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ORIGINAL ARTICLE

Assessment of metallic pollution status of surface water and aquatic macrophytes of earthen dams in Ilorin, north-central of Nigeria as indicators of environmental health



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KEYWORDS

Aquatic plants; Contamination; Earthen dams; Environmental health; Pollution index

Abstract The functional quality of an aquatic ecosystem is a reflection of the health of the environment. Therefore, the present study evaluates the trace metal contamination (Pb, Cd, Ni and Mn) of water and aquatic macrophytes in Asa, Agba, Unilorin and Sobi (Moro) earthen dams, northcentral Nigeria to evaluate the level of anthropogenic impact on the immediate environment. The concentrations of trace metals in samples of water and available macrophytes from the earthen dams were determined by Atomic Absorption Spectrophotometry. Trace metal contamination of surface water in the earthen dams was assessed using metal index (MPI) and metal pollution index (HPI). The biological accumulation factor of trace metals in the aquatic macrophytes was extrapolated from trace metal concentrations in the water and macrophyte samples. The results of the MPI revealed gross metal contamination of the surface water by Pb and Cd (>6.0 for both metals) in the four earthen dams; while Agba and Sobi dams were slightly contaminated by Ni (MPIs = 1.43 and 1.14 respectively). All the earthen dams were considered safe from Mn contamination (MPI < 1.0). Considering the HPI, the four earthen dams fall within the critical pollution threshold for trace metals (HPI > 100), but Asa dam (HPI = 2682.4) was the most contaminated. The biological accumulation factor of Mn in the macrophytes indicated Ceratophyllum demersum, Pycreus lanceolatus and Pistia stratiotes as moderate accumulators of Mn, and can be used as bioindicators in monitoring Mn pollution of aquatic ecosystem. The obtained results in this study showed that the earthen dams are polluted by Pb, Cd and Ni which pose human health risks to the inhabitants through drinking water. © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

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1. Introduction

Water is an important natural resource which plays a vital role in human existence (Ahmed et al., 2011). It is a dynamic system, containing living as well as non-living components, organic, inorganic, soluble as well as insoluble substances that constitute life support systems. Changes in the water quality are known to

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affect the equilibrium of the aquatic environment, causing it to become unfit for designated uses. The availability of freshwater through surface and groundwater resources has become critical as only 1% of freshwater that is available for drinking, agriculture and domestic purposes is exposed to arrays of contamination (Karthika and Dheenadayalan, 2015).

Contamination of freshwater bodies by trace metals is one of the major environmental issues in developing countries in recent times (Goher et al., 2014a). Natural contamination such as chemical weathering and soil leaching is a gradual process whereas release of contaminants from anthropogenic sources is rapid and on the rise (El-Bouraie et al., 2010). Anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfills, mining and rural agricultural activities (Hashim et al., 2011; Yang et al., 2012). Trace metal contamination of fresh water is a major threat to environmental health and a factor in geochemical cycling of metals (Kabata-Pendias and Pendias, 1992). It is of great concern due to their long biological half-lives, non-biodegradability and potential toxicity to the environment (Aktar et al., 2010; Jiang et al., 2012; Goher et al., 2014b; Singare et al., 2012). Contaminants like Hg, Cd, As, Pb, Sb, Cr and Sr are very toxic even at low concentrations; and being non-biodegradable, bioaccumulation in the human body can cause damages to nervous system and internal organs (Lohani et al., 2008). Other contaminants such as Cu, Fe, Mn, Ni and Zn that are essential micronutrients also pose detrimental effects to the functioning of living tissues at higher concentrations (Bruins et al., 2000).

The Nigerian inland water bodies have been subjected to various forms of degradation due to pollution (Sabo et al., 2013). Riverine systems in Ilorin, the capital and commercial hub of Kwara state, north-central Nigeria, are not an exception in this menace. The level of contamination of surface water of lake dams within Ilorin metropolis has been worsened by the indiscriminate deposition of wastes from multifarious sources into river and water channels which eventually end up in lake dams. Lake dams (Asa, Agba, Unilorin and Sobi lake dams) within Ilorin metropolis provide water for the populace of Ilorin city and the immediate communities for the purposes of drinking, domestic and industrial uses. Although, various studies have assessed the trace metal status in sections of River Asa (Ahaneku and Animashaun, 2013; Ibrahim et al., 2013; Oyedeji et al., 2013); no attempts have been made to assess the quality of the surface water in Asa lake dam using water quality index (WQI) and biological analysis approaches. In addition, there is paucity of information on the pollution index of trace metals in Agba, Unilorin and Sobi lake dams. Therefore, this study was conducted to assess the metal pollution status of surface water and aquatic macrophytes of the four lake dams in Ilorin metropolis using water quality index and biological analysis approach to evaluate the health of the environment.

2. Materials and methods

2.1. Study area

The study area is Ilorin metropolis, north-central Nigeria. The four lakes with earthen dams that provide drinking water for the inhabitants of Ilorin metropolis were chosen for this study (Fig. 1). These water reservoirs are Asa dam, Agba dam,

Unilorin dam and Sobi dam. Asa dam is located on River Asa (8° 44" N; 4° 56" E) at approximately 5 km from the city centre. The dam has an overall length of 597 m and storage capacity of 43 million m³ with lake extension of 18 km. The length and breadth of the spillway are about 65 m and 14 m respectively with discharge capacity of 79,000 cm³ (Araoye, 2009; Ayanshola, 2013). Agba dam is located on River Agba (8° 47" N; 4° 60" E) which is one of the tributaries of River Asa. The dam is 17.8 m high, with the length of 570 m and has a reservoir capacity of 1344 million litres (Busari et al., 2014). The University of Ilorin dam (Unilorin dam) is located on River Oyun (8° 46" N; 4° 67" E), with the primarily purpose of water supply to the University community. The dam has a reservoir capacity of 1,800,000 m³, live storage capacity of 1,540,000 m³ and the length of the river is 48 km. The spillway has a length of 50 m, height of 7.7 m and maximum flood discharge of 434.8 m³/s (Sule et al., 2011). Sobi dam (9° 58" N; 8° 25" E) is located on River Moro (a tributary of River Asa); and it is the second largest dam in Ilorin with yield capacity of 14,000 m³/day (Ayanshola, 2013). It was constructed primarily to supply portable water to the Nigerian Army cantonment situated at Sobi, Ilorin.

2.2. Sampling and chemical analysis

Sampling activities were carried out at the four lake dams in the year 2014. Ten samples of dam water were collected at each earthen dam in a pre-acid washed glass bottles and acidified immediately on-site to pH < 2.0 with nitric acid (Sigma Aldrich) after filtration. Water samples were collected at the inflowing (3 samples), intermediate (4 samples) and outflowing (3 samples) points of the four dams. Macrophyte species were collected at the dam sites based on availability, as the macrophytes were mostly floating and submerged types which only survive close to the bank. Physico-chemical parameters of the water samples such as the pH, electrical conductivity (EC) and turbidity were determined on-site using digital multiparameter portable meters (HI-98129 & 93414 models, Hanna Instruments). Other parameters were determined later in the laboratory according to the standard method of APHA (1985).

Available macrophytes in each of the dams were collected and identified either immediately at the site or later at the Department of Plant Biology herbarium, University of Ilorin, Nigeria. The acidified water sample (50 ml) was digested in 5 ml concentrated HNO₃ (Sigma Aldrich) and allowed to evaporate slowly on a hot plate; thereby reducing the volume to 20 ml. The digested water sample was allowed to cool, then filtered using Whatman filter paper No 42 and diluted to 50 ml volume with distilled water. The air-dried samples of the macrophytes were pulverized into powder and digested using HNO₃ + HClO₄ acid mixture according to Hseu (2004). Concentrations of trace metals (Pb, Cd, Ni and Mn) in the digest were measured using atomic absorption spectrophotometer (Buck Scientific model 210 VGP, USA). Quality control and quality assurance procedures were carried out to ensure reliability and integrity of the results.

2.3. Water quality index

The metal index (MPI) of water samples in the lake dams was calculated to determine the level of trace metal contamination 326 C.O. Ogunkunle et al.

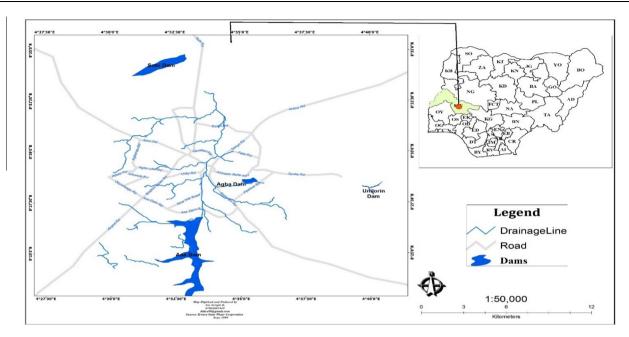


Figure 1 Map of Ilorin showing the location of the lake dams. Inset: map of Nigeria showing the states.

of the surface water in order to assess the suitability of the water quality for drinking (Tamasi and Cini, 2004; Caerio et al., 2005).

$$MPI = \sum_{i}^{n} Ci/MACi$$
 (1)

MPI = Metal index, Ci is the metal concentration (mg L $^{-1}$) in water sample and MACi (mg L $^{-1}$) is the maximum allowable concentration (WHO, 2004). The higher the value of MPI, the more harmful the water is to human health (Bakan et al., 2010). MPI is classified into six (6) classes: class 1, very pure < 0.3; class II, Pure 0.3-1.0; class III, Slightly affected 1.0–2.0; class IV, Moderately affected 2.0–4.0; class V, Strongly affected 4.0–6.0 and class VI, Seriously affected > 6.0 (Lyulko et al., 2001; Caerio et al., 2005).

Metal pollution index (HPI) of the surface water of the lake dams was assessed to provide information on the composite influence of individual element on the totality/overall quality of water in the dams. The calculation of HPI follows three steps viz-a-viz Eqs. (2)–(4) (Prasad and Kumari, 2008; Prasad and Mondal, 2008):

The unit weightage (Wi) of *i*th parameter is a value inversely proportional to the recommended standard (Si) of the corresponding parameter and calculated thus

$$Wi = K/Si \tag{2}$$

where K is the constant of proportionality and Si is the recommended standard of individual ith element in water (mg L⁻¹) (adopted standard is the WHO limit).

Individual quality rating is expressed as sub index of ith parameter (Qi) in Eq. (3)

$$Qi = 100Vi/Si$$
 (3)

where Vi is the monitored value of the *i*th element and Si is the recommended standard limit in water (mg L^{-1}).

The metal pollution index (HPI) is calculated thus as in Eq. (4)

$$HPI = \sum_{i}^{i} QiWi / \sum_{i}^{i} Wi$$
 (4)

Value of HPI > 100 indicates critical metal pollution of water (Prasad and Bose, 2001); however, a modified scale of three classes was proposed by (Edet and Offiong, 2002) as low, medium and high for HPI values of <15, 15–30 and >30 respectively.

2.4. Biological accumulation factor of macrophyte

Biological accumulation factor (BAF) of macrophyte gives the accumulation affinity of macrophytes for specific metal (Nowell et al., 1999)

$$BAF = \sum_{i=0}^{n} Cm/Wi$$
 (5)

Cm is the trace metal content of biomass $(mg kg^{-1})$ of macrophyte and Wi $(mg L^{-1})$ is the concentration of trace metal in water sample.

2.5. Data analysis

Data were subjected to descriptive analysis using the Statistical Package for Social Sciences (SPSS) 16.0 version.

3. Results and discussion

3.1. Physico-chemical and dissolved trace metal level of surface water in the four lake dams

The results of the physico-chemical parameters of surface water in the four lake dams are presented in Table 1. The pH of water samples from the four dams was slightly alkaline, indicating abundance of carbonates of calcium and magnesium (Begum et al., 2009) which may likely result in reduction of metal

toxicity in the water (Aktar et al., 2010). Electrical conductivity (EC), turbidity, hardness, nitrate ion and sulphate ion were below the permissible limits of WHO (2004) and NIS (2007). Pb concentrations in the surface water of the four dams showed that Asa and Unilorin lake dams had the highest concentrations $(0.65 \pm 0.21 \text{ mg L}^{-1} \text{ and } 0.53 \pm 0.17 \text{ mg L}^{-1} \text{ respectively})$ at p < 0.05. The concentration of Pb in Agba lake dam (0.46 \pm 0.19 mg L^{-1}) did not differ significantly from Pb concentrations obtained in Sobi (0.39 \pm 0.17 mg L⁻¹) lake dam at p < 0.05. Furthermore, Cd concentration in the surface water of Asa lake dam was rated highest (0.05 \pm 0.01 mg L⁻¹) whereas, concentrations of Cd in the other three dams did not differ significantly (Agba = Unilorin = Sobi) at p < 0.05. Concentrations of Ni in all the four lake dams were statistically the same at p < 0.05. Mn concentration was significantly higher in Unilorin lake dam $(0.36 \pm 0.12 \text{ mg L}^{-1})$ than the other dams following this pattern: Unilorin dam $(0.36 \pm 0.12 \text{ mg/l}) > \text{Sobi dam}$ $(0.26 \pm 0.08 \text{ mg L}^{-1}) > \text{Agba} \quad \text{dam} \quad (0.17 \pm 0.05 \text{ mg L}^{-1})$ = Asa dam $(0.12 \pm 0.02 \text{ mg L}^{-1})$ at p < 0.05.

The observed variability in concentrations of Pb and Cd may be due to the patronage of the dams, as anthropogenic activities like farming, municipal wastes disposal around these water bodies may be responsible for the elevated metal contents. Trace metals are usually present at low concentrations in aquatic environments but their concentrations may be raised due to anthropogenic inputs like municipal wastes, fertilizer and pesticides application and industrial effluents (Muller et al., 2008; Ntakirutimana et al., 2013). The various anthropogenic activities coupled with land-use pattern (vehicular activities, fertilizer and pesticides use, urban farming and domestic wastes disposals) around these dams must have contributed to the pollution status of Pb and Cd in the dam. Run-offs into these lake dams could also increase the metal loads (especially Pb and Cd) because Karouna-Renier and Sparling (2001) have reported that run-offs from developed/ built-up can increase metal concentrations in water bodies. The fact that there was no significant difference in Ni concentrations in the four dams suggests the absence of anthropogenic input of Ni. The differential levels of Mn in the four dams may be due to the soil geochemistry/geology; most importantly the high Mn concentration in Unilorin lake dam has earlier been reported to be geogenic in nature (Adekola et al., 2008). In addition, the low variability in the concentrations of Mn obtained in all the dams is an indication of little external inputs of Mn in the water. High variability in the analytical data of metal concentrations in surface waters has been reported to be indicative of an external source (Krishna et al., 2009).

Concentrations of Pb and Cd in surface water of Asa, Agba, Unilorin and Sobi lake dams exceeded the maximum allowable concentrations (0.01 mg L⁻¹ for Pb and 0.003 mg L⁻¹ for Cd) stipulated by (WHO, 2004) and (NIS, 2007) for drinking water respectively. The elevated levels of Pb and Cd in the four dams are of utmost concern due to their environmental toxicological threats as these dams supply portable water to different sections of the populace of Ilorin and its environ. However, concentration of Ni and Mn at the four lake dams were within the permissible limits of WHO (2004) whereas concentration of Mn at Asa, Agba and Sobi lake dams exceeded Nigerian standard for drinking water quality limit of 0.2 mg L^{-1} (NIS, 2007). Comparing with similar studies in Nigeria, concentrations of Cd and Mn in water samples from the four dams were lower than reported concentrations (Cd = 0.114 mg L^{-1} and $Mn = 0.651 \text{ mg L}^{-1}$) for River Benue in north-east Nigeria (Haliru et al., 2014); and the reported concentrations (Cd = 1.10 mg L^{-1} and Mn = 2.29 mg L^{-1}) for River Warri in south-south Nigeria (FEPA, 1991). Considering the use of the surface water for irrigation purpose, levels of Pb, Cd and Ni in surface water of the four lake dams exceeded the limits prescribed by FEPA (1991) while Mn only exceeded FEPA limit at Unilorin and Sobi dams (0.36 and 0.26 mg L^{-1} respectively).

Table 1 Physico-chemical parameters of water samples from water dams in Ilorin, north-central Nigeria.

					Metal concentration (mg L ⁻¹)		Metal concentration (mg L ⁻¹)					
	pН	EC dS/m	Turbidity (NTU)	Hard- ness	BOD	Cl ⁻	NO ₃	SO ₄ ⁺	Pb	Cd	Ni	Mn
Asa lake dam	7.81	0.61	1.80 ± 0.5	18.5	64.2	128.0	1.06	50.8	0.65	0.05	0.07	0.12
	± 0.25	± 0.11		\pm 6.8	\pm 12.4	\pm 30.4	± 0.4	± 10.8	$\pm 0.21^{a}$	$\pm 0.01^{a}$	$\pm 0.03^{a}$	$\pm 0.02^{c}$
Agba lake dam	7.74	0.71	1.81 ± 0.5	16.2	72.0	144.0	1.09	54.7	0.46	0.03	0.09	0.17
	$\pm~0.11$	$\pm~0.22$		$\pm~10.1$	$\pm~20.9$	$\pm~26.0$	$\pm~0.7$	\pm 12.6	$\pm 0.19^{b}$	$\pm 0.01^{b}$	$\pm 0.04^{a}$	$\pm 0.05^{c}$
Unilorin lake dam	7.57	0.58	1.85 ± 0.9	14.4	64.0	124.0	1.08	51.8	0.53	0.02	0.07	0.36
	± 0.10	$\pm~0.14$		\pm 8.9	$\pm~20.3$	± 20.1	$\pm~0.7$	± 12.6	$\pm 0.17^{ab}$	$\pm 0.01^{b}$	$\pm 0.04^{a}$	$\pm 0.12^{a}$
Sobi lake dam	7.62	0.66	1.96 ± 0.6	16.7	70.4	136.0	1.08	50.7	0.39	0.02	0.08	0.26
	$\pm~0.19$	$\pm~0.13$		\pm 8.9	± 15.1	\pm 29.7	$\pm~0.6$	± 18.9	$\pm 0.17^{b}$	$\pm 0.01^{b}$	$\pm~0.04^{a}$	$\pm 0.08^{b}$
Drinking H ₂ O quality, WHO*	6.5–8.5	0.9	5.0	100	NA	NA	50	250	0.01	0.003	0.07	0.4
Drinking H ₂ O quality,	6.5-8.5	1.0	5.0	150	NA	250	50	100	0.01	0.003	0.02	0.2
Nigeria +												
Irrigation H ₂ O quality,	NA	NA	NA	NA	NA	NA	NA	NA	0.02	0.01	0.2	0.2
Nigeria + +												
Freshwater quality for aquatic + + +												
CMC, acute	NA	NA	NA	NA	NA	860	NA	NA	0.0650	0.0020	0.470	NA
CCC, chronic	6.5–9.0	NA	NA	NA	NA	230	NA	NA	0.0025	0.00025	0.052	NA

*WHO (1989, 2004, 2006); *NSDWQ maximum limit (2007); *+*(FEPA, 1991); *+*+*USEPA (2006); NA – not available. NA – not available; CMC – critical maximum concentration; CCC – criterion continuous concentration a,b,c p < 0.05.

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The presence of Pb, Cd and Ni in high concentrations may render the usage of the surface water for irrigation environmentally-unfriendly. There is possibility of accumulation of these trace metals in the soil which may be transferred up the food chain through the consumption of crops. This may also affect the acceptability of the agricultural produce for sale or consumption.

Comparing the results with the criteria maximum concentration (CMC) and criterion continuous concentration (CCC) for aquatic life (USEPA, 2006); Pb and Cd concentrations in the surface water of the dams were several folds higher than FEPA recommended limits (FEPA, 1991). CMC value for Ni was higher by at least multiple of 5 units than Ni concentrations in the four dams whereas CCC value was contrarily higher than monitored Ni concentrations in the dams. This indicates that there is possibility of unacceptable effects on aquatic organisms due to Pb and Cd exposures in the four lake dams. Fig. 2 showed dendrogram of three clusters of trace metals in the dams. Cd and Ni formed a cluster while Pb and Mn formed different clusters. This possibly reflects different routes of introduction of Pb and Mn into the dams while Cd and Ni could possibly be from the same source. This Cd-Ni relationship could be linked to indiscriminate disposal of batteries into drainages and rivers (USEPA, 2015). Cd and Ni can also find their way into rivers through run-offs as they are deposited in roadside dust from vehicle break-linings, tyres and fossil fuels (Carrero et al., 2010).

3.2. Metallic pollution status of surface water of the lake dams

Metal pollution index (MPI) of water samples (Table 2) revealed gross metal contamination by Pb and Cd in the four dams $[MPI_{Pb}: Asa (65.0) > Unilorin (53.0) > Agba (46.0)$ > Sobi (39.0) and MPI_{Cd}:Asa (16.67) = Unilorin (10.0) = Agba (10.0) > Sobi (6.67)]. These MPI values signal that the surface water of the four lake dams was seriously affected (class VI) by Pb and Cd based on the classification of Caerio et al. (2005) and Lyulko et al. (2001). MPI_{Mn} of surface water of the four dams and MPI_{Ni} of surface water of both Asa and Unilorin dams were below 1.0, (class II); indicating the surface water is pure. MPI_{Ni} in surface water of Agba and Sobi lake dams (MPIs = 1.43 and 1.14 respectively) falls into class III which is "slightly affected" by Ni. Mean concentrations of monitored metals were also used to determine the HPI values for the four dams (Table 3). The highest HPI value was recorded in Asa dam (HPI = 2682.4), and the following trend of HPI was observed for the four dams: $HPI_{Asa} = 2682.4 >$ $HPI_{Agba} = 1768.9 > HPI_{Unilorin} = 1674.9 > HPI_{Sobi} = 1364.1.$ Based on the scales proposed by Prasad and Bose (2001) and Edet and Offiong (2002); HPI values for all the dams fall

Table 2 Trace metal index (MPI) of surface water in the studied dams.

Dam	Metal	$\sum_{n}^{i} MPI$			
	Pb	Cd	Ni	Mn	
Asa dam	65.00	16.67	1.00	0.30	82.97
Agba dam	46.00	10.00	1.43	0.85	58.28
Unilorin dam	53.00	10.00	1.00	0.90	64.90
Sobi dam	39.00	6.67	1.14	0.65	47.46
MPI Warning threshold	1.0	1.0	1.0	1.0	

within the critical pollution (HPI > 100) and high metal pollution (HPI > 30). This observed critical/high metal pollution of the four dams is an indication that there is a great deterioration in the quality of the environment and this portends great potential ecological and human health risk.

3.3. Biological accumulation of trace metals in aquatic macrophytes

Concentrations and corresponding biological accumulation factor (BAF) for trace metals in the available macrophytes from the dams are shown in Table 4. There were variations in the macrophytes encountered in the dams; Ceratophyllum demersum L. and Pycreus lanceolatus (Poir) C.S. Clarke were encountered in Asa and Agba Lake dams while Eichhornia crassipes (Mart.) Solms and Pistia stratiotes L. were present in Sobi dam. Azolla Africana Desv., C. demersum L., Eclipta prostrata (L.) L. and Ludwigia abyssinica A. Rich. were encountered in Unilorin dam (Table 4). The variation in the distribution of aquatic macrophytes is influenced by factors such as flow velocity, water temperature, light, sediment composition (Barko et al., 1986) as well as plant habit, morphology, and dispersal of propagules (Morris, 2012).

Concentrations of Pb in biomass of all the macrophytes ranged from $13.3 \pm 4.0 \,\mathrm{mg}\,\mathrm{kg}^{-1}$ in *E. crassipes* (Sobi dam) to $98.5 \pm 19.0 \,\mathrm{mg}\,\mathrm{kg}^{-1}$ in *P. lanceolatus* (Agba dam). Kabata-Pendias and Pendias (1992) reported that Pb concentration in uncontaminated plant ranged between 0.05 and $3.0 \,\mathrm{mg}\,\mathrm{kg}^{-1}$; therefore it is inferred that Pb concentrations in the macrophytes were in the toxic range. None of the macrophytes seems to be a hyper-accumulator of Pb from the perspective of phytoremediation as the highest BAF (BAF = 214) recorded in *P. lanceolatus* (Agba dam) was not within hyper-accumulator threshold. A hyper-accumulator should concentrate 100 folds of a particular metal in its tissue on a fresh weight basis; which implies BAF should be more than 1000 (Zayed et al., 1998).

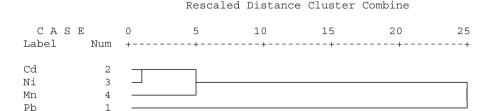


Figure 2 Dendrogram cluster of Trace metals in all the lake dams using Ward's method.

Table 3	Individual quality	rating and metal	pollution index (HF	I) of water dams in Ilorin	, north-central Nigeria.
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	Pb	Cd	Ni	Mn		
K	1	1	1	1		
Weightage (W)	100	333.3	14.3	2.5	$\sum_{n}^{i} Wi = 450.1$	
Quality rating (Q)					$\sum_{n=1}^{i} Q_{i}Wi$	HPI
Asa dam	6500	1667.7	100	30.0	1,207,349.4	2682.4
Agba dam	4600	1000	128.6	42.5	796,201.5	1768.9
Unilorin dam	5300	666.7	100	90.0	753,866.1	1674.9
Sobi dam	3900	666.7	114.3	65.0	614,008.1	1364.1

Table 4 Trace metal concentrations and biological accumulation factor (BAF) in macrophytes in the lake dams.

Metal	Threshold ^a (%)	Aquatic macrophytes	Family	Habit	Dam site	Concentration (mg kg ⁻¹ dw)	BAF	Percent
Pb	0.1	Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Asa	60.0 ± 18.0	92	0.0060
		Pycreus lanceolatus	Cyperaceae	Emergent species	Agba	$98.5 \pm 19.0^{**}$	214	0.0099
		Eichhornia crassipes	Pontederiaceae	Floating species	Sobi	$13.3 \pm 4.0^*$	34	0.0013
		Pistia stratiotes	Araceae	Floating species	Sobi	45.0 ± 24.0	115	0.0045
		Azolla africana	Azollaceae	Floating species	Unilorin	20.0 ± 8.0	38	0.0020
		Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Unilorin	47.5 ± 10.0	90	0.0048
		Eclipta prostrata	Asteraceae	Emergent species	Unilorin	17.5 ± 5.0	33	0.0018
		Ludwigia abyssinica	Onagraceae	Submerged species	Unilorin	30.0 ± 22.0	57	0.0030
Cd	0.01	Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Asa	$4.5 \pm 2.0^*$	90	0.0005
		Pycreus lanceolatus	Cyperaceae	Emergent species	Agba	5.4 ± 2.4	180	0.0005
		Eichhornia crassipes	Pontederiaceae	Floating species	Sobi	6.0 ± 1.2	300	0.0006
		Pistia stratiotes	Araceae	Floating species	Sobi	$4.5 \pm 2.0^*$	225	0.0005
		Azolla africana	Azollaceae	Floating species	Unilorin	6.0 ± 2.0	300	0.0006
		Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Unilorin	6.0 ± 1.0	300	0.0006
		Eclipta prostrata	Asteraceae	Emergent species	Unilorin	4.8 ± 2.0	240	0.0005
		Ludwigia abyssinica	Onagraceae	Submerged species	Unilorin	$7.5 \pm 1.0^{**}$	375	0.0008
Ni	0.1	Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Asa	17.8 ± 2.0	254	0.0018
		Pycreus lanceolatus	Cyperaceae	Emergent species	Agba	$25.3 \pm 8.3^{**}$	281	0.0025
		Eichhornia crassipes	Pontederiaceae	Floating species	Sobi	10.3 ± 4.0	129	0.0010
		Pistia stratiotes	Araceae	Floating species	Sobi	$3.3 \pm 1.1^*$	41	0.0003
		Azolla africana	Azollaceae	Floating species	Unilorin	6.5 ± 2.0	93	0.0007
		Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Unilorin	4.5 ± 3.0	64	0.0005
		Eclipta prostrata	Asteraceae	Emergent species	Unilorin	12.0 ± 3.0	171	0.0012
		Ludwigia abyssinica	Onagraceae	Submerged species	Unilorin	13.7 ± 5.0	196	0.0014
Mn	1.0	Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Asa	79.8 ± 24.7	665	0.0080
		Pycreus lanceolatus	Cyperaceae	Emergent species	Agba	146.5 ± 81	862	0.0147
		Eichhornia crassipes	Pontederiaceae	Floating species	Sobi	70.5 ± 13.4	271	0.0071
		Pistia stratiotes	Araceae	Floating species	Sobi	157.2 ± 40.4	605	0.0157
		Azolla africana	Azollaceae	Floating species	Unilorin	$37.7 \pm 15.4^*$	105	0.0038
		Ceratophyllum demersum	Ceratophyllaceae	Submerged species	Unilorin	$277.0 \pm 89.2^{**}$	770	0.0277
		Eclipta prostrata	Asteraceae	Emergent species	Unilorin	133.2 ± 47.3	370	0.0133
		Ludwigia abyssinica	Onagraceae	Submerged species	Unilorin	170.5 ± 66.2	474	0.0171

^{*} Significant highest concentration at 0.05 level.

Biomass concentrations of Cd were relatively low in all the macrophytes. Concentration of Pb in *L. abyssinica* (7.5 \pm 1.0 mg kg⁻¹) from Unilorin dam rated highest at p < 0.05 and the least concentration (4.5 \pm 2.0 mg kg⁻¹; p < 0.05) was recorded for *C. demersum* (Asa dam) and *P. stratiotes* (Sobi dam). Though relatively high BAF values were obtained

in L. abyssinica (BAF = 375), C. demersum (BAF = 300), A. africana (BAF = 300) and E. prostrata (BAF = 240) at Unilorin dam; and E. crassipes (300) and P. stratiotes (225) at Sobi dam the values did not meet the criterion for hyperaccumulator according to Zayed et al. (1998) and Xing et al. (2013). The reported percent accumulated Cd for C. demersum

^{**} Significant least concentration at 0.05 level.

^a Threshold for hyper-accumulator (Xing et al., 2013).

^b Trace metal concentration (%) in plants.

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in this study was consistent with the reports of Xing et al. (2013) for *C. demersum* (0.0001%) in Dianchi Lake, China.

Biomass concentration of Ni in the macrophytes also varied according to plant species. Significantly least concentration $(3.3 \pm 1.1 \text{ mg kg}^{-1}; p < 0.05)$ was recorded in *P. stratiotes* (Sobi dam) while the highest concentration $(25.3 \pm 8.3 \text{ mg kg}^{-1}; p < 0.05)$ was obtained in *P. lanceolatus* (Agba dam). None of the macrophytes can be regarded as a hyperaccumulator of Ni according to Xing et al. (2013); however *P. lanceolatus* and *C. demersum* could be regarded as accumulator of Ni based on their BAF values (BAFs = 281 and 254 respectively).

Biomass concentration of Mn in C. demersum at Unilorin dam (277.0 \pm 89.2 mg kg⁻¹; p < 0.05) was the highest; while the least biomass concentration was obtained in A. africana $(37.7 \pm 15.4 \text{ mg kg}^{-1}; p < 0.05)$ at Unilorin dam. Mn has a range of 20–300 mg kg⁻¹ in most plants, and the level could be raised as high as 1500 mg kg⁻¹ without deleterious effects in some plants (Pais and Jones, 2000). Therefore, it can be concluded that the macrophytes accumulated Mn within normal growth range. BAF values of Mn were close to hyperaccumulator threshold in P. lanceolatus (BAF = 862) at Agba dam, C. demersum (BAFs = 770 and 665) at both Unilorin and Asa dams respectively and P. stratiotes (BAF = 605) at Sobi dam. From this result, P. lanceolatus, C. demersum and P. stratiotes appear to be moderate accumulators of Mn, hence bioindicators of Mn pollution in aquatic environment. These species, based on their underlined potential can also be engaged in phytoremediation of Mn-polluted water. Furthermore, L. abyssinica (BAF = 474) and E. prostrata (BAF = 370), both at Unilorin dam and E. crassipes (BAF = 271) at Sobi dam could also be regarded as just accumulators of Mn.

4. Conclusion

Chronic trace metal poisoning has become a worldwide public health issue. It is evident from the study that the four lake dams within Ilorin metropolis were grossly contaminated by Pb and Cd thus exposing the inhabitants and aquatic lives to serious health challenges. Though Ni and Mn concentrations were within permissible levels by World Health Organization, there is possibility of increased health risk from long-term exposure to water from Agba and Sobi dams as revealed by their MPIs. The Cd and Ni contaminants in these lakes were possibly deposited from a common source. Assessing water quality standard using the distribution of macrophytes may be misleading, as these aquatic plants have evolved survival strategies in such polluted environments as in the case of low Pb accumulation despite the high pollution index of the metal in the dams. This study also suggests C. demersum, P. lanceolatus and P. stratiotes as moderate accumulator of Mn in metal-polluted aquatic environment; the underlined potential of these macrophytes can be employed in biomonitoring and phytoremediation of Mn in aquatic ecosystems. There is the need for urgent action to restore the standard of drinking water from the dams in Ilorin metropolis through strict regulation and public enlightenment on the health consequences of trace metal contaminants in the earthen dams.

References

- Adekola, F.A., Bale, R.B., Abdus-Salam, N., Eletta O.A.A., Olaniyan,
 J.O., Baba, A.A., 2008. Manganese pollution of the University of
 Ilorin Dam, Nigeria: Source, identification and geochemistry. A-50
 page Technical Report of Investigation submitted to Academic
 Unit, University of Ilorin, Nigeria.
- Ahaneku, I.E., Animashaun, I.M., 2013. Determination of water quality index of river Asa, Ilorin, Nigeria. Adv. Appl. Sci. Res. 4 (6), 277–284.
- Ahmed, S.I., Sabo, A., Maleka, D.D., 2011. Trace metals' contamination of stream water and irrigated crop at Naraguta-Jos, Nigeria. ATBU J. Environ. Technol. 4 (1), 49–56.
- Aktar, M.W., Paramasivam, M., Ganguly, M., Purkait, S., Sengupta, D., 2010. Assessment and occurrence of various heavy metals in surface water of Ganga River around Kolkata: a study for toxicity and ecological impact. Environ. Monit. Assess. 160 (1–4), 207–213.
- American Public Health Association (APHA), 1985. Standard Methods for the Examination of Water and Wastewater, 15th ed. American Public Health Association Inc., New, York, N.Y.
- Araoye, P.A., 2009. The seasonal variation of pH and dissolved oxygen (DO₂) concentration in Asa lake Ilorin, Nigeria. Int. J. Phys. Sci. 4 (5), 271–274.
- Ayanshola, A.M., 2013. Evaluation of supply reliability and sustainability of household water use in Ilorin, Kwara State, Nigeria. Unpublished PhD Thesis submitted to the Department of Civil Engineering, University of Ilorin, Ilorin.
- Bakan, G., Boke-Ozkoc, H., Tulek, S., Cuce, H., 2010. Integrated environmental quality assessment of Kızılırmak River and its coastal environment. Turkish J. Fish. Aquat. Sci. 10, 453–462.
- Barko, J.W., Adams, M.S., Clesceri, N.L., 1986. Environmental factors and their consideration in the management of submersed aquatic vegetation: a review. J. Aquat. Plant Manage. 24, 1–10.
- Begum, A., Ramaiah, M., Khan, H.I., Veena, K., 2009. Heavy metal pollution and chemical profile of Cauvery River water. E-J. Chem. 6 (1), 47–52.
- Bruins, M.R., Kapil, S., Oehme, F.W., 2000. Microbial resistance to metals in the environment. Ecotoxicol. Environ. Saf. 45 (3), 198– 207
- Busari, T.I., Ejieji, C.J., Abegunrin, T.P., 2014. A study of storage capacity degradation of agba reservoir in Ilorin, Kwara State, Nigeria. USEP. J. Res. Inf. Civil Eng. 11 (1), 397–408.
- Caerio, S., Costa, M.H., Ramos, T.B., Fernandes, F., Silveira, N., Coimbra, A., Painho, M., 2005. Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. Ecol. Ind. 5, 155–169.
- Carrero, J.A., Goienaga, N, Barnita, O., Artetxe, U., Arana, G., Hernandez, A., Becerril, J.M., Madariaga, J.M., 2010. Diagnosing the impact of traffic on roadside soils through chemometric analysis on the concentrations of more than 60 metals by ICP/MS. In: Rauch, S., Morrison, G.M. and Monzon, A. (Eds.), Highways and Urban Environment. Proceedings of the 9th Highway and Urban Environment Symposium, Alliance for Global Sustainability Book Series 17, Springer, Dordrecht. pp. 329–336.
- Edet, A.E., Offiong, O.E., 2002. Evaluation of water quality pollution indices for heavy metal contamination monitoring. a study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria). GeoJournal 57, 295–304.
- El-Bouraie, M.M., El Barbary, A.A., Yehia, M.M., Motawea, E.A., 2010. Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. Suo 61 (1), 1–12.
- Federal Environmental Protection Agency (FEPA), 1991. Proposed National Water Quality Standards. Federal Environmental Protection Agency, Nigeria.
- Goher, M.E., Hassan, A.M., Abdel-Moniem, I.A., Fahmy, A.H., El-Sayed, S.M., 2014a. Evaluation of surface water quality and heavy

- metal indices of Ismailia Canal, Nile River, Egypt. Egypt. J. Aquat. Res. 40, 225–233.
- Goher, M.E., Farhat, H.I., Abdo, M.H., Salem, S.G., 2014b. Metal pollution assessment in the surface sediment of Lake Nasser, Egypt. Egypt. J. Aquat. Res. 40, 213–224.
- Haliru, H.A., Ling, L.P., Suhaiza, S.O., 2014. Physicochemical quality assessment of pollutants in river Benue water in Jimeta/Yola metropolitan, Adamawa State, North Eastern Nigeria. Am. J. Environ. Prot. 3 (2), 90–95.
- Hashim, M.A., Mukhopadhyay, S., Sahu, S.J., Sengupta, B., 2011. Remediation technologies for heavy metal contaminated ground-water. J. Environ. Manage. 92 (10), 2355–2388.
- Hseu, Z.Y., 2004. Evaluating heavy metal contents in nine composts using four digestion methods. Bioresour. Technol. 95, 53–59.
- Ibrahim, K.O., Okunlola, I.A., Abdurrahman, A., 2013. Trace metal indices in the characterization of hydro-geochemical condition of surface water along Asa River, Ilorin, Kwara State, Nigeria. Int. J. Geol. Earth Environ. Sci. 3 (1), 29–35.
- Jiang, X., Wang, W.W., Wang, S.H., Zhang, B., Hu, J.C., 2012. Initial identification of heavy metals contamination in Taihu Lake, a eutrophic lake in China. J. Environ. Sci. 24, 1539–1548.
- Kabata-Pendias, A., Pendias, H., 1992. Trace Elements in Soils and Plants, second ed. CRC Press, Boca Ratón, Florida, 315p.
- Karouna-Renier, N.K., Sparling, D.W., 2001. Relationships between ambient geo- chemistry, watershed land-use and trace metal concentrations in aquatic invertebrates living in storm water treatment ponds. Environ. Pollut. 112, 183–192.
- Karthika, I.N., Dheenadayalan, M.S., 2015. Study of ground water quality at selected locations in Dindigul district, India. J. Adv. Chem. Sci. 1 (2), 67–69.
- Krishna, A.K., Satyanarayanan, M., Govil, P.K., 2009. Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India. J. Hazard. Mater. http:// dx.doi.org/10.1016/j.jhazmat.2008.12.131.
- Lohani, M.B., Singh, S., Rupainwa, D., Dhar, D.N., 2008. Seasonal variations of heavy metal contamination in river Gomti of Lucknow city region. Environ. Monit. Assess. 147 (1), 253–263.
- Lyulko, I., Ambalova, T., Vasiljeva, T., 2001. To Integrated Water Quality Assessment in Latvia. MTM (Monitoring Tailor-Made) III. In: Proceedings of International Workshop on Information for Sustainable Water Management. Netherlands, pp. 449–452.
- Morris, K., 2012. Wetland connectivity: understanding the dispersal of organisms that occur in Victoria's wetlands. Arthur Rylah Institute for Environmental Research Technical Report Series No. 225. Department of Sustainability and Environment, Heidelberg, Victoria, Australia. pp. 26–32.
- Müller, B., Berg, M., Yao, Z.P., Zhang, X.F., Wang, D., Pfluger, A., 2008. How polluted is the Yangtze River? Water quality downstream from the Three Gorges Dam. Sci. Total Environ. 402, 232– 247.
- Nigerian Industrial Standard (NIS), 2007. Nigerian Standard for Drinking Water Quality. Nigerian Industrial Standard 554, 13–14.
- Nowell, L.H., Capel, P.D., Dileanis, P.D., 1999. Pesticides in Stream Sediment and Aquatic Biota: Distribution, Trends, and Governing Factors. CRC Press, Boca Raton, Florida, 1040 pp.

- Ntakirutimana, T., Du, G., Guo, J.S., Gao, X., Huang, L., 2013.Pollution and potential ecological risk assessment of heavy metals in a lake. Polish J. Environ. Stud. 22 (4), 1129–1134.
- Oyedeji, S., Fatoba, P.O., Ogunkunle, C.O., Akanbi, G.M., 2013. Water hyacinth and duckweed as indicator of heavy metal pollution in River Asa. J. Ind. Pollut. Control 29 (2), 155–162.
- Pais, I., Jones, J.B., 2000. The Handbook of Trace Elements. Luice Press, Florida, St.
- Prasad, B., Bose, J.M., 2001. Evaluation of heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas. Environm. Geol. 41, 183–188.
- Prasad, B., Kumari, S., 2008. Heavy metal pollution index of ground water of an abandoned open cast mine filled with fly ash: a case study. Mine Water Environ. 27 (4), 265–267.
- Prasad, B., Mondal, K.K., 2008. The impact of filling an abandoned open cast mine with fly ash on ground water quality: a case study. Mine Water Environ. 27 (1), 40–45.
- Sabo, A., Gani, A.M., Ibrahim, A.Q., 2013. Pollution status of heavy metals in water and bottom sediment of River Delimi in Jos, Nigeria. Am. J. Environ. Prot. 1 (3), 47–53.
- Singare, P.U., Mishra, R.M., Trivedi, M.P., 2012. Sediment contamination due to toxic heavy metals in Mithi River of Mumbai. Adv. Anal. Chem. 2 (3), 14–24.
- Sule, B.F., Salami, A.W., Bilewu, S.O., Adeleke, O.O., Ajimotokan, H. A., 2011. Hydrology of River Oyun and Hydropower Potential of Unilorin Dam, Ilorin, Kwara State, Nigeria. N.Y. Sci. J. 4 (1), 69–78
- Tamasi, G., Cini, R., 2004. Heavy metals in drinking waters from mount Amiata (Tuscany, Italy), possible risk from arsenic for public health in the province of Siena. Sci. Total Environ. 327, 41–51.
- USEPA, 2006. National Recommended Water Quality Criteria, Office of Water, EPA-822-R-02-047. Environmental Protection Agency, Washington, U.S.
- USEPA, 2015. Batteries. From < http://www.epa.gov/epawaste/conserve/materials/battery.htm (accessed July 16, 2015).
- WHO, 1989. Health guidelines for the use of wastewater in agriculture and aquaculture: Report of a WHO Scientific Group. WHO Technical Report 778. World Health Organization, Geneva, Switzerland, 74p.
- WHO, 2004. Guidelines for drinking water quality, 3rd ed. World Health Organization, 516 p.
- WHO, 2006. Guidelines for drinking-water: incorporating first addendum, 3rd ed. In: Recommendations, vol. 1. World Health Organization, Geneva, 515 pp.
- Xing, W., Wu, H., Hao, B., Huang, W., Liu, G., 2013. Bioaccumulation of heavy metals by submerged macrophytes: looking for hyperaccumulators in eutrophic lakes. Environ. Sci. Technol. 47, 4695–4703.
- Yang, Y., Chen, F., Zhang, L., Liu, J., Wu, S., Kang, M., 2012. Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf. Mar. Pollut. Bull. 64, 1947–1955.
- Zayed, A., Gowthaman, S., Terry, N., 1998. Phytoaccumulation of trace elements by wetland plants: Duckweed. J. Environ. Qual. 27, 715–721.