater than the concentrations of Pb from Edagberi Creek (0.0006–0.003) (Edori and Iyama 2020a, b), and above the 0.010 mg/L⁻¹ WHO limit in water (WHO 2008). The inimical effect of high levels of Lead (Pb) in higher animals include acute damage to the brain, especially in adult and children, but most especially, obstruct the proper mental development of infants (Saheed and Abimbola 2021). Pb has also been reported to cause heart-related diseases (Kopper et al. 1988).

The LR recorded the highest zinc concentration (0.129 mg/L⁻¹) while the least concentration of zinc (0.024 mg/L) was recorded in both upper and middle

ivers, with a mean value of 0.059 mg/L. This finding was similar to the findings of Ayobahan et al. (2014), Ogwo et al. (2014) and Oluyemi et al. (2014) who recorded zinc values in the range between 0.17 and 1.49, 0.011–0.021 and 0.03–0.22 respectively. Zn concentrations of this study were less than those in Wiser and Elbe Rivers (Pache et al. 2008), and the recent researches like the Buriganga river (Bhuiyan et al. 2015), the Nakdong River (Chung et al. 2016), Yellow River (Yan et al. 2016), and Bortala River (Zhang et al., 2016c).

In a bid to determine the level of heavy metal chemistry in Nworie inland aquatic ecosystem, a standard comparison of data results with other global water standards was done. The mean concentration of Cd 0.053 mg/L was above WHO, SON, EPA, EC, and WPCL standard in Table 6. Cr was below SON, WHO, EPA, and EC but higher than 0.020 stipulated by WPCL (2004). Zn was lower than all the guidelines in Table 6. Pb was also above all the water guidelines except 10.00 mg/L given by EC (1998), Ni was slightly raised above SON, WPCL, WHO (0.020 mg/L) but below 20 mg/L by EC in the table above. While Fe in water sample were above the SON and WHO guidelines but below 0.500 and 0.450 mg/L given by EPA and WPCL respectively. Above all, the excessive concentration of heavy metals above the environmental standards in the study river could be connected to anthropogenic sources, which is in tandem with the findings of Bhuiyan et al. (2011) in lagoon and canal water in the Dhaka, Bangladesh Fu et al. (2014) in Jialu River, China.

The elemental concentrations in Nworie surface water therefore occurred in descending abundance: $Pb^{2+} \geq Fe^{2+} \geq Cu^{2+} \geq Zn^{2+} \geq Cd^{2+} \geq Cr^{2+} \geq Ni^{2+}$

Table 7 shows that Nworie river recorded relatively low level of selected heavy metals when compared to other rivers of the world. Although cadmium content was recorded in Nworie river but not in other rivers like wise As and Mn that were not indicated in the studied Nworie inland water.

Correlation matrix of heavy metals in inland surface water

Table 8 shows a correlation matrix of the heavy metals. A correlational matrix can help identify the source and transport of metals among heavy metals. (Suresh, et al. 2011; Wang et al. 2012), The correlation between the main metals indicated the presence of anthropogenic sources (Fu et al. 2014; Maanan et al. 2015). The inter-relationship between the heavy metal levels in Nworie inland aquatic ecosystem is presented in Table 8 and the closer the elements lines lay together; the stronger is the mutual correlation (Ter Braak and Smilauer 2002). The correlation relationship showed close positive association between Cd^{2+} and Fe^{2+} ($r=0.816$), Cd^{2+}/Pb^{2+} ($r=0.603$),

Table 7 A comparative global heavy metals concentrations of rivers to Nworie river

Rivers	Cu	Cd	As	Cr	Ni	Zn	Mn	Pb	Fe	Refs
Nworie River, Nigeria	0.301 (0.001–0.003)	0.053	–	0.049	0.024	0.059 (0.014–0.55)	–	0.787 (0.004–0.06)	0.443 (0.37–1.23)	This Study
Uruan River, Nigeria	–	–	–	–	–	–	–	–	–	Denise E. M. and John (2004)
Weihe River, Xian, China	(18.23–69.34)	–	(18.43–39.93)	(60.54–142.93)	(15.43–62.38)	(71.32–143.64)	(519.25–1212.79)	(15.62–36.39)	–	Ahamad et al. (2020)
Zijiang River, Hunan, China	(18.37–59.01)	–	(6.90–74.34)	(48.47–95.32)	(21.50–52.29)	(42.41–251.61)	(570.75–2106.73)	(12.70–104.32)	–	Zhang et al. (2018a, b)
Jialu River, China	(8.82–107.61)	–	(2.39–14.57)	(40.04–96.39)	(19.75–80.26)	(42.39–210.00)	NA	(14.79–51.17)	–	Fu et al. (2011)
Korotoa River, Bangladesh	76	–	25	109	95	NA	NA	58	–	Islam, et al. (2015)
Axios River, Greece	93	–	40	180	188	271	NA	140	–	Karageorgis et al. (2003)
River Po, Italy	90.1	–	NA	NA	16198.5	645	NA	98.5	–	Farkas et al. (2007)
Gomti River, India	245.33	–	NA	88.7	76.08	343.47	834.7	156.2	–	Singh et al. (2005)
Chenab River, Pakistan	(5.80–9.40)	–	NA	NA	NA	(11.7–50.5)	(245–851)	(2.4–32.4)	–	Hanif et al. (2016)
Almendaras River, Cuba	420.8	–	NA	23.4	NA	708.8	NA	189	–	Olivares-Rieumont et al. (2005)
Nile River Egypt	81	–	NA	274	NA	221	2810	23.2	–	Rifaat (2005)
South Platte River, USA	480	–	31	71	NA	3700	6700	270	–	Heiny, and Tate (1997)
Tees River, UK	76.9	–	NA	NA	NA	1920	5240	6880	–	Hudson-Edwards et al. (1999)

Table 8 Correlation matrix of heavy metals in surface water of nworie micro watershed

Element	Cd ²⁺	Cr ²⁺	Cu ²⁺	Fe ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺
Cd ²⁺	1.000						
Cr ²⁺	− 0.309	1.000					
Cu ²⁺	− 0.515 ^a	0.013	1.000				
Fe ²⁺	0.816 ^b	− 0.162	− 0.856 ^b	1.000			
Ni ²⁺	0.381	0.302	− 0.918**	0.700 ^b	1.000		
Pb ²⁺	0.603 ^b	0.005	0.185	0.319	− 0.239	1.000	
Zn ²⁺	0.681 ^b	− 0.236	− 0.916 ^b	0.940 ^b	0.712 ^b	0.062	1.000

^a Significant correlation at 0.05 p level

^b Significant correlation at 0.01 plevel

Cd²⁺/Zn²⁺ ($r=0.681$), Fe²⁺ /Ni²⁺ ($r=0.700$) and Fe²⁺ / Zn²⁺ ($r:0.940$) which were significant. While copper have negative relationship with Fe²⁺ ($r=−0.856$) and Zn²⁺ ($r:−0.916$) respectively. Iron (Fe²⁺) shows high positive association with Nickel (Ni²⁺) ($r=0.700$), Zinc (Zn²⁺) ($r=0.940$) respectively. Nickel (Ni) shows positive correlation with Zn²⁺ ($r=0.712$). Others showed a relatively weak correlation among themselves in the surface water. The significant positive correlations found between metals in the river may not have similar behaviors in other aspects, and this is in tandem with the findings of Nguyen et al. (2005) of Lake Balaton, Zhang et al. (2018a; b) in Zhanjiang Bay, China. Elements that correlated significantly did not necessarily originate from common source, or neither are the elements source and pathway dependently correlated (Jørgensen et al. 2005; Ma et al. 2016). The result is consistent with the finding of Li et al. (2017) who with the use of multivariate statistical tools that includes correlation, reported, Cd, Cu, Pb and Zn levels in soils to emanate from anthropogenic sources, while Cr and Ni chiefly come from natural processes such as from parent materials (Lian et al. 2019).

Principal component analysis (PCA) for Nworie inland surface water samples

Table 9 x-rays a varimax rotated PCA of the chemistry of Nworie river performed with SPSS 19.0. The PCA was used chiefly to show the relationship existing among the major ions, identify the sources of the ions as well as the validity of the elements of concern, according to the Bartlett's test (Ahamad et al. 2020). Principal Components, alongside their respective plots were harnessed and rotated in space (Tables 9, Figs. 2 and 3). Three factors in the study area with high eigen-values > 1 were harnessed (Figs. 4, 5), which totals 89.41% of the cumulative. Accordingly, Liu et al. (2003), Çiçek et al. (2019) classified “strong” (>0.75), “moderate” (0.75–0.50), and “weak” (0.50–0.30) in order of factor loadings values. The first principal component (PC1) shows upto 61% of the total

Table 9 Principal component analysis (PCA) for surface water samples

	PC ₁	PC ₂	PC ₃
pH	− 0.157	0.763	− 0.223
Turbidity	0.765	− 0.41	− 0.006
Hardness as (CaCO ₃)	0.923	− 0.334	0.046
COD	0.969	0.09	0.107
DO	0.987	0.022	− 0.02
Chloride	− 0.593	− 0.383	0.641
Calcium	0.973	0.181	− 0.041
Magnesium	0.521	0.74	− 0.016
Potassium	0.835	− 0.385	0.006
Sodium	0.542	− 0.18	0.796
Sulphate	0.187	0.842	− 0.314
Nitrate	− 0.24	0.932	0.075
Phosphate	− 0.53	− 0.738	− 0.195
Cadmium	0.944	0.039	0.265
Chromium	0.874	− 0.012	− 0.289
Copper	0.93	0.33	0.022
Iron	0.964	0.208	0.093
Lead	− 0.878	− 0.244	0.062
Zinc	0.952	0.149	0.159
Nickel	− 0.869	− 0.225	− 0.249
Total Eigenvector	12.191	4.184	1.506
% of Variance	60.953	20.922	7.532
Cumulative %	60.953	81.875	89.407

Values in bold make up the parameters with positive and negative loadings

variance and is characterized by highly positive loading values of turbidity (0.785), hardness (0.923), COD (0.969), DO (0.987) calcium (0.973), potassium (0.835), Cd (0.944), Cr (0.874), copper (0.93), iron (0.964), and zinc (0.952). Accordingly, high COD and low DO may suggest increased level of organic matter content and nutrients load in water (El-Gamel and Shafik 1985; EL-Naggar et al. 1998), while lead (− 0.878) and nickel (− 0.869) were negatively loaded. The loading in PC₁ may be as a result of the use of agricultural chemicals like pesticides,

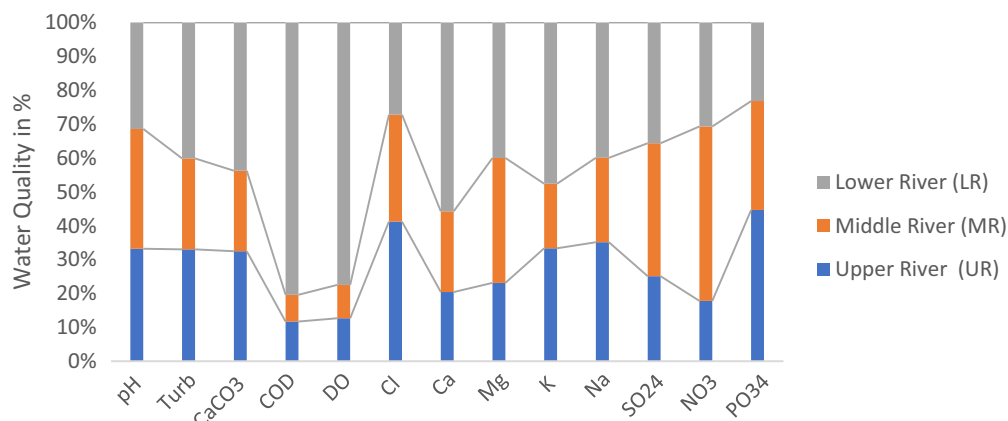


Fig. 2 Water tracers of inland river at different stages

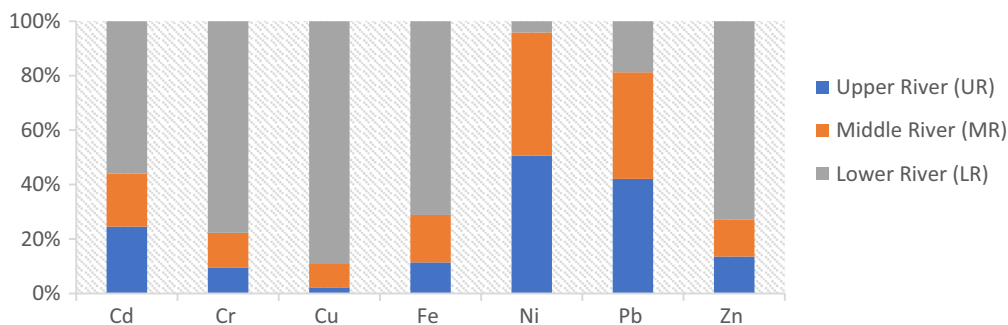


Fig. 3 Heavy metal concentrations in inland Aquatic Ecosystem at different stages

manure, and fertilizers, in the soil within the watershed leading to increased release of Cd, Cr, Cu, Ni, Pb, Zn, K, Fe, Ni etc. (Duzgoren-Aydin, and Weiss 2008; Cai et al. 2012; Xue et al. 2014; Dai et al., 2015; Ubuoh et al. 2022a, b.). A number of the metals are essential nutrients in crop production though in trace amounts, and are provided chiefly by inorganic and commercial fertilizers so as to enhance soil quality and fertility. A few metals like Pb, Cd, and Cr, are not needed by plant for growth and development and thus, not intentionally introduced (Lian et al. 2019), but are suggested to have come from vehicular flow and workshops during sand mining. The result is in tandem with the previous reports by researchers, implicating industrial and vehicular processes to be responsible for the release of Zn, Cu, and Pb, into the soils and the environment (Imperato et al. 2003), with Cu arising primarily from machine production plants, Zn (a hardness additive) emanating from tire dust, while Pb comes from automobile exhaust emissions and coal combustion (Duzgoren-Aydin, and Weiss 2008; Cai et al. 2012). Zinc pigment, is also used in production of plastic (Gakwisiri et al. 2012; Chi et al. 2017), and is found in solid wastes

(Ubuoh et al., 2013). The break through on the removal of leaded petrol has greatly reduced the amount of Pb in the environment, although, the wearing and tearing of vehicle brake pads and tires still release Pb into the environment, therefore implicating vehicular source as a source of pollution (Imperato et al. 2003). The second principal component (PC₂) shows upto 20.9% of the total variance, indicating high loading of pH (0.763), Sulphate (0.842) and nitrate (0.932). Only phosphate is negatively loaded (-0.738). This suggested to have originated from agriculture (Ubuoh et al. 2022a, b), resulting in nutrients enrichment and eutrophication in water. The third principal component (PC₃) explains 7.53% of the total variance, and was equally loaded with chloride (0.641) and Sodium (0.796) positively (Figs. 4 and 5). values in bold make up the parameters with positive and negative loadings

Contamination factor (C_f)

From Table 10, C_f for Cd²⁺ fell within 0.316–0.908, with a mean of 1.08, Cr²⁺ ranged from 3.3×10^{-3} to 5.4×10^{-4} , with a mean value of 1.4×10^{-3} , Cu²⁺ ranged from $0.032 - 8 \times 10^{-4}$, with a mean value 0.012, Fe²⁺

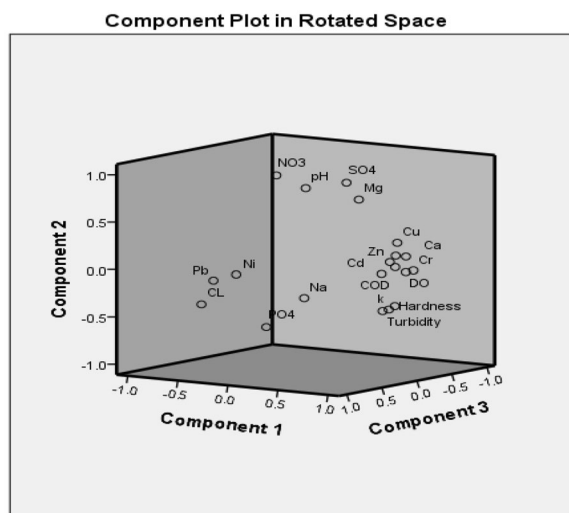


Fig. 4 whiskers plot showing the three components

ranged from 0.024 to 5.8×10^{-3} , with a mean value 0.011 , Ni^{2+} ranged from 1.5×10^{-4} to 1.9×10^{-4} , with a mean value of 1.3×10^{-3} , Pb^{2+} ranged from 0.022 to 0.050 , with a mean of 0.039 , and Zn^{2+} ranged from 1.8×10^{-3} to 3.3×10^{-4} , with a mean value of 1.4×10^{-3} . The implication is that the heavy metals recorded a low contamination factors in the river. (Hakason 1980). Based on the mean of heavy metals in surface water of Nworie inland river contamination factor is in order of: $\text{Cd}^{2+} \geq \text{Pb}^{2+} \geq \text{Cu}^{2+} \geq \text{Fe}^{2+} \geq \text{Zn}^{2+} \geq \text{Ni}^{2+} \geq \text{Cr}^{2+}$. with Cadmium as the major contamination factor and at

variance with the finding of Leghouchi et al. (2009) who observed highest content of Chromium from the tannery of Jijel in the Mouttas river (Algeria).

Degree of contaminant (Cdegree) and the pollution load (PLI)

Table 10 showed that the LR recorded the highest degree of contaminant with a value of 1.899 while the middle river had the lowest (0.689), with a mean value of 1.14 and degree of contaminant ≤ 8 indicating low. This is in slight disagreement with the findings of Edori and Iyama (2020a, b) who obtained low to moderate contamination degree of heavy metals in Edagberi Creek. The order of contamination degree of each sampling point was in order of: $\text{LR} \geq \text{UR} \geq \text{MR}$, with (LR) having highest degree of contaminants, suspected to be due to human activities along the river course, which is consistent with the finding of Zhang et al. (2013), Zhang et al. (2015), Goody et al. (2016), and Kong et al. (2018) who reported that human activities such as rapid agricultural and economic development are the leading causes of collective pollution of surface water of the rivers.

The values of pollution index (PLI) ranged from 1.3×10^{-4} to 2.2×10^{-5} , with a mean value of 1.7×10^{-4} , which is less than 1 ($0 < \text{PLI} \leq 1$), and signifying no heavy pollution status of the river, greater than the PLI values that ranged from 0.0996 to 0.194 , and falling within the bracket of which goes to show that the river is not heavily polluted but moderately polluted with heavy metals most especially cadmium. This is also in tandem with the findings in Edagberi Creek (Edori and Iyama 2020a, b).

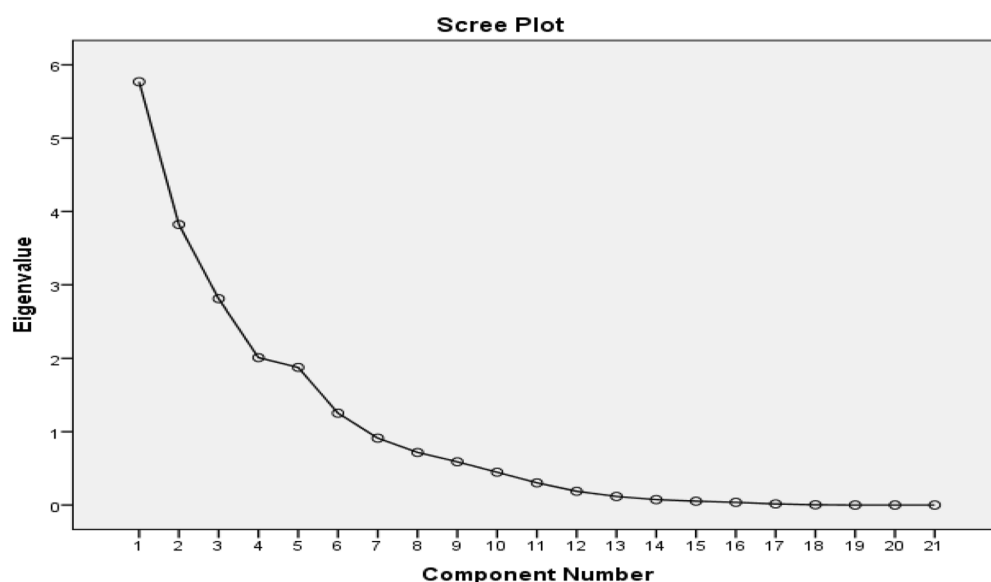


Fig. 5 Screen plot for PCA of Nworie Inland Surface water in the study area

Table 10 Risk assesment of heavy metals in Nworie inland aquatic ecosystem

Stations	Contamination factor (C _f),							C _d	PL1
	Cd ²⁺	Cu ²⁺	Fe ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺	Mn ²⁺		
UR	0.796	4 × 10 ⁻⁴	3.8 × 10 ⁻³	1.9 × 10 ⁻⁴	0.050	3.3 × 10 ⁻⁴	0.1–9.72	0.1–0.067	1.6 × 10 ⁻⁴
MR	0.632	5.4 × 10 ⁻⁴	5.8 × 10 ⁻³	1.9 × 10 ⁻³	0.046	3.3 × 10 ⁻³	–	–	2.2 × 10 ⁻⁵
LR	1.816	3.3 × 10 ⁻³	0.024	1.5 × 10 ⁻⁴	0.022	1.8 × 10 ⁻³	–	–	1.3 × 10 ⁻⁴
Mean	1.081	1.4 × 10⁻⁴	0.011	1.3 × 10⁻³	0.039	1.4 × 10⁻³	–	–	1.7 × 10⁻⁴
Edori and lyama (2020a, b)	0.167–0.267	0.06–0.30	0.003–0.029	0.093–0.25	0.06–0.30	0.0067–0.025	–	–	0.0996–0.194
Remarks	LC: cf > 1	LC: cf < 1	LC: cf < 1	LC: cf < 1	LC: cf < 1	LC: cf < 1	LC: cf < 1	LC _{cf} < 8	NP > 1

Heavy metals with cf < 1 points to low contamination (LC), heavy metals with < 8 indicates low degree of contamination (LCD). While pollution load index (PLI) < 1 shows no pollution (Hakason, 1980)

Potential risk (LPER) and the ecological risk index is below 150 which indicates low ecological risk. (LER)

The pollution load ranged from 1.6×10^{-4} in the upper river to 2.2×10^{-5} in the middle river, in decreasing order of $UR \geq MR \geq LR$, with a mean PL of 1.7×10^{-4} . The values obtained of the pollution load were less than one (1) which implies no pollution. This means that the water at the different course streams were not polluted by the heavy metals. The result of the study is in contrast with the finding of Abdullah et al. (2016), who reported the high values of PLI index of the river due to metals at the Balok in Kuantan, Malaysia, and the pollution load in a river was also observed by Panda et al. (2020) in Salandi River—Downstream, Bhadrak, Odish.

Table 11 summarizes the ecosystem risk assessment results of the heavy metals in Nworie Inland river. From the summary, the ecosystem risk assessment of heavy metals were ranked in the following order: $Cd^{2+} \geq Pb^{2+} \geq Cu^{2+} \geq Zn^{2+} \geq Cr^{2+} \geq Ni^{2+}$, and were below the remark (40), indicating low ecological risk factor. The result is in tandem with the findings of El-Amier et al. (2018), who observed low potential ecosystem risk (< 40) of all metals in Idku Lake. Accordingly, the result of Er of the study differs with the finding of El-Amier et al. (2022), who observed very high ecosystem risk (> 320) in water body. Going forward to quantifying the overall potential ecosystem risk associated with heavy metals in Nworie water, the value of the risk index (Ir) ranged from 9.738 in the middle river to 27.520 in the lower river, and the range was below 150 indicating low ecological risk index (Hakason, 1980). The result of Ir also differs from the finding of El-Amier et al. (2022) who observed that the risk index values in the lake showed very high ecosystem risk (> 600) in Lake Qarun Wetland, Egypt, with Cd^{2+} accounting for most of the total risk factor, but below ≤ 40 of Er, which is consistent with the finding of Yuguda et al. (2020) in river water and sediment in Gashua Towa, Yobe, Nigeria. The result is against the finding of Zang et al. (2018) who observed Cd with high risk that associated with public health concern worldwide. The risk index numbers obtained in this present study are less significant compared with other studies conducted in wetland in Iran (Yavar Ashayeri and

Keshavarzi 2019) as well as the studies conducted on the coast of the Persian Gulf respectively.

Table 11: shows that ecological risk factor of heavy metals in water is between $\sum_i \leq 40$ which indicates low.

Conclusion

The study assessed the effect of anthropogenic activities on water chemistry and associated potential ecological risk in Nworie inland River, Imo State, Nigeria. The result of the physicochemical tracers indicated that water was slightly acidic and hard (Ca^{2+}), with high level of $CaCO_3$, phosphorus and low dissolved oxygen all above the WHO critical limits. Heavy metals such as Cd^{2+} , Cr^{2+} , Fe^{2+} , Ni^{2+} and Pb^{2+} were above some of the critical global limits. Metals content in Nworie inland River were in decreasing abundance: $Pb^{2+} \geq Fe^{2+} \geq Cu^{2+} \geq Zn^{2+} \geq Cd^{2+} \geq Cr^{2+} \geq Ni^{2+}$, which suggest an increase of human activities and organic waste disposal into the river over the years. Positive and negative correlations exist between physicochemical tracers and elements in water respectively originating from complex human activities. Principal component analysis (PCA), was significantly loaded with $CaCO_3$, COD, DO, Ca, PO_4 , Cu, Fe, Zn in PC1 due to agricultural activities and vehicular flows. In PC2, was loaded with SO_4 , and Significantly loaded with NO_3 , leading to nutrients enrichment and eutrophication due to organic wastes dump in the river and fertilizer application. PC3 was moderately loaded with Cl and Na. Contamination factor (C_f) was high for cadmium but low for other heavy metals in decreasing order: $Cd^{2+} \geq Pb^{2+} \geq Cu^{2+} \geq Fe^{2+} \geq Zn^{2+} \geq Ni^{2+} \geq Cr^{2+}$. Degree of contaminant and the pollution load (PLI) recorded moderately respectively. Contamination degree is in order of: Lower River (LR) \geq Upper River (UR) \geq Middle River (MR). The ecological risk factor was low in order: $Cd^{2+} \geq Pb^{2+} \geq Cu^{2+} \geq Fe^{2+} \geq Zn^{2+} \geq Ni^{2+} \geq Cr^{2+}$, with moderate risk index. The moderate to low contamination and ecological risk calculated in this study could be generally attributed to the self-purification properties of a flowing river or stream which helps to reduce pollution load and associated risk. However, the high cadmium concentrations could be associated with rising urban

Table 11 Ecosystem risk factor (Er) and index (Ir) of heavy metals In Nworie Inland aquatic ecosystem Inland

Stations	(E _r) Cd^{2+}	(E _r) Cr^{2+}	(E _r) Cu^{2+}	(E _r) Ni^{2+}	(E _r) Pb^{2+}	(E _r) Zn^{2+}	Ir
UR	11.940	8×10	4×10^{-3}	9.5×10^{-3}	0.249	$3.3 \times 10^{-}$	12.204
MR	9.480	1.1×10^{-3}	0.016	8.5×10^{-3}	0.232	3.3×10^{-4}	9.738
LR	27.24	6.6×10^{-3}	0.160	7.5×10^{-4}	0.111	1.8×10^{-3}	27.520
Mean	16.22	2.8×10^{-3}	0.053	6.3×10^{-3}	0.197	8.2×10^{-3}	16.48
Remarks	LPER $\sum_i \leq 40$	LPER $\sum_i \leq 40$	LPER $\sum_i \leq 40$	LPER $\sum_i \leq 40$	LPER $\sum_i \leq 40$	LPER $\sum_i \leq 40$	LER $I_r < 150$

activities and would pose a deleterious effect to the lives of the people and the ecosystem as a whole.

Therefore, there is need for constant monitoring of the River in order to guide against aquatic ecosystem degradation and ensure water quality sustainability for man and aquatic lives. Above all, activities like agricultural practices, mechanic workshops and solid wastes should not be allowed within Nworie watershed. This should be accomplished by regulatory agencies for compliance, alongside sound environmental practice in every aspects of operation including accelerated erosion control practice.

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Author contributions

UEA: Term, Conceptualization, Methodology, supervision, NFU: writing original draft, writing review and editing, Investigation, correspondence OCC: software, project administration, visualization, CPC: Resources, data curation. All author read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interest

The authors declare that they have no competing interests.

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