Scientific African 7 (2020) e00259

Contents lists available at ScienceDirect

Scientific African

journal homepage: www.elsevier.com/locate/sciaf

Assessing the spatial and temporal variability and related environmental risks of toxic metals in Lake Asejire, south-western Nigeria

Beaven Utete [a,b,*], Bernadette.T. Fregene [b]

[a] Department of Wildlife Ecology and Conservation, Chinhoyi University of Technology, P. Bag 7724, Chinhoyi, Zimbabwe
[b] Department of Aquaculture and Fisheries Management, University of Ibadan, Ibadan, Oyo State, Nigeria

ARTICLE INFO

Article history:
Received 26 February 2019
Revised 7 November 2019
Accepted 19 November 2019

Editor: DR B Gyampoh

Keywords:
Biotoxicity
Heavy metal
Tissue accumulation
Ecological risk assessment
Lake Asejire
Nigeria

ABSTRACT

Lake Asejire in Nigeria is polluted with untreated effluent from nearby aquacultural, urban, agricultural and industrial zones. The metal laden effluent pose a hazard to the health of fish and fish consumers in the lake. This study aimed to (1) assess the spatial and seasonal variations in the levels of cadmium, cobalt, copper, iron, lead, nickel, mercury and zinc in water, sediments and gills and stomach tissues of mud catfish, *Clarias gariepinus* and Nile tilapia, *Oreochromis niloticus;* and (2) evaluate environmental risks posed by heavy metals in Lake Asejire. Potential ecological risks of heavy metals were assessed using the pollution loading, geoaccumulation and potential ecological risk indices. Levels of Fe, Co, Cu, Cd, Pb, Ni and Zn were high in water and sediments and in some cases exceeded the Nigerian Standards for Drinking Water Quality and World Health Organisation threshold values. There were significant ($p < 0.05$) seasonal variations in the levels of all metals in water and sediments. Significantly high Fe, Co, Cd, Pb, Ni and Zn levels recorded in gills and stomach tissues of mud catfish and Nile tilapia relate well with metal levels in water and sediments. The geoaccumulation index reflected heavy Cu and Zn contamination in sediments whereas Cd pose serious ecological risks to aquatic organisms in the lake. Accurate assessment of the spatial and temporal variability of heavy metal levels in Lake Asejire is crucial for pollution control and environmental management.

Introduction

Metals are part of the natural organic and inorganic complexes found among soils, aquatic sediments, and mostly occur in trace concentrations ([2,36,37,40,45]). Concentrations of toxic heavy metals may exceed allowed levels in urban and peri–urban lakes due to pollution from proximal catchments [23,32,48]. Metropolitanisation of most catchments in African countries such as Nigeria largely through rapid industrialisation, urbanisation, and stochastic modifications of land-use and land-cover increase the heavy metal concentrations in lakes and reservoirs diminishing their ecosystem service value ([6];

* Corresponding author at: Department of Wildlife Ecology and Conservation, Chinhoyi University of Technology, P. Bag 7724, Chinhoyi, Zimbabwe.
E-mail address: beavenu@yahoo.co.uk (B. Utete).

https://doi.org/10.1016/j.sciaf.2019.e00259

Strayer and Findlay, 2010). Moreso, increased effluent discharges from agricultural and industrial zones and urban settlements elevate concentrations of toxic heavy metals in lakes [16,43,44]. Aquatic systems are subject to changing conditions and are practically never at equilibrium [26,42]. Thus, a correct interpretation of the discharge, fate (accumulation in the aquatic chain), toxicity and environmental effect of heavy metal complexes is to consider the significance of reactivity, fluxes of the compounds, and more importantly, their exchange between abiotic and biotic phases through interfacial processes in time and space ([8]; Jansen et al., 2002; [9,46]).

Excess concentrations of toxic heavy metals in freshwater ecosystems have been implicated in several metal-related diseases, fish deaths and food poisoning in man [19]. Most toxic heavy metals, such as Cd, Cr, Pb and Hg have no known physiological benefit (Alloway, 1990; [51]). Some deadly diseases like eyelid oedema, brain tumours, and nasal disorders, gastrointestinal, muscular, reproductive, neurological and genetic malfunctions are caused by some metals [51]. Despite the toxicity associated with metals, some of them like Zn and Fe have essential functions in the blood and immune system [25]. Toxicity of metals relates to the bioavailability and reactive forms or species and the associated medium or phase in aquatic systems [1,28]. Biogeochemical behaviour, bioaccumulation, bioavailability, environmental mobility and potential ecological risks depend on the chemical species and its redox dynamics in different phases in freshwater systems (Luoma and Rainbow, 2005; [18,47]). Secondary and tertiary pollution in aquatic systems arise from discharge of heavy metals from sediments and decomposing tissues of biological organisms [54]. It is imperative to detect and monitor the spatio-temporal concentrations of metals in various components of the aquatic system [49].

Lake Asejire receives metal laden effluent from the vast industries and urban areas mainly located in the metropolitan Ibadan City located 30 km away to the east in Oyo State, Nigeria [3,20]. Urban soils in Ibadan metropolitan are heavily contaminated by trace toxic heavy metals which runoff as effluent and enters the lake [21,34]. Metal contamination by traditional cassava farming and processing activities is rife in the catchment of the main tributary River Osun [24]. Cassava processing release cyanide related toxins which pose serious risks to aquatic organisms and human livelihoods dependent on water and fisheries resources in the lake [3,4]. Protection of the integrity of aquatic ecosystems and ambient water quality in Nigerian lakes is vital to sustain life, livelihoods, development and avert deleterious heavy metal contamination hazard risks [5,21].

This study aimed to (1) assess the spatial and seasonal variations in the levels of cadmium, cobalt, copper, iron, lead, nickel, mercury and zinc in water, sediments and gills and stomach tissues of mud catfish, *Clarias gariepinus* and Nile tilapia, *Oreochromis niloticus;* and (2) evaluate environmental risks posed by heavy metals in Lake Asejire. We hypothesised that there were: no significant spatial and temporal variations in concentrations of metals in different phases: water, sediments and fish tissues within the same system, and no potential ecological risks posed by metals in Lake Asejire in Ibadan metropolitan, Nigeria.

Materials and methods

Study area

Lake Asejire (Fig. 1), a man-made lake was constructed on Osun River, in Egbeda Local Government Area of Oyo State, Southwest Nigeria. Osun River is one of the West African rivers which do not drain into River Niger but discharges into coastal lagoons and creeks bordering the Atlantic Ocean [4,5]. Lake Asejire lies on 04°07′East and 07°21′North at an altitude of 137 m above sea level, covering a length of 19.5 km [4]. The lake, located about 30–33.8 km from Ibadan, has numerous other inflows joining at different points [10]. Ogunleye (1982) reported that Osun River was dammed at Asejire in 1972 for the purpose of providing potable water to Asejire and Osegere water treatment plants in Ibadan metropolis, and its surrounding communities.

The lake has an approximate gross storage of 7403 MI. The construction of the lake divides the fishing area into two main zones, namely the upstream and the downstream [20]. State laws and catchment regulations totally banned farming in the drainage basin and advocated for planting trees on the littoral and drawdown zones to reduce erosion and siltation in Lake Asejire. The south-western part of Nigeria where the lake is located has no distinct dry, cold or rainy seasons as it is predominantly equatorial and there are rains almost all year round with high temperatures [4]. Therefore, the reservoir has plentiful water supply and remains almost full throughout the year with minimal hydrological fluctuations [4]. There are numerous manufacturing industries, aquacultural enterprises, cassava farming and processing activities, white water recreational sports, capture fisheries and peripheral settlements which release metal laden effluent into the lake. Metals threaten the ambient water quality, aquatic biodiversity, aesthetic and economical value of the lake. Consequent effects may cascade to the health, economic and social well-being of water and fisheries dependent livelihoods in Lake Asejire.

Sample collection and quality assurance

We selected five sites which covered as much of the lake as possible (Fig. 1). The rationale was to accurately estimate the variation in metal levels across the whole lake. Site 1 is the uppermost site adjacent to predominantly cassava farming communities. Site 2 is located adjacent to rural communities whose members are mostly fishermen, and site 3 represent the middle point of the lake. Site 4 is located near the main Nigerian Bottling Company plant and some commercial aquacultural companies in Asejire. Site 5 is located at the dam wall, where there is a combined water intake tower for the Oyo State

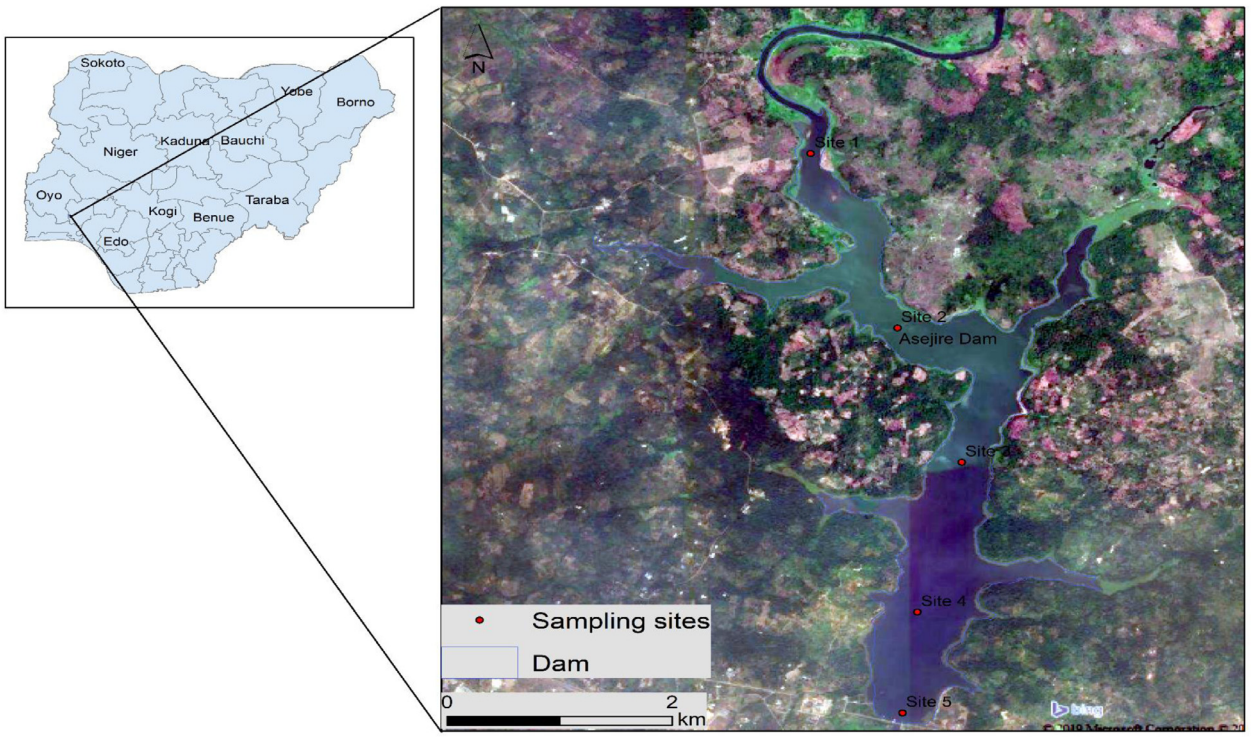

Fig. 1. Map of the sampling sites in Lake Asejire Oyo State, south western Nigeria.

Water works water treatment plants in the catchment and Asejire hydroelectric power plant. Once off sampling of water, sediment and fish was done in April, July and November 2017. The sampling seasons were chosen so as to cover the early or low rainy period late March-April, rainy period May-August and the early dry period late November.

In Lake Asejire, three replicate water samples were collected at each site using a 5 L Ruttner sampler at a maximum depth of 1 m, and these were combined into one sample in 500 ml sterilised polyethene bottles. There was no analysis of the depth profile of water in the lake. The 500 ml bottles were stored in ice packed cooler boxes for further analysis in the laboratory. At each site, in-situ measurements of pH, conductivity, turbidity, temperature and dissolved oxygen (DO) were taken using a raft of appropriate meters such as the pH, turbidimeter, Conductivity and DO metre (HACH, LDO, Germany). Water transparency (Secchi depth, SD) at each site was measured using a 20 cm diameter Secchi disc which combines alternating black and white quadrants. Fine and coarse grained sediments were collected at the same site as water using a polypropylene coring device suspended by an extensible rope, with a 0.1 m internal diameter. Multiple 10 cm cores were collected at each site and were thoroughly mixed to create an integrated sample which was stored in sterilised polyethene bags. Integrated sediment samples were stored at 4 °C in a refrigerator for a maximum of 48 h in the laboratory in preparation for metal digestion and analysis.

Mud catfish and Nile tilapia were collected from the same sampling sites for water and sediments using fine meshed monofilament gillnets. Some augment fish samples were collected from fishermen, fish marketers and fish traders on site at Lake Asejire. For each sampling trip we collected at least 15 fish specimens for each species in order to get truly representative samples which the local fish consumers buy and eat.

Extraction and analysis of metals in collected samples

Extraction and analysis of toxic heavy metals in the two fish species and the water and sediment phases were done following methods by Greenberg et al. [12], and Nhiwatiwa et al. [33]. Collected water samples were filtered through 0.45 µm sized Whatman G/F filters into sterilised 100 ml flasks in order to remove solid microparticles and algae. The filtered water sample was acidified with nitric acid to a pH < 2. Heavy metals in water were then quantified using the flame atomic absorption spectrometry (FAAS). A multiple step acid digestion protocol to extract heavy metals was adopted for sediments and fish tissues following methods by Greenberg et al. [12]. The procedure for heavy metals comprises of consecutive steps: Step 1. Disaggregation: sediments were oven dried at 180–185 °C in a hooded muffle furnace and large aggregates were broken into smaller granules. Step 2. Digestion: 20 ml nitric acid and 5 ml perchloric acid were added to 5.00 g of the oven dried sediment sample and the mixture was heated until fume production and cooled to room temperature of 22–24 °C. Step 3. Acidification: 20 ml of 50% hydrochloric acid was added to the mixture from the first digestion. The acidified mixture

Table 1
Water quality parameters measured in Lake Asejire, Nigeria 2017. The NSDWQ and WHO approved values in water are added for comparison.

Location	Month	DO (mg/L)	Temp (°C)	Turbidity (NTU)	EC (µS/cm)	pH	Secchi depth (m)
AS1	April	5.22 ± 0.34	33.6 ± 1.71	4.11 ± 0.27	321.01 ± 88.24	8.32 ± 0.22	1.31 ± 0.11
	July	5.53 ± 0.65	31.4 ± 3.22	4.17 ± 0.34	237.89 ± 45.11	7.23 ± 0.31	1.08 ± 0.38
	Nove	4.71 ± 0.63	28.6 ± 1.91	3.65 ± 0.45	189.53 ± 55.12	8.01 ± 0.28	0.94 ± 0.23
AS2	April	4.11 ± 0.66	30.8 ± 1.45	4.49 ± 1.63	298.33 ± 93.24	7.22 ± 0.19	1.42 ± 0.45
	July	5.92 ± 0.51	31.3 ± 1.71	3.82 ± 0.37	235.77 ± 62.53	7.88 ± 0.15	0.88 ± 0.31
	Nove	5.11 ± 1.23	29.7 ± 2.34	3.97 ± 0.88	216.62 ± 47.17	8.44 ± 0.73	0.72 ± 0.25
AS3	April	4.87 ± 0.56	32.8 ± 1.87	3.03 ± 0.49	322.72 ± 85.67	8.21 ± 0.65	1.01 ± 0.47
	July	4.23 ± 0.72	32.3 ± 1.79	2.89 ± 0.67	268.43 ± 99.37	7.18 ± 0.42	1.18 ± 0.34
	Nove	5.07 ± 0.85	29.7 ± 1.45	3.77 ± 0.34	356.67 ± 101.15	8.05 ± 0.66	1.85 ± 0.68
AS4	April	3.11 ± 0.33	28.5 ± 1.78	3.01 ± 0.67	333.64 ± 97.08	6.92 ± 0.33	0.74 ± 0.55
	July	4.03 ± 0.64	30.4 ± 2.01	4.32 ± 0.49	256.23 ± 88.16	7.76 ± 0.17	0.89 ± 0.49
	Nove	4.69 ± 1.32	29.6 ± 2.11	3.72 ± 0.54	242.17 ± 72.53	7.49 ± 0.36	1.69 ± 0.53
AS5	April	3.97 ± 0.53	29.8 ± 1.87	3.34 ± 0.47	211.25 ± 47.82	7.33 ± 0.14	1.45 ± 0.27
	July	3.74 ± 0.63	28.2 ± 1.62	3.22 ± 0.66	317.35 ± 95.34	7.27 ± 0.28	1.71 ± 0.19
	Nove	4.01 ± 0.84	29.7 ± 1.35	3.97 ± 0.73	342.59 ± 77.16	7.33 ± 0.55	1.04 ± 0.23
	NSDQW	5.0	28–30	5	1000	6.5–8.5	N/A
	WHO	5.0–6.59	25.3	5	1000	6.59–8.5	N/A

was heated until boiling and then cooled to room temperature. This acidified mixture was filtered and distilled water added to a 100 ml mark. Step 4. Estimation of metals: Digested sediments were analysed for metals using the FAAS [12].

For fish samples, 3.00 g of wet weight of the gill and edible stomach muscle tissues were dried in separate clay crucibles at a temperature of 120 °C until they reached a constant weight between 1.00–1.5 g. The dry gill and stomach muscle tissues were digested using 5 ml perchloric acid and 10 ml nitric acid in sterilised digestion flasks. The digestion flasks were heated in an oven at 130–145 °C until all materials dissolved and then allowed to cool at room temperature. Care was taken to ensure a gradual increase in temperature as the concentration of heavy metals such as mercury, cadmium and lead is lowered due to the volatization at higher temperatures [49]. Levels of metals in the digested fish tissues, water and sediments were estimated using the multicathode hollow lamp fast sequential AAS Spectra-AA 232 FS (Varian, Germany).

Quality control

Calibration was performed using standard analytical solutions. Standard solutions were prepared by serial dilutions of 1000 mg/L PerkinElmer Pure single element-standards in 2% nitric acid (v/v). Before analysis, the detection method was validated with reference materials: Merck 100,473 for water, LKSD-1 for sediments and ERM-CE278K for fish. Recovery rate was >95% for all elements with a 90% recovery rate for mercury with low RSD values <5%. Detection limits of the FAAS for the analysed metals were: 0.005 mg/L for Cu, Zn; 0.2 mg/L for Ni, Co; 0.04 mg/L for Cr, Pb; 0.03 mg/L for Fe and 0.001 mg/L for Hg. Procedural blanks and standards were prepared and used for quality control of heavy metal estimation. At every stage of analysis after 10 samples of sediments and water, a reagent blank with concentration below detectable limits was prepared. For repeatability and accuracy, each sample was analysed in triplicate with a standard deviation (SD $<$ 0.05) for all metals and SD $<$ 0.001 for mercury. All acids used for digestion were standard analytical grade acids. The multiple step acid analysis used for the FAAS was to ensure accuracy and precision in quantification and estimation of heavy metals in water, sediments and fish samples as they are pertinent to the health of humans who use water and consume fish.

All glassware used in this study, were soaked for 12–24 h in acid water (1% solution of hydrochloric or nitric acid) before being washed by distilled and deionised water in preparation for acid digestion procedures. All the water used for serial dilutions and preparation of blanks and topping up during acid digestion process was purified using a combination of technologies which included osmosis, ion exchange and ultraviolet photo oxidation in the laboratory at the University Of Ibadan Department Of Chemistry.

Statistical analysis

Physicochemical parameters in Lake Asejire

Mean (±SD) values of water quality parameters comprising temperature, dissolved oxygen (DO), electrical conductivity (EC), Secchi depth, turbidity and pH at the sampled sites were calculated and compared to the Nigerian Standards for Drinking Water Quality (NSDQW) and World Health Organisation (WHO) values and the results are indicated in Table 1. Kolmogorov-Smirnov test indicated that the water quality data were non-parametric ($p > 0.05$). Hence the Kruskal-Wallis Anova was used to assess the spatial and temporal variations in the water quality data and results are summarised in Table 1.

Spatial-temporal variations of metal concentrations in water, sediments and fish tissue

The Kolmogorov-Sminorv normality test applied on the raw metal values in water, sediments and fish indicated that the data were non-parametric ($p > 0.05$). Thus, spatial and temporal differences for the metal levels were analysed using the non-parametric Kruskal Wallis Anova at $p < 0.05$ significance level in SPSS version 21. Further, levels of metals in water from Lake Asejire were compared to the Nigerian Standards for Drinking Water Quality (NSDQW) and the World Health Organisation standards [39,52,53]. Levels of metals in sediments in Lake Asejire were compared to the USEPA sediment criteria [39] whereas metal levels in fish were compared to the FAO [11] legal limits for hazardous substances in fish and fishery products.

Pollution status and potential ecological risks of metals in water and sediments

For each sampling effort or month, three replicate water and sediment samples were collected per site in Lake Asejire. The three replicate levels of each metal determined per site were then averaged and used for further statistical analysis. To determine the lake's pollution status and potential ecological risk posed by each heavy metal, the pollution load index (PLI), and geological accumulation index method (Igeo) by Müller [30,31] and potential ecological risk evaluation method (PERI) by Hakanson [15] were used respectively.

The pollution load index (PLI) in water is defined as the n^{th} root of the multiplications of specific metal concentrations (CF_{metals}):

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots CFn)1/n$$

Values of PLI > 1 imply that heavy metal pollution exists. Otherwise, if PLI < 1, there is no heavy metal pollution [38].

The geo-accumulation index (Igeo) is defined by the following equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5} \times B_n\right)$$

Where: C_n is level of metal n and B_n is background level of the metal (n) usually adopted from sediment quality guidelines (SDQ). Constant factor K is a background matrix correction factor due to lithospheric effects, which is usually defined as 1.5 [30,31]. Classification of geo-accumulation index is presented in Table A1.

In the Potential Ecological Risk index (PERI) method by Hakanson [15], potential ecological risk coefficient E^i_r of a single element, and potential ecological risk index RI of the multielement are calculated using the following equations:

$$Cif = Cis/Cin$$

$$Eir = TirxCif$$

$$RI = \sum i = 1nEir$$

Where:

C^i_f is the pollution coefficient of a heavy metal of "i" or the monomial contamination factor;
C^i_s is the measured level of sedimentary heavy metal;
C^i_n is the background level of sedimentary heavy metal;
T^i_r is the toxic response factor for the given heavy metal of "i", which accounts for the toxic requirement and the sensitivity requirement;
RI is the sum of all risk factors for heavy metals in sediments.

The average shale background level of global sediments was selected as the reference baselines in this study. This study adopted the Hakanson [15], PERI classification criteria shown in Table A2. In order to obtain the sediment/water (S/W) ratio or bioconcentration factor (BCF) that is the ratio of metal levels in sediment phase to that in water phase, the equation used was:

$$Sediment/water\ ratio = \frac{Level\ of\ metal\ in\ sediments}{Level\ of\ metal\ in\ water}$$

If the S/W Ratio or BCF is greater than 1000, it was considered as extremely high and those under 200 were considered as low. BCF between 200–1000 was considered as moderately high. The sediment-water criterion for this study was derived from the Solids-water coefficient (Ksw) method used by Van der Kooij et al. [41], and Shea (1998). The Criterion maximum concentrations (CMC) and criterion continuous concentration (CCC) for metals in water for Asejire were also analysed to assess the potential ecological risks to humans and fish.

Table 2
Sediment/Water ratio of Bioconcentration Factor (BCF) of metals in Lake Asejire, Nigeria 2017. High BCF>1000 are marked with a double asterik** and those in the moderately high (200 < BCF < 1000) criterion are marked by a single asterik*.

Site	Season	Fe	Co	Zn	Cu	Cd	Pb	Ni	Hg
AS1	April	3.87	451.07*	3241.11**	66.65	20.36	34.58	65.38	9.00
AS1	July	3.88	233.40*	171.48	24.70	21.60	1.54	438.60*	0.09
AS1	November	13.51	326.67*	2437.50**	131.25	26.67	201.30*	580.00*	0.00
AS2	April	5.05	452.00*	1339.58**	87.41	49.50	40.88	100.96	5.50
AS2	July	6.31	122.86	339.14*	37.32	59.45	6.04	970.13*	0.10
AS2	November	13.11	550.00*	1920.00**	175.66	21.47	125.57	213.79*	0.00
AS3	April	5.32	357.57*	2535.00**	65.77	23.22	42.76	72.85	0.00
AS3	July	8.05	320.20*	300.71*	38.30	69.20	3.07	658.75*	0.14
AS3	November	14.48	142.5	1725.00**	101.43	13.33	245.56*	115.33	0.00
AS4	April	4.34	452.00*	810.00*	79.77	30.53	48.98	90.35	0.50
AS4	July	6.62	245.10*	154.60	34.60	21.42	3.11	784.63*	0.05
AS4	November	5.90	176.5	1315.00**	241.88*	31.88	94.71	609.09*	0.00
AS5	April	1.70	239.00*	588.00*	46.64	7.18	31.35	38.19	0.05
AS5	July	3.57	152.55	138.87	28.58	28.54	5.18	402.78*	0.13
AS5	November	7.12	175.13	9150.00**	90.56	11.25	31.48	123.33	0.00

Results

Water quality parameters in Lake Asejire

DO levels were low at AS4 and AS5 in all months sampled (Table 1). Almost all temperature values recorded were above the NSDWQ and WHO threshold values (Table 1). All turbidity, pH and electrical conductivity levels fell within the NSDWQ AND WHO thresholds (Table 1). There were no significant spatial and temporal differences (Kruskal Anova, $p > 0.05$) for all the physicochemical parameters in Lake Asejire.

Heavy metals in water

Comparatively higher Fe, Ni and Cd levels in water were recorded at almost all sites in April (Fig. 2a, e, g; Table A3). Higher Co levels were recorded in July at AS2, AS3, AS4 and AS5 (Fig. 2b; Table A3). Signficantly higher levels of Zn, Cu, Hg and Pb were also recorded in July in Lake Asejire (Fig. 2d, e, f, h; Table A3). The values of Fe, Co, Cu, Cd, Pb and Ni in most cases exceeded the NSDWQ and WHO maximum allowable values for water. There were significant (Kruskal Anova, $p < 0.05$) seasonal variations in the values of all metals assessed in water. However, no significant (Kruskal Anova, $p > 0.05$) spatial heterogeneity was observed for all metals in water in the lake (Table A3).

Heavy metals in sediments

Significantly high Co, Zn, Pb, and Ni values were recorded in sediments at all sites and in most cases they exceeded the USEPA threshold values (Fig. 3b, c, f, g; Table A4). Relatively low values of Fe, Cu, Cd and Hg were recorded in sediments at most sites (Table A4). There were no significant (Kruskal Anova, $p > 0.05$) spatial variations in the values of all metals. Significant seasonal (Kruskal Anova, $p < 0.05$) heterogeneity was observed for all metals except Fe and Pb in sediments in Lake Asejire (Table A4).

Phase relations of metals in Lake Asejire

Analysis of the BCF indicated that Co and Zn had extremely high values > 1000 whereas the BCFs for Cu, Ni and Pb were moderately high in some seasons (Table 2). There were exceptionally higher BCFs for Zn at AS1 in April (BCF = 3241.111), November (BCF = 2437.5), AS3 in April (BCF = 2535), and at AS5 in November (BCF = 9150). For most metals, the BCF > 0.1 implying that their levels are higher in sediments relative to the water phase. Only mercury had some BCFs < 0.1 in most cases where it was not detected. The BCF hierarch for metals in Lake Asejire was; Zn>Co>Ni>Pb>Cu>Cd>Fe>Hg.

Heavy metals in fish tissues

Significantly high Fe, Co, Zn, Cd, Pb and Ni values were recorded in the gills and stomach muscle tissues of both fish species (Table 3). In most cases, the highest values of metals in the gills and stomach tissues were recorded in April with the lowest values mostly recorded in November (Table 3). The high values of Co, Zn and Cd in the gills and stomach muscle tissues of the mud catfish and Nile tilapia exceeded the maximum allowed FAO (1993) limits (Table 3). There was significant temporal (Kruskal Anova, $p < 0.05$) variation in the levels of all metals except Hg in the gills and stomach tissues of mud

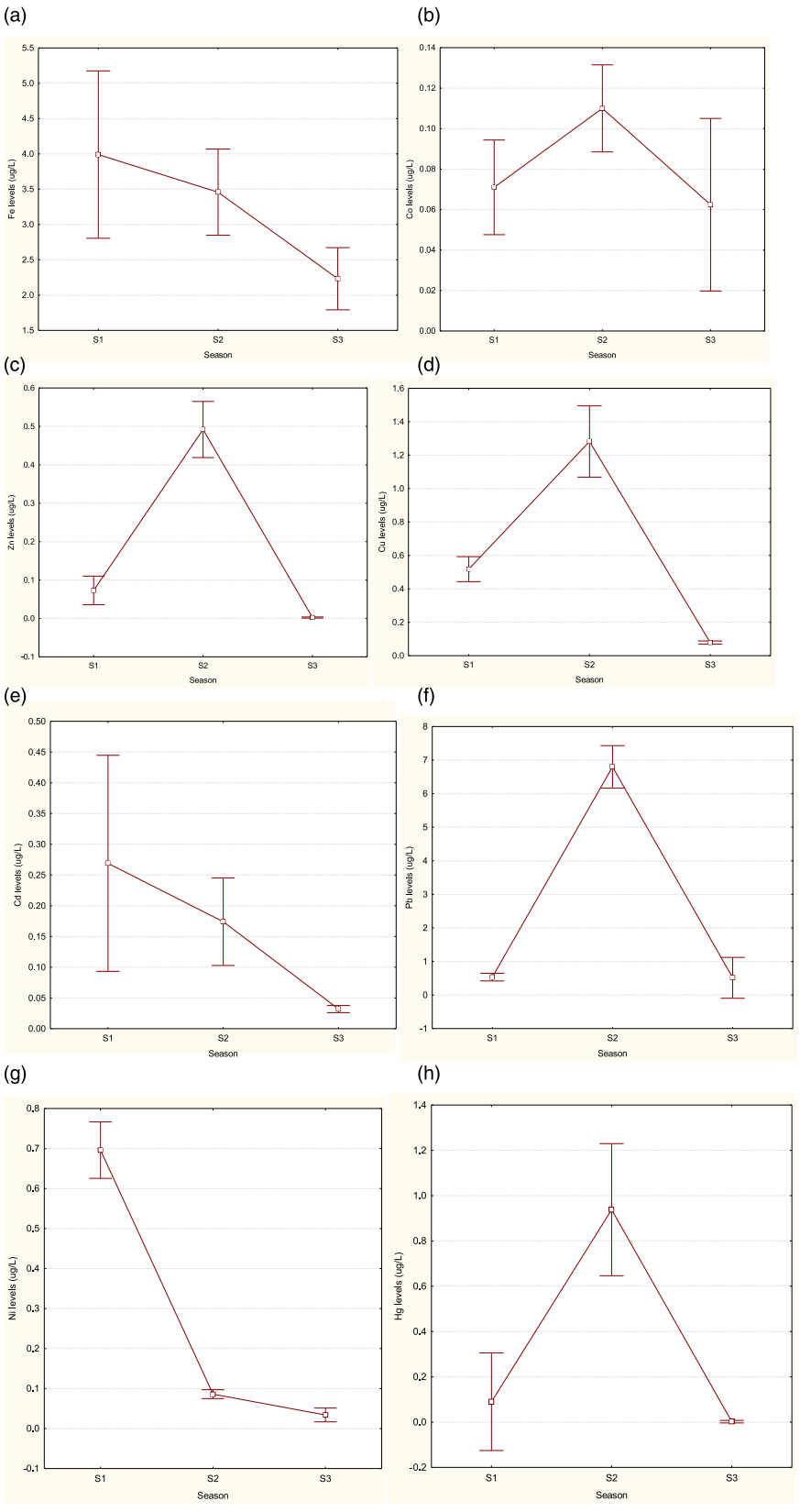

Fig. 2. (a, b, c, d, e, f, g, h). The Mean ± 0.95 Conf. Interval for levels of Fe, Co, Zn, Cu, Cd, Pb, Ni and Hg in the water phase of Lake Asejire, Nigeria 2017. S1 = April; S2 = July and S3 = November.

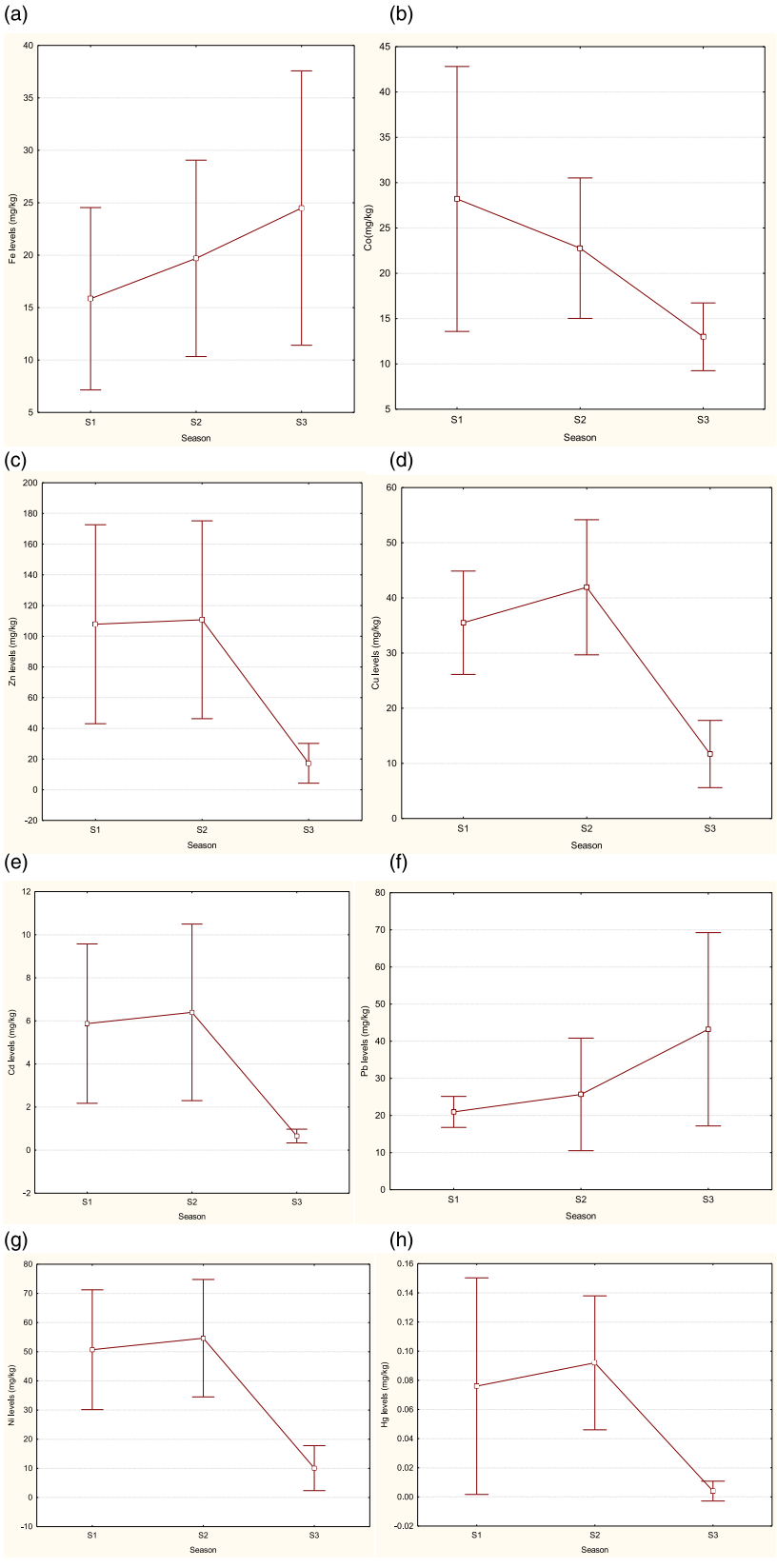

Fig. 3. (a, b, c, d, e, f, g, h). The Mean ± 0.95 Conf. Interval for levels of Fe, Co, Zn, Cu, Cd, Pb, Ni and Hg in the sediment phase of Lake Asejire, Nigeria in April = S1, July = S2 and November = S3 in 2017.

Table 3
Metal concentrations (μg/g) in tissues of the African Sharptooth mud catfish ($N = 45$; 0.523 ± 0.27 kg) and Nile Tilapia ($N = 45$; 0.28 ± 0.11 kg) sampled in Lake Asejire, Nigeria in April, July and November2017. FAO (1993) for metal tissue accumulation limits are also shown for comparison.

Catfish/Tissue	Month	Fe	Co	Zn	Cu	Cd	Pb	Ni	Hg
Gill	April	1649 ± 844.12	21.54 ± 14.66	65.77 ± 23.47	29.36 ± 7.23	3.15 ± 0.09	4.85 ± 0.47	28.96 ± 9.08	0.01 ± 0.00
	July	673.33 ± 478.16	45.81 ± 11.71	48.68 ± 10.5	30.31 ± 2.04	2.63 ± 0.56	9.66 ± 0.69	36.34 ± 10.47	0.01 ± 0.006
	Nove	317 ± 70.48	5.82 ± 0.51	67.1 ± 13.39	41.13 ± 20.67	0.29 ± 0.07	0.92 ± 0.61	1.35 ± 0.97	0.04 ± 0.02
Muscle	April	270.72 ± 83.31	90.70 ± 32.69	39.24 ± 8.00	19.56 ± 15.55	2.28 ± 0.41	3.14 ± 0.53	27.56 ± 12.07	0.02 ± 0.001
	July	216.45 ± 12.64	27.85 ± 6.56	30.05 ± 2.40	25.3 ± 3.86	2.21 ± 0.46	4.72 ± 0.45	25.62 ± 1.98	0.001 ± 0.00
	Nove	181.59 ± 8.68	2.64 ± 0.55	40.75 ± 2.17	32.40 ± 1.40	0.25 ± 0.02	1.83 ± 0.07	1.30 ± 0.42	0.01 ± 0.00
Tilapia/Tissue									
Gill	April	462.88 ± 30.40	12.16 ± 4.16	76.66 ± 42.22	34.07 ± 12.56	2.69 ± 1.25	4.74 ± 1.47	32.84 ± 23.02	0.02 ± 0.01
	July	266.87 ± 42.64	40.23 ± 2.26	47.49 ± 0.34	35.12 ± 0.65	3.19 ± 0.41	10.41 ± 0.68	28.78 ± 2.44	0.01 ± 0.00
	Nove	294.33 ± 6.51	6.02 ± 0.16	72.67 ± 2.08	60.46 ± 1.52	0.26 ± 0.01	1.83 ± 0.05	1.05 ± 0.03	nd
Stomach Muscle	April	283.33 ± 68.02	12.83 ± 2.02	34.52 ± 1.56	42.61 ± 3.39	3.27 ± 0.36	4.65 ± 0.42	39.32 ± 1.19	0.02 ± 0.012
	July	133.44 ± 12.27	8.92 ± 0.08	40.65 ± 2.08	40.93 ± 1.69	2.51 ± 0.23	11.41 ± 0.54	33.79 ± 1.19	0.004 ± 0.001
	Nove	169.58 ± 3.18	3.02 ± 0.02	56.49 ± 1.62	59.11 ± 1.02	0.22 ± 0.03	1.76 ± 0.03	1.02 ± 0.02	nd
FAO limits			0.5	30	100	0.5			30

*Note**mud catfish (0.231–0.657 kg; 0.17–1.23 m) and Nile tilapia (0.112–0.348 kg; 0.09–0.22 m).

Table 4
Criterion maximum concentration (CMC) and criterion continuous concentration (CCC) for metals in water of Lakes Asejire highlighted for comparison purposes. Note (1000 μg/L = 1 ppm). Marked concentrations surpass either the CMC or CCC*.

Metal/Analyte	Freshwater CMC (μg/L)	Freshwater CCC (μg/L)	Concentration ranges (ppm) in Lake Asejire
Cadmium	2.0	0.25	0.03 ± 0.01–0.51 ± 0.14
Mercury	5.00	< 4.5	0.02 ± 0.01–1.16 ± 0.07
Copper	13	9.0	0.08 ± 0.01–1.53 ± 0.53
Lead	65	2.5	0.50 ± 0.01–7.38 ± 0.24
Nickel	470	52	0.02 ± 0.01–0.78 ± 0.05
Zinc	120	120	0.001 ± 0.00–0.54 ± 0.04
Iron	750	1000	1.96 ± 0.02–5.14 ± 1.22
Cobalt	5	< 5	0.02 ± 0.01–0.14 ± 0.01

Table 5
Pollution load index (PLI) for metals in surface sediments of Lake Asejire, Nigeria 2017.

Site	April	July	November
AS1	0.003	0.042	0.089
AS2	0.003	0.020	0.062
AS3	0.001	0.008	0.002
AS4	0.0002	0.005	0.003
AS5	0.0001	0.007	0.084
Mean	0.001	0.016	0.048

catfish. Significant seasonal heterogeneity (Kruskal Anova, $p < 0.05$) in the levels of Co, Cd, Pb and Ni was observed in the gills and stomach muscle tissues of Nile tilapia from Lake Asejire.

Environmental risks posed by heavy metals

For the freshwater phase, the CMC for all metals in Lake Asejire were within the prescribed thresholds (Table 4). The highest CCC values of Cd (0.51 ± 0.14 ppm) recorded at AS5, and that of Pb (7.38 ± 0.24 ppm) recorded at AS3 were higher than the prescribed CCC values (Table 4). Relatively, both the CMC and CCC values for all the metals indicated that the water was suitable to sustain aquatic life and humans could use it for purposes like irrigation, industry and domestic washing but not for drinking and cooking without thorough treatment first.

The pollution loading index (PLI) indicated no metal contamination in the sediments of Lake Asejire (Table 5). The more affirmative geoaccumulation index (I_{geo}) reflected moderate Pb, Ni and Zn, and extreme Cu contamination in the sediments of Lake Asejire (Table 6). Kruskal Anova indicated no significant ($p > 0.05$) spatial differences in the geoaccumulation index for all metals in the sediment of the lake. Whereas there were significant ($p < 0.05$) seasonal heterogeneity in the I_{geo} values for Co ($p = 0.007$), Zn ($p = 0.0090$), Cu ($p = 0.0075$), Cd ($p = 0.00087$), Pb ($p = 0.084$) and Ni ($p = 0.0087$) in the

Table 6
Geoaccumulation index (I_{geo}) for metals in surface sediments of Lake Asejire, Nigeria 2017.

Site	Season	Fe	Co	*Zn	*Cu	Cd	Pb	Ni	Hg
AS1	S1	1.69	1.35	3.83	939.75	−0.100	2.414	2.635	−0.523
AS1	S2	1.72	1.12	3.64	1029.9	−0.063	2.229	2.642	−0.574
AS1	S3	1.98	0.82	2.66	315	−0.796	2.887	2.241	−1.477
AS2	S1	1.70	1.48	3.88	1416	0.338	2.532	2.867	−0.436
AS2	S2	1.81	1.06	3.92	1713	0.376	2.854	2.889	−0.398
AS2	S3	2.09	0.91	2.952	400.5	−0.921	3.106	2.093	0
AS3	S1	1.96	1.22	3.772	1104.9	0.098	2.577	2.682	−0.301
AS3	S2	2.02	1.33	3.855	1378.8	0.141	2.578	2.722	−0.331
AS3	S3	1.99	0.88	2.207	213	−1.097	2.566	1.539	0
AS4	S1	1.67	1.18	3.481	1053	−0.038	2.611	2.769	−1.477
AS4	S2	1.84	1.21	3.557	1173	0.011	2.551	2.798	−0.778
AS4	S3	1.59	1.07	3.089	580.5	−0.690	2.692	2.127	0
AS5	S1	1.44	0.98	3.283	811.5	−0.136	2.557	2.474	−1.176
AS5	S2	1.56	1.05	3.403	994.5	−0.130	2.718	2.559	−0.632
AS5	S3	1.72	0.97	3.108	244.5	−1.046	2.840	1.568	−1.477

Note * moderate to extreme contamination.

Table 7
Potential Ecological Risk Assessment (PERI) in Lake Asejire. Er > 40; RI > 150*. Note *appreciable to serious ecological risk.

Site	Season	Fe	*Co	Zn	Cu	*Cd	Pb	Ni	Hg
AS1	S1	2.94	169.15	2.08	3.48	397	3.11	2.88	0.3
AS1	S2	3.17	116.7	1.32	3.81	432	2.03	2.92	0.27
AS1	S3	5.75	49	0.14	1.17	80	9.26	1.16	0.03
AS2	S1	3.01	226	2.30	5.24	1089	4.09	4.91	0.38
AS2	S2	3.9	86	2.52	6.34	1189	8.51	5.17	0.4
AS2	S3	7.44	60.5	0.27	1.48	60	15.32	0.83	0
AS3	S1	5.46	125.15	1.81	4.09	627	4.53	3.21	0.5
AS3	S2	6.26	160.1	2.19	5.11	692	4.53	3.51	0.48
AS3	S3	5.82	57	0.05	0.79	40	4.42	0.23	0
AS4	S1	2.80	113	0.93	3.9	458	4.90	3.92	0.03
AS4	S2	4.17	122.55	1.10	4.34	514	4.27	4.19	0.17
AS4	S3	2.31	88.25	0.38	2.15	102	5.91	0.89	0
AS5	S1	1.63	71.7	0.59	3.01	366	4.33	1.99	0.07
AS5	S2	2.20	83.9	0.77	3.68	371	6.27	2.42	0.23
AS5	S3	3.16	70.05	0.39	0.91	45	8.31	0.25	0.03

sediments of Lake Asejire. The potential ecological risk index (PERI) indicated that Co and Cd posed appreciable and serious ecological risks respectively to aquatic organisms in the lake (Table 7). Kruskal Anova indicated no significant ($p > 0.05$) spatial variation in the PERI for all metals assessed in the lake. However, there were significant seasonal variations in the PERI values for Co ($p = 0.0226$), Zn ($p = 0.0090$), Cu ($p = 0.0075$), Cd ($p = 0.0087$), Ni ($p = 0.0087$) and Hg ($p = 0.0120$) in the lake.

Discussion

Analysis of pertinent parameters indicated that water quality in Lake Asejire is beneficial and suitable to support most freshwater aquatic organisms. However, the low DO amounts at AS4 and AS5 indicated oxygen depleting activities, processes or compounds in water. Site AS4 is located near the main Nigerian Bottling Company plant, Coca Cola industries and some commercial aquacultural companies in Asejire which could be releasing DO depleting effluent [24]. Low DO levels at the dam wall site, AS5, reflected the effects of stratification in reservoirs which create high DO zones in the epilimnion and low DO zones in the hypolimnion [50]. Underwater or bottom water release into the hydropower intake towers induces partial turn over in the water column depleting oxygen at the epilimnion resulting in low DO levels at the surface. Thus, hydropower facilities or even dam walls with release gates have low DO levels especially in the epilimnion, a phenomenon which explains the low DO values recorded at AS5 in the present study.

Levels of toxic metals such as Fe, Co, Cu, Cd, Pb and Ni exceeded the NSDWQ and WHO approved values in water. Only Hg and Zn levels in water were within acceptable thresholds in the lake. It must be pointed out use of the surface water < 1 m in depth may limit the accuracy of the results as a depth analysis would have revealed a more complete state of

heavy metal pollution in the water column of the lake ([49]). Use of surface water studies provide a quick insight into the pollution status of lake or reservoir [50]. Sediments were polluted by Co, Zn, Pb and Ni whose values exceeded the USEPA thresholds. Previous studies by Lameed and Obadara [24], Aladesanmi et al. [3] in the lake showed contamination of the water phase with Mg, Ni, Ca, Cu, Co, Mn, and Fe. Odewande and Abimbola [34] and Godwin [14] indicated that the sediment phase is contaminated by Fe, Zn, Cd, Ca, Mg, Ni, Mn and Pb in the lake. Anthropogenic sources we suspect to be responsible for elevated levels of metals in Lake Asejire include the manufacturing, aquacultural, agricultural industries and peripheral domestic settlements [21,22]. Of note is that the present study detected the presence of the highly toxic and lethal mercury element in water and sediments of the lake. Although it must be pointed out that the study used the less accurate FAAS method in estimating mercury which has been done elsewhere by Oluyemi and Olabanji [35] for fish tissues in Nigeria. In as much as the less accurate FAAS method detected Hg in water, sediments and fish tissues in Lake Asejire, for future studies it is vital to use more accurate methods of estimating the metal. However, the most important aspect is the ability of the FAAS to detect the presence of Hg which would enable water resources managers to implement guided conservation and remedial strategies. This element (Hg) is less studied in water and sediments of the lake (see [10,14]). Presence of mercury in the lake may be related to the cassava processing which releases cyanide compounds and the effluent from the fizzy drink manufacturing concerns nearby [13,29]. However, at this stage of the study, due to its short term nature to pin point the exact source of mercury in the lake may be not very accurate as only term studies will pin point the exact source of such toxic metals ([29].

Levels of all metals indicated no significant spatial heterogeneity in water and sediments of Lake Asejire. However, there was significant seasonal variation in the levels of all metals in water and sediments at all sites which partially confirmed our first hypothesis. This can be related to the specific features of each sample site and the geographic distribution, and the nature and seasonality of the effluent discharged from the main pollution sources [1]. A lake is a lateral and vertical continuum of sites with unique metal absorption and desorption properties [50], thus there is most likely to be differences in metal absorption rates at sites even in the same lake [27]. The varying bioconcentration factors indicated higher levels of all metals in the sediment phase relative to the water phase in the lake. Heavy metals accumulate in benthic sediments through complex physical and chemical adsorption and dissolution pathways depending on the physicochemical conditions of the water body, metal species' reactivity and the sediment matrix ([25]; Jansen et al., 2002; [7,17,47]). Metals in the sediment phase represent sources of secondary and tertiary pollution when redox conditions alter in most lakes although in most cases seasonal lake turn over releases metals from sediments into the water phases [54].

High Fe, Co, Zn, Cd, Pb and Ni values, which exceed the FAO (1993) limits, were recorded in the gills and stomach muscle tissues of both fish species mostly in April in Lake Asejire. Lowest levels of all metals in the fish tissues of both species were recorded in November in the lake. There were high standard deviations in the levels of Fe in all the tissues for both fish species over the sampling periods indicating a wide seasonal variation of iron in the sediments and water in Lake Asejire. This relates to the seasonal human activities in the catchment which release varying amounts of Fe into the lake. High levels of metals in fish tissues relate to the high levels of metals in water and sediments in the lake. This is largely expected as metals enter fish (and accumulate in tissues) through different pathways such as the gills, skin, eyes, reproductive apertures, fins and food (Luoma and Rainbow, 2005). Metal accumulation in fish pose a health hazard to the fish itself as most metals disrupt the normal physiological, respiratory, reproductive and biochemical processes. Moreso, accumulation of metals in edible fish tissues pose a serious hazard to humans who consume the contaminated fish. Noteworthy is the variation in the seasonal heterogeneity of metal levels i) between tissues in similar fish species, ie mud catfish, and ii) between similar tissues in different fish species. The first observation relates to the seasonal fluctuations in the levels of metals in water, sediments and food sources for the mud catfish which can be linked to the seasonality of polluting activities in the catchment [19]. The second observation relates to dissimilarities in metal depuration rates, age at capture, condition factor, reproductive status, feeding ecology and genetic traits unique among different species which influences metal accumulation in fish tissues [22]. It may be imperative to note that the use of higher temperatures 90–120 °C in drying of fish tissues may also cause lower readings as some heavy metals tend to volatise at increased temperatures, a factor which may lead to some inconsistences on the actual estimation of the concentration of the heavy metals [33].

The CMC and CCC for freshwater indicated that water in Lake Asejire was suitable to sustain aquatic life and humans could use it for purposes like farm irrigation, heavy industry and domestic washing but not for drinking and cooking without treating it first [32]. For sediment analysis, the pollution load index showed no considerable metal contamination. However, the more robust and affirmative geoaccumulation index showed heavy Cu and Zn contamination in sediments of the lake. Only the highly toxic Cd posed serious ecological risk to hydrobionts in Lake Asejire and this partially confirmed our second hypothesis. Although we detected other toxic metals like Pb and Hg in sediments, it appears that determination of sediment toxicity is challenging due to site-specific factors affecting pollutants distribution and bioavailability, especially when contamination levels are close to expected non-effect concentrations [14,16,23].

Conclusion and recommendations

Levels of metals in water and sediments of Lake Asejire were significantly high and in some cases exceeded the stipulated local and international thresholds. Whilst there were no significant spatial heterogeneity in the metal levels in both water and sediments, the significant temporal variations noted for all metals in water, sediments and in some fish tissues reflects

the negative impacts of seasonal fluctuations of anthropogenic activity on the water quality and habitat integrity of the reservoir. The fact that some metals eg Cd pose serious ecological risk to hydrobionts in the lake necessitates for urgent remedial action and mitigation of heavy metal pollution. Moreso, metal contamination of edible gills and stomach muscles in the Nile tilapia and mud catfish implies a potential serious health hazard to the fish themselves and humans who are the consumers of fish from Lake Asejire. Thus, it is prudent to ensure control and effective monitoring of the discharge of effluents from surrounding manufacturing, agricultural and aquacultural industries and domestic settlements. This will help to conserve aquatic biodiversity and optimise the water ecosystem services provision from Lake Asejire for the benefit of lake dependent livelihoods.

Declaration of Competing Interest

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Acknowledgments

This research was supported by funding from the Department for International Development (DfID) under the Climate Impact Research Capacity and Leadership Enhancement (CIRCLE) programme implemented by the African Academy of Sciences (AAS) and the Association of Commonwealth Universities (ACU). Special gratitude goes to all staff at the Aquaculture and Fisheries Management at University of Ibadan, Nigeria for all the logistical help in field and laboratory work. Our sincere gratitude to Exeverino Chinoitezvi and Blessing Kavhu of Parks and Wildlife Zimbabwe (ZIMPARKS), and the Department of Wildlife Ecology and Conservation at Chinhoyi University of Technology for assistance with the map.

Appendices

Table A1
The mean (± SD) concentrations (µg/L), and a summary of the Kruskal-Wallis ANOVA output for the heavy metals in water from Lake Asejire, Nigeria 2017. The NSDWQ and WHO approved values in water are added for comparison.

Location	Month	Fe	Co	Zn	Cu	Cd	Pb	Ni	Hg
AS1	April	3.34 ± 0.51	0.10 ± 0.01	0.07 ± 0.05	0.5 ± 0.02	0.19 ± 0.04	0.6 ± 0.05	0.72 ± 0.02	0.04 ± 0.01
	July	4.09 ± 0.03	0.1 ± 0.03	0.54 ± 0.04	1.39 ± 0.04	0.2 ± 0.02	6.59 ± 0.80	0.10 ± 0.04	0.88 ± 0.17
	Nove	2.13 ± 0.55	0.03 ± 0.01	0.004 ± 0.00	0.08 ± 0.01	0.03 ± 0.00	0.23 ± 0.08	0.03 ± 0.01	nd
AS2	April	2.98 ± 0.25	0.1 ± 0.01	0.12 ± 0.02	0.54 ± 0.08	0.22 ± 0.03	0.50 ± 0.01	0.73 ± 0.01	0.02 ± 0.01
	July	3.09 ± 0.02	0.14 ± 0.01	0.52 ± 0.03	1.53 ± 0.53	0.20 ± 0.02	7.10 ± 1.18	0.08 ± 0.01	1.16 ± 0.07
	Nove	2.84 ± 0.02	0.02 ± 0.01	0.001 ± 0.00	0.076 ± 0.01	0.03 ± 0.01	0.61 ± 0.02	0.06 ± 0.01	nd
AS3	April	5.14 ± 1.22	0.07 ± 0.01	0.05 ± 0.03	0.56 ± 0.16	0.27 ± 0.08	0.53 ± 0.05	0.66 ± 0.06	nd
	July	3.89 ± 0.89	0.10 ± 0.02	0.51 ± 0.05	1.20 ± 0.02	0.10 ± 0.03	7.38 ± 0.24	0.08 ± 0.01	1.01 ± 0.11
	Nove	2.01 ± 0.02	0.08 ± 0.01	0.002 ± 0.001	0.07 ± 0.01	0.03 ± 0.01	0.09 ± 0.03	0.03 ± 0.01	nd
AS4	April	3.22 ± 1.82	0.05 ± 0.03	0.08 ± 0.06	0.44 ± 0.16	0.15 ± 0.07	0.5 ± 0.16	0.65 ± 0.28	0.02 ± 0.01
	July	3.15 ± 0.05	0.10 ± 0.02	0.50 ± 0.01	1.13 ± 0.01	0.24 ± 0.01	6.87 ± 0.21	0.08 ± 0.001	1.08 ± 0.06
	Nove	1.96 ± 0.02	0.1 ± 0.01	0.002 ± 0.00	0.08 ± 0.01	0.03 ± 0.01	0.31 ± 0.04	0.02 ± 0.01	0.01 ± 0.00
AS5	April	4.81 ± 0.85	0.06 ± 0.01	0.07 ± 0.01	0.58 ± 0.06	0.51 ± 0.14	0.69 ± 0.03	0.78 ± 0.05	0.4 ± 0.24
	July	3.07 ± 0.06	0.11 ± 0.02	0.39 ± 0.04	1.16 ± 0.10	0.13 ± 0.02	6.05 ± 1.31	0.09 ± 0.03	0.56 ± 0.68
	Nove	2.22 ± 0.03	0.08 ± 0.02	0.003 ± 0.00	0.09 ± 0.01	0.04 ± 0.01	1.32 ± 0.02	0.03 ± 0.01	nd
	NSDQW	0.05	0.003	1.0	0.3	0.01	0.02	0.001	3.0
	WHO	0.05	0.01	2.0	0.3	0.01	0.05	0.001	3.0
Determinant		Fe	Co	Zn	Cu	Cd	Pb	Ni	Hg
Site, H		1.267	0.205	0.368	0.392	0.276	1.127	0.778	0.684
P value		0.867	0.995	0.985	0.98	0.991	0.890	0.941	0.953
Season, H,		9.620	6.963	12.545	12.522	10.016	9.637	12.681	11.616
P value		0.0081*	0.03*	0.002*	0.002*	0.0067*	0.0081*	0.0018*	0.0030*

*Note**. Significant results are denoted by an asterik*.

Table A2
The mean (± SD) concentrations, and a summary of the Kruskal-Wallis ANOVA output of heavy metals in sediments (mg/kg) of Lake Asejire, Nigeria 2017. The USEPA values are added for normative comparison.

Location	Month	Fe	Co	Zn	Cu	Cd	Pb	Ni	Hg
AS1	April	14.71 ± 10.27	33.83 ± 21.39	145.85 ± 92.84	31.325 ± 15.66	3.97 ± 0.44	15.56 ± 4.14	43.15 ± 23.83	0.09 ± 0.01
	July	15.86 ± 11.10	23.34 ± 11.01	92.6 ± 36.63	34.33 ± 15.67	4.32 ± 0.08	10.16 ± 5.42	43.86 ± 16.43	0.08 ± 0.01
	Nove	28.77 ± 11.12	9.8 ± 3.48	9.75 ± 4.21	10.5 ± 5.83	0.8 ± 0.02	46.3 ± 11.37	17.40 ± 2.11	0.01 ± 0.00
AS2	April	15.05 ± 0.39	45.2 ± 4.60	160.75 ± 42.07	47.2 ± 13.65	10.89 ± 1.77	20.44 ± 1.66	73.70 ± 16.83	0.11 ± 0.01
	July	19.50 ± 2.40	17.2 ± 3.59	176.35 ± 49.71	57.1 ± 13.65	11.89 ± 1.92	42.87 ± 1.66	77.61 ± 20.93	0.12 ± 0.01
	Nove	37.22 ± 12.73	12.1 ± 4.87	19.2 ± 9.03	13.35 ± 3.97	0.6 ± 0.02	76.6 ± 15.83	12.40 ± 4.82	nd
AS3	April	27.32 ± 0.62	25.03 ± 4.71	126.75 ± 5.30	36.83 ± 2.79	6.27 ± 1.96	22.66 ± 5.49	48.08 ± 12.69	0.15 ± 0.07
	July	31.32 ± 0.62	32.02 ± 5.69	153.36 ± 1.21	45.96 ± 3.46	6.92 ± 2.17	22.66 ± 5.49	52.7 ± 10.68	0.14 ± 0.04
	Nove	29.10 ± 8.73	11.4 ± 4.27	3.45 ± 1.02	7.1 ± 3.72	0.4 ± 0.02	22.1 ± 5.86	3.46 ± 1.05	nd
AS4	April	13.98 ± 8.80	22.6 ± 13.11	64.8 ± 42.57	35.1 ± 13.72	4.58 ± 2.38	24.49 ± 9.35	58.73 ± 45.64	0.01 ± 0.000
	July	20.84 ± 4.80	24.51 ± 12.81	77.3 ± 46.10	39.1 ± 5.23	5.14 ± 2.86	21.34 ± 8.64	62.77 ± 48.39	0.05 ± 0.01
	Nove	11.56 ± 4.82	17.65 ± 6.93	26.3 ± 11.43	19.35 ± 8.43	1.02 ± 0.03	29.55 ± 10.64	13.4 ± 7.34	nd
AS5	April	8.16 ± 0.06	14.34 ± 0.78	41.16 ± 1.35	27.05 ± 1.06	3.66 ± 0.78	21.63 ± 0.80	29.79 ± 2.04	0.02 ± 0.0
	July	10.96 ± 1.63	16.78 ± 0.78	54.16 ± 2.89	33.15 ± 6.58	3.71 ± 0.42	31.33 ± 0.93	36.25 ± 5.49	0.07 ± 0.01
	Nove	15.81 ± 4.32	14.01 ± 3.09	27.45 ± 7.34	8.15 ± 2.38	0.45 ± 0.12	41.55 ± 15.32	3.7 ± 1.02	0.01 ± 0.001
Determinant	USEPA	50	0.99	31.6	20,000	35.8	22.7	0.02	0.121
Site, H,		7.97	1.80	1.83	3.00	2.70	2.07	2.97	2.57
P value		0.09	0.77	0.77	0.56	0.61	0.72	0.56	0.63
Season, H		2.78	7.58	9.42	9.78	9.50	4.84	9.50	8.85
P value		0.25	0.02*	0.01*	0.01*	0.01*	0.09	0.01*	0.012*

*Note**. Significant results are denoted by an asterik*.

Table A3
Geoaccumulation Index and the criteria used for decision making adopted from Muller [31].

I_{GEO}	Class	Pollution status
0	0	Practically uncontaminated
1	0–1	Uncontaminated to moderately contaminated
1–2	2	Moderately contaminated
2–3	3	Moderately to heavily contaminated
3–4	4	Heavily contaminated
4–5	5	Heavy to extremely contaminated
>5	6	Extremely contaminated

metal	Hg	Cr	Ni	Co	Cu	Zn	Fe	Cd	Pb
C_n^i/ (ppm)/	3	25	15	1	45	70	5	0.3	25
T_r^i	10	2	1	5	5	1	1	30	5

Table A4
Potential ecological risk assessment criteria.

Risk range (E_r and RI)	Classification
$E_r < 40$; RI < 150	Low ecological risk
$40 < E_r \leq 80$; $150 < RI < 300$	Moderate ecological risk
$80 < E_r \leq 160$; $150 < RI < 300$	Appreciable ecological risk
$160 < E_r \leq 320$; $300 < RI < 600$	High ecological risk
$E_r > 320$; $300 < RI < 600$	Serious ecological risk
$E_r > 320$; $RI \geq 600$	Significantly high serious ecological risk

References

[1] A.A. Adrian, Speciation of heavy metals in environmental water, J. Analyt. Bioanalyt. Chem. 372 (2000) 448–452.
[2] N. Agca, E. Ozdel, Assessment of spatial distribution and possible sources of heavy metals in the soils of sariseki-dortyol district in hatay province (Turkey), Environ Earth Sci. 71 (2014) 1033–1047.
[3] T.O. Aladesanmi, Oluwatosin G. Oladipo, A.G Ali., Aquatic environmental contamination: the fate of Asejire Lake in south-western Nigeria, African J. Environ. Sci. Technol. 7 (6) (2013) 482–489.
[4] A.A. Ayoade, S.O. Fagade, A.A. Adebisi, Dynamics of limnological features of two man-made lakes in relation to fish production, Afr. J. Biotechnol. 5 (10) (2006) 1013–1021.
[5] A.A. Ayoade, Population characteristics of *schilbe mystus* (Linnaeus, 1758), from two different habitats: Asejire and Oyan lakes southwestern Nigeria, J Fish Aquat Sci 6 (2011) 571–577.
[6] C.S. Bentivegna, J.E. Alfano, S.M. Bugel, K. Czechowicz, Influence of sediment characteristics on heavy metal toxicity in an urban marsh, Urban Habitats 2 (2004) 91–111.
[7] H.J. Bing, J. Zhou, Y.H. Wu, X.X. Wang, H.Y. Sun, R. Li, Current state, sources, and potential risk of heavy metals in sediments of three gorges reservoir, china, Environ. Pollut. 485 (2016) 485–496.
[8] P.L. Brown, S.J. Markich, Evaluation of the free ion activity model of metal-organism interaction: extension of the conceptual model, Aquat. Toxicol. 51 (2000) 177–194.
[9] M.T.D. Cronin, J.D. Walker, J.S. Jaworska, M.H.I. Comber, C.D. Watts, A.P. Worth, Use of QSARs in international decision-making frameworks to predict ecologic effects and environmental fate of chemical substances, Environ. Health Perspect. 111 (2003) 1376–1390.
[10] A.B.M. Egborge, The suspended matter content of Lake Asejire, a new impoundment in Nigeria, Trop Ecol 22 (2) (1981) 263–270.
[11] Food and Agriculture Organization, Compilation of legal limits for hazardous substances in fish and fishery products, FAO Fishery Circular (1983) 5–100 No. 464. pp.
[12] A.E. Greenberg, J.J. Connors, D. Jenkin, Standard Methods For the Examination of Water and Wastewater, 15th Ed., American Public Health Association, Washington DC, 1980.
[13] E.A. Godwill, C.J. Ihekwoaba, U.S. Ilo, M. Unaegbu, L.E. Ayuk, A.G. Osuji, Determination of some soft drink constituents and contamination by some heavy metals in Nigeria, Toxicol Rep 2 (2015) 384–390.
[14] A.I. Godwin, Assessment of heavy metals associated with bottom sediment of asejire reservoir, southwest Nigeria, Int. Lett. Natural Sci. 55 (2016) 9–16.
[15] L. Hakanson, An ecological risk index for aquatic pollution control. a sedimentological approach, Water Res. 14 (1980) 975–1001.
[16] L. Herngren, A. Goonetilleke, G.A. Ayoko, Understanding heavy metal and suspended solids relationships in urban stormwater using simulated rainfall, J. Environ. Manage. 76 (2005) 149–158.
[17] P. Huang, T. Li, A. Li, X. Yu, N. Hu, Distribution, enrichment and sources of heavy metals in surface sediments of the north yellow sea, Cont. Shelf Res. 73 (2014) 1–13.
[18] H.S. Hundal, Chemical Speciation of Heavy Metals in Ground and Surface Waters, 4th Ed, Punjab Agricultural University, Lothian, India, 2006 1 – 2.
[19] A.T.A. Ibrahim, T.E. Wassif, M.S. Alfons, Heavy metals assessment in water, sediments and some organs of *oreochromis niloticus* under the impact of sewage water, J. Heavy Metals Toxicity Diseases 1 (1) (2016) 1–7.
[20] M.O. Ipinmoroti, Ichyofauna diversity of lake asejire: ecological implication, Int. J. Fish Aquacult. 5 (10) (2013).
[21] A. Jenyo-Oni, A.H. Oladele, Heavy metals in water, sediments and selected aquatic organisms in Lake Asejire, Nigeria, Eur. Scient. J. 12 (24) (2016) 339–351.
[22] A.A.A Jimoh, A. Ojesanmi, R.A. Olowu, The study of concentrations of some heavy metals in relation to size of *macrobrachium vollenhovenii* (Herklots, 1857) in Asejire lake, Oyo state, southwest Nigeria, Journal of Research and Review in Science (2017) 215–220.
[23] P. Kelderman, W.M.E. Drossaert, M. Zhang, L. Galione, C. Okwonko, I.A. Clarisse, Pollution assessment of the canal sediments in the city of delft (The netherlands), Water Res. 34 (2000) 936–944.
[24] G.A. Lameed, P.G. Obadara, Eco-Development impact of coca-cola industry on biodiversity resources at Asejire area, Ibadan; Nigeria, J. Fisher. Int. 1 (2–4) (2006) 55–62.
[25] E. Latiff, Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrophotometer after a four-stage sequential extraction procedure, J. Analyt. Chim. Acta 413 (2000) 33–40.
[26] M. Lindström, Urban land use influences on heavy metal fluxes and surface sediment concentrations of small oxbows, Water Air Soil Pollut 126 (2001) 363–383.
[27] J. Lisa, T. Sullivan, B. Kinsella, A. Furey, F. Regan, Occurrence of selected metals in wastewater effluent and surface water in Ireland, Anal Lett 50 (4) (2017) 724–737, doi:10.1080/00032719.2016.1194854.
[28] L. Mingbiao, L. Jianqiang, C. Weipeng, W. Maolan, Study of heavy metals speciation in branch sediment of Poyang lake, Environ Sci. (Ruse) 14 (2008) 58–65.
[29] S. Mombo, C. Dumat, M. Shahid, E. Schreck, A socio-scientific analysis of the environmental and health benefits as well as potential risks of cassava production and consumption, in: Environmental Science and Pollution Research, Springer Verlag, 2016, pp. 1–15, doi:10.1007/s11356-016-8190-z.
[30] G. Müller, Index of geoaccumulation in sediments of the Rhine river, J. Geol. 2 (3) (1969) 108–118.
[31] G. Müller, Die schwermetallbelastung der sedimente des neckars und seiner nebenflusse: eine bestandsaufnahme, Chem. Zeitung 105 (1981) 157–164.
[32] G. Nabulo, O.H. Oryem, G.W. Nasinyama, D. Cole, Assessment of Zn, Cu, Pb and Ni contamination in wetland soils and plants in the Lake Victoria basin, Int. J. Environ. Sci. Technol. 5 (1) (2008) 65–74.
[33] T. Nhiwatiwa, M. Barson, A.P. Harrison, B. Utete, R.G. Cooper, Metal concentrations in rivers in Zimbabwe, African J. Aquat. Sci. 3 (2011) 243–252.
[34] A.A. Odewande, A.F. Abimbola, Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria, Environ. Geochem. Health 30 (2008) 243–254.
[35] E.A. Oluyemi, I.O. Olabanji, Heavy metals determination in some species of frozen fish sold at ILE-IFE main market, south west Nigeria, Ife J. Sci. 13 (2) (2011) 355–362.
[36] N.C. Sawyer, L.M. Clair Perry, P. Gene, Chemistry For Environmental Engineering, 4th Ed, 1994, pp. 3–9. New York.
[37] E. Tipping, WHAM - a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by Humic substances, Comput. Geosci. 20 (1994) 973–1023.
[38] D.L. Tomlinson, J.G. Wilson, C.R. Harris, D.W. Jeffrey, Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index, Helgolaender Meeresunter 33 (1980) 566–575.
[39] USEPA, National Primary Drinking Water Regulations, Environmental Protection Agency, United States, 2000.
[40] M. Varol, Assessment of heavy metal contamination in sediments of the tigris river (Turkey) using pollution indices and multivariate statistical techniques, J. Hazard. Mater. 195 (2011) 355–364.
[41] L.A.Van Van Der Kooij, D.Van De Meent, C.J. Leeuwen, W.A. Bruggeman, Deriving quality criteria for water and sediment from the results of aquatic toxicity tests and product standards: application of the equilibrium partitioning method, Water Res. 25 (6) (1991) 679–705.
[42] H.P. Van Leeuwen, Speciation dynamics and bioavailability of metals, J. Radioanal. Nuclear Chem. 246 (2000) 487–492.
[43] J.D. Villanueva, P. Le Coustumer, F. Huneau, M. Motelica-Heino, T.R. Perez, R. Materum, M.V.O. Espaldon, S. Stoll, Assessment of trace metals during episodic events using dgt passive sampler: a proposal for water management enhancement, Water Resources Manag. 27 (12) (2013) 4163–4181, doi:10.1007/s11269-013-0401-5.
[44] J.D. Villanueva, P. Le Coustumer, A. Denis, A. Abuyan, H. Frederic, Trends of labile trace metals in tropical urban water under highly contrasted weather conditions, Environmental Science and Pollution Research, Springer Verlag, Germany, 2015, doi:10.1007/s11356-015-4835-6.

[45] J.P.M. Vink, Measurement of heavy metal speciation over redox gradients in natural water-sediment interfaces and implications for uptake by benthic organisms, Environ. Sci. Technol. 36 (2002) 5130–5138.
[46] J.P.M. Vink, The origin of speciation: trace metal kinetics over natural water / sediment interfaces and the consequences for bioaccumulation, Environ. Pollut. 157 (2009) 519–527.
[47] K. Yulia, M.S. Ann, S. Marie, Adsorption of Cd, Cu, Ni, Pb, and Zn on sphagium peat from solutions with low metal concentrations, J. Hazard. Mater. 152 (2008) 885–891.
[48] Y. Wang, Z. Yang, Z. Shen, Z. Tang, J.;. Niu, F. Gao, Assessment of heavy metals in sediments from a typical catchment of the yangtze river, china, Environ. Monitor. Assess. 172 (2011) 407–417.
[49] W. Wepener, J.H.J. van Vuren, H.H. du Preez, Uptake and distribution of a copper, iron and. zinc mixture in gill, liver and plasma of a freshwater teleost, Tilapia Sparrmanii. Water SA 27 (2001) 99–108.
[50] R.G. Wetzel, Limnology: Lake and River Ecosystems, 3rd ed., Academic Press, San DiegoCA, 2001.
[51] World Health Organisation, Guidelines For Drinking-Water Quality, Vol. 1, 3rd Ed., 2008 ISBN 978 92 4 154761 1.
[52] WHO, Guidelines For Drinking Water Quality, 4th Edition, World Health Organization, Geneva, Switzerland, 2011.
[53] WHO/UNICEF, Progress On Drinking Water Sanitation. 2012, Update WHO, Geneva and UNICEF, New York, 2012.
[54] W. Wu, Z.X. Xu, X.W.;. Yin, D.P. Zuo, Assessment of ecosystem health based on fish assemblages in the WEI river basin, china, Environ. Monitor. Assessm. 186 (2014) 3701–3716.

Further Reading

Nigeria Environmental Standard and Regulatory Enforcement Agency (NESREA), Guidelines and Standards for Environmental pollution Control in Nigeria, 2011, pp. 12–28. Abuja, Nigeria.