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SEASONAL ASSESSMENT, TREATMENT AND REMOVAL OF HEAVY METAL CONCENTRATIONS IN A TROPICAL DRINKING WATER RESERVOIR

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Abstract

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Heavy metals are present in low concentrations in reservoirs, but seasonal anthropogenic activities usually elevate the concentrations to a level that could become a health hazard. The dry season concentrations of cadmium, copper, iron, lead, mercury, nickel and zinc were assessed from three sites for 12 weeks in Oyun reservoir, Offa, Nigeria. Triplicate surface water samples were collected and analysed using atomic absorption spectrophotometry. The trend in the level of concentrations in the three sites is site C > B > A, while the trend in the levels of the concentrations in the reservoir is Ni > Fe > Zn > Pb > Cd > Cu > Hg. Ni, Cd, Pb and Hg were found to be higher than the WHO guidelines for the metals in drinking water. The high concentration of these metals was from anthropogenic watershed run-off of industrial effluents, domestic sewages and agricultural materials into the reservoir coming from several human activities such as washing, bathing, fish smoking, especially in site C. The health effects of high concentration of these metals in the reservoir were highlighted. Methods for the treatment and removal of the heavy metals from the reservoir during water purification such as active carbon adsorption, coagulation-flocculation, oxidation-filtration, softening treatment and reverse osmosis process were highlighted. Other methods that could be used include phytoremediation, rhizofiltration, bisorption and bioremediation. Watershed best management practices (BMP) remains the best solution to reduce the intrusion of the heavy metals from the watershed into the reservoir.

Key words: heavy metals, anthropogenic, health hazard, treatment, watershed.

Introduction

Heavy metals are usually present in low concentrations naturally in water bodies, originating from weathering of minerals, rocks and aquatic environments. Heavy metals occurring naturally are not normally harmful to the quality, productivity, biodiversity and utilization of water bodies as they are only present in very small amounts (Sanayei et al., 2009), and some are even essential to maintenance of life. But various run-offs and leaching of anthropogenic activities from water shed, urbanization, industrial and domestic discharges, agricultural activities, exploration of resources, etc. have led to an increase in the concentrations of these metals in many water bodies such as rivers, lakes and reservoirs. This has posed severe threats to humans and biodiversity using and present in such water bodies with attendant effects on the health of humans, assemblages, conservation and productivity of fishes and other fauna.

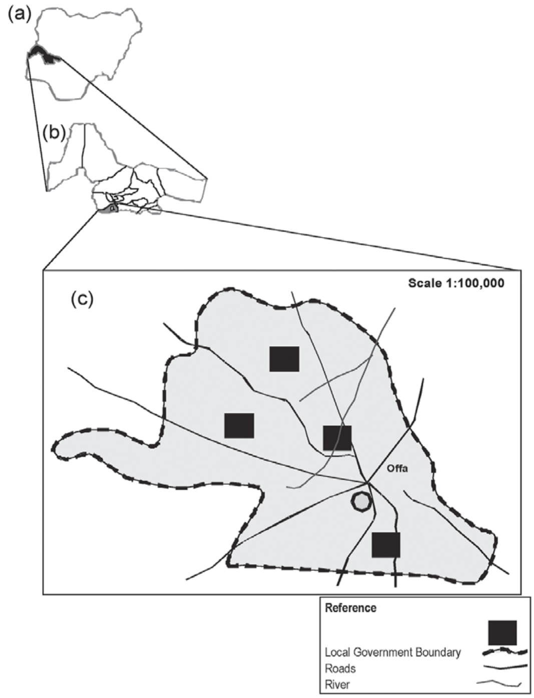

Fig. 1a. Reservoir location in Offa (c), Kwara State (b), Nigeria (a).

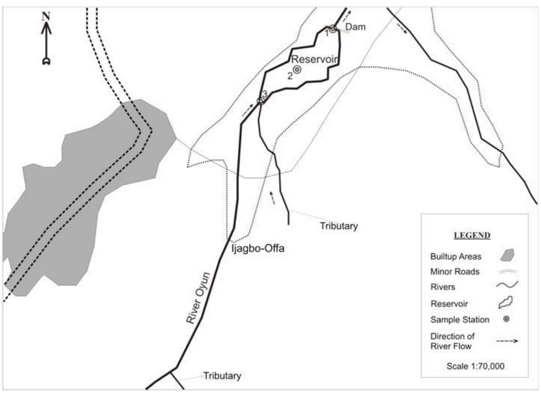

Fig. 1b. Map of Oyun Reservoir Showing the Sampling Stations.

Pollution by heavy metals such as lead, arsenic, cobalt, chromium, zinc, iron, cadmium, copper, manganese, nickel and mercury often affect the quality, productivity and utilization of water bodies. According to Prasad (2008), the primary sources of heavy metals pollution in lakes and reservoirs is the inputs from rivers, sediments and the atmosphere. Heavy metal pollution could be a long-term and irreversible process, because many of the metals are retained relatively strongly in the surface water and soil and do not readily leach out. Also, they have high ability to incorporate in the food chain and bioaccumulate in the body of organisms.

Because of the problems of heavy metals in water to humans and biodiversity, many regulatory bodies such as WHO and U.S. EPA have set maximum contaminant levels (MCL) for various metal ions in drinking water, such that if the levels of these metals are higher than the recommended limits, they become a threat to their quality, productivity and utilization.

Drinking water, which usually comes from man-made lakes and reservoirs, is one of the important sources for heavy metals contamination in humans. The levels and effects of heavy metals pollution in water bodies such as rivers, lakes and reservoirs and have been studied by many workers including Salem et al. (2000), Järup (2003), Idowu et al. (2004), Adekola, Eletta (2007), Mohod, Dhote (2013), among several others.

Water quality, influence of watershed activities on the water quality and fish assemblages, phytoplankton, zooplankton, fisheries potentials, problems, challenges, and management, conservation of fish species, use of biomanipulation to control eutrophication, seasonal influence of limnological variables on plankton dynamics, threatened fishes, fish fauna and general limnology of Oyun reservoir, Offa, Nigeria, an important shallow tropical drinking water reservoir, has been described by Mustapha (2008; 2009a,b,c,d,e,f; 2010a,b,c,d; 2011). The levels of heavy metal concentrations in the reservoir, however, have not yet been assessed.

The present work is aimed at dry season assessment of the concentration levels, sources, possible effects of elevated concentration above the WHO (2011) guidelines on human health and treatment and removal options of some heavy metals in a shallow tropical African water reservoir, which serves as a drinking water reservoir for an estimated population of about 300,000 people.

Material and methods

Study site description

The reservoir used for this study is Oyun reservoir, located in Offa, Nigeria (8°30'05" N and 8°15'55" E) (Fig. 1a). The reservoir was created purposely to provide portable drinking water for domestic and industrial uses to an estimated population of about 300,000 people.

It is a dam reservoir on Oyun River, created in 1964 (expanded in 1983 and 1995 with further expansions proposed) by damming the Oyun River. The reservoir is eutrophic (Mustapha, 2008) with diverse species of littoral plant occupying the shoreline length. Subsistence and commercial fishing activities is also carried out on the reservoir. The reservoir has a maximum length of 128 m, maximum width of 50 m and maximum depth of 8.0 m, and a mean depth of 2.6 m. The surface area is 6.9×10^5 m^2 while the water volume is 3.50×10^6 m^3. The net storage capacity is 2.9×10^6 m^3. The reservoir is subjected to temporal fluctuations in water volume with high water volume in the rainy season and less water in the dry season due to high evaporation. The water retention time is between four and five months in the rainy season (May–October), with an average precipitation between 1,000 mm and 1,200 m, while the water residence time in the dry season (December–April) is between one and two months with average rainfall of about 100 and 200 mm. The morphometric characteristics of the reservoir are listed in Table 1.

Samplings

Triplicate surface water samples were collected from 10 cm depth and stored in a pretreated 1-litre plastic (polyethylene) screw-capped bottles. The bottles were treated with 5% nitric acid and rinsed with distilled water before use. The samples were transported to the laboratory in an ice chest within 24 hours and were stored at –5 °C in a freezer prior to analysis.

Sampling was done weekly from three stations designated 1 (C), 2 (B) and 3 (A) for 12 weeks between January 2014 and April 2014 to assess the level of heavy metals concentrations in the reservoir during the dry season. Station 1 (C) was at the dam axis where a lot of human activities such as washing, bathing and fish landing take place. Station 2 (B) was at the mid-section of the reservoir, which represented the area of lentic water, while Station 3 (A) was at the head water of the reservoir, which represented the lotic section of the reservoir (Fig. 1b).

Heavy metal analyses of cadmium, copper, iron, lead, mercury, nickel and zinc were done at the water quality laboratory of the Department of Agronomy, University of Ibadan, Ibadan, Nigeria, using Perkins-Elmer Atomic Absorption Spectrophotometer model DV 210/211 according to the spectrophotometer operating manual with 0.001 mg/l as the detection limit.

Statistical analysis

The results were presented as mean ±SD. One-way ANOVA and Duncan multiple range test were used to evaluate the significant difference in the concentration of the heavy metals with respect to different sites and the weeks. A probability at level of 0.05 or less was considered significant. Standard errors were also estimated.

T a b l e 1. Morphometric characteristics of Oyun Reservoir, Offa, Nigeria.

Elevation (m)	15
Surface area (m^2)	13.4 x 10^5
Volume (m^3)	3.50 x 10^6
Mean depth (m)	2.6
Maximum depth (m)	8.0
Mean depth to maximum depth ratio	0.325
Hydraulic residence time (days)	12
Length of Shoreline (km)	10
Shoreline Development	2.43

Results

The results of the total mean variations in the level of each heavy metal concentration across the three sites in Oyun reservoir between January and April 2014 is presented in Table 2. Among the heavy metals, Nickel had the highest mean concentration of 0.50±0.12 mg/l recorded in site C, while Mercury had the least mean concentration of 0.000±0.001 mg/l recorded from site A. However, there was no significant differences (*P*>0.05) in the means concentrations of the heavy metals across the three sites (Table 3). The trend in the level of heavy metal concentrations among the three sites is site C > B > A, while the trend in the levels of the concentrations of the heavy metals in the reservoir is Ni > Fe > Zn > Pb > Cd > Cu > Hg. The mean concentration of each heavy metal across the three sites is presented in Figs 2a–g.

T a b l e 2. Mean variations in the concentration of each heavy metal across the three sites.

Sites	Fe(mg/l)	Ni(mg/l)	Cu(mg/l)	Cd(mg/l)	Pb(mg/l)	Zn(mg/l)	Hg(mg/l)
SITEA	0.37±0.144[a]	0.39±0.115[a]	0.08±0.025[a]	0.21±0.109[a]	0.28±0.087[a]	0.40±0.094[a]	0.00±0[a]
SITEB	0.42±0.163[a]	0.35±0.091[a]	0.12±0.037[a]	0.21±0.101[a]	0.31±0.087[a]	0.37±0.135[a]	0.007±0[a]
SITEC	0.33±0.164[a]	0.50±0.124[a]	0.10±0.028[a]	0.29±0.147[a]	0.28±0.086[a]	0.29±0.086[a]	0.01±0.001[a]

All groups with the same symbol across the each column indicate they are the same at P<0.05

T a b l e 3. Total Mean concentration of heavy metals across the three sites.

	SITEA	SITEB	SITEC
Mean	0.251±0.038[a]	0.258±0.040[a]	0.261±0.042[a]

All groups with the same symbol across the each column indicate they are the same at P<0.05

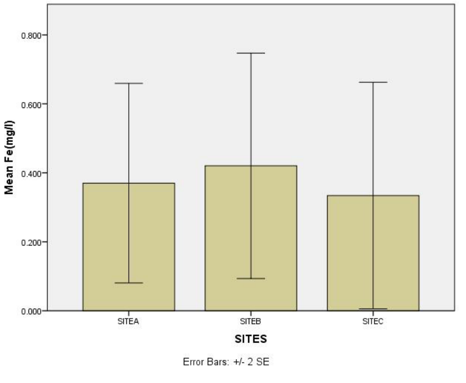

Fig. 2a. Mean concentration of iron across the three sites in Oyun reservoir.

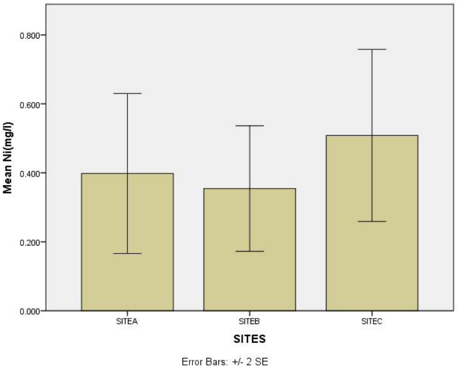

Fig. 2b. Mean concentration of nickel across the three sites in Oyun reservoir.

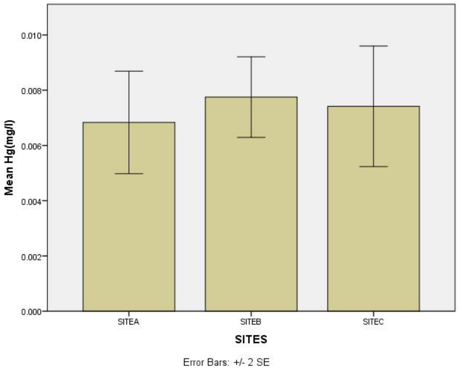

Fig. 2c. Mean concentration of mercury across the three sites in Oyun reservoir.

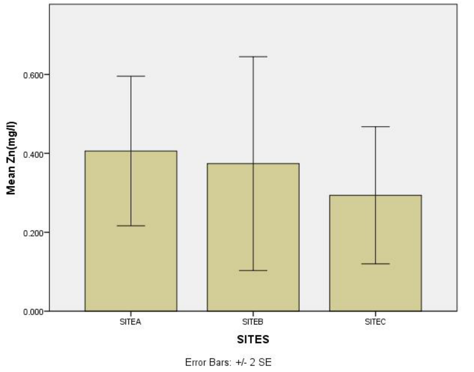

Fig. 2d. Mean concentration of zinc across the three sites in Oyun reservoir.

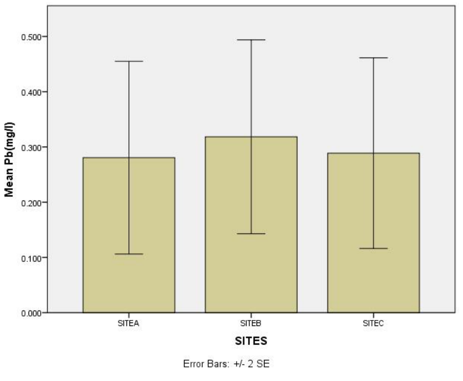

Fig. 2e. Mean concentration of lead across the three sites in Oyun reservoir.

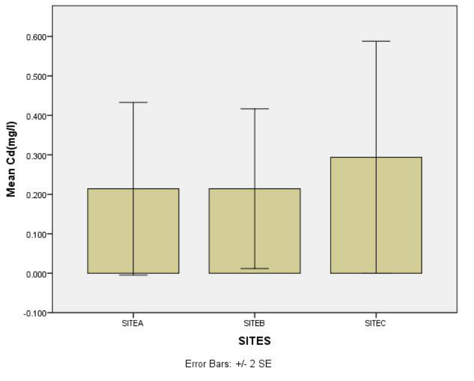

Fig. 2f. Mean concentration of cadmium across the three sites in Oyun reservoir.

The total weekly mean concentration of the heavy metals across the three sites is presented in Table 4, while weekly mean concentration of each heavy metal between January and April 2014 is presented in Table 5. The concentrations of the heavy metals appeared to be high in week 4 except for iron and nickel in which the highest concentration was found in week 5. There was significant differences ($P<0.05$) in the weekly concentration of the heavy metals.

The weekly mean concentration in the level of each heavy metal across the sites in the reservoir is shown in Figs 3a–g.

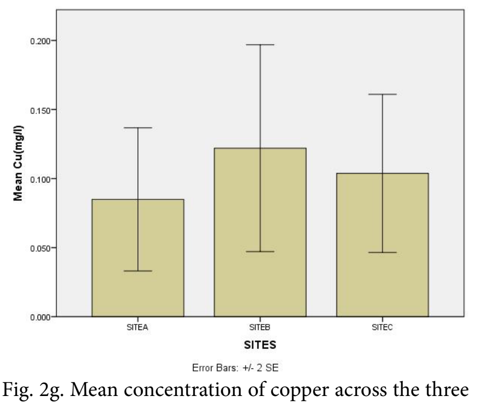

Fig. 2g. Mean concentration of copper across the three sites in Oyun reservoir.

T a b l e 4. Weekly mean concentrations of all heavy metals across the three sites.

Weeks	SITEA	SITEB	SITEC
WEEK1	0.56 ± 0.223^{c}	0.50 ± 0.239^{b}	0.67 ± 0.265^{bc}
WEEK2	0.17 ± 0.087^{abc}	0.09 ± 0.031^{a}	0.11 ± 0.052^{abc}
WEEK3	0.46 ± 0.182^{bc}	0.43 ± 0.127^{ab}	0.57 ± 0.150^{c}
WEEK4	0.19 ± 0.064^{abc}	0.28 ± 0.083^{ab}	0.34 ± 0.162^{abc}
WEEK5	0.06 ± 0.027^{ab}	0.04 ± 0.021^{a}	0.05 ± 0.026^{ab}
WEEK6	0.27 ± 0.187^{abc}	0.27 ± 0.171^{ab}	0.36 ± 0.250^{abc}
WEEK7	0.09 ± 0.034^{ab}	0.10 ± 0.040^{a}	0.15 ± 0.064^{abc}
WEEK8	0.38 ± 0.133^{abc}	0.37 ± 0.132^{ab}	0.35 ± 0.129^{abc}
WEEK9	0.15 ± 0.042^{abc}	0.22 ± 0.071^{a}	0.18 ± 0.068^{abc}
WEEK10	0.43 ± 0.132^{bc}	0.36 ± 0.145^{ab}	0.29 ± 0.086^{abc}
WEEK11	0.20 ± 0.132^{abc}	0.22 ± 0.209^{a}	0.17 ± 0.144^{abc}
WEEK12	0.00 ± 0.001^{a}	0.007 ± 0.0006^{a}	0.007 ± 0.001^{a}

All groups with the same symbol across the each column indicate that they are the same at $P<0.05$

T a b l e 5. Weekly concentrations of each heavy metal.

WEEKS	Fe(mg/l)	Ni(mg/l)	Cu(mg/l)	Cd(mg/l)	Pb(mg/l)	Zn(mg/l)	Hg(mg/l)
WK1	0.116 ± 0.008^{abc}	0.084 ± 0.003^{a}	0.234 ± 0.041^{b}	0.359 ± 0.026^{d}	0.003 ± 0.003^{a}	0.194 ± 0.020^{ab}	0.003 ± 0.001^{a}
WK2	0.267 ± 0.027^{abcd}	0.395 ± 0.134^{ab}	0.223 ± 0.075^{b}	0.069 ± 0.022^{ab}	0 ± 0^{a}	0.158 ± 0.061^{ab}	0.007 ± 0^{bc}
WK3	0.416 ± 0.161^{bcd}	0.500 ± 0.101^{ab}	0.132 ± 0.047^{ab}	0.116 ± 0.019^{abc}	0.660 ± 0.064^{c}	0.042 ± 0.009^{a}	0.005 ± 0.001^{ab}
WK4	0.576 ± 0.158^{d}	0.872 ± 0.077^{b}	0.216 ± 0.094^{b}	1.493 ± 0.176^{e}	0.800 ± 0.065^{c}	0.799 ± 0.309^{cd}	0.013 ± 0.001^{d}
WK5	1.930 ± 0.079^{e}	0.873 ± 0.205^{b}	0.040 ± 0.013^{a}	0.024 ± 0.006^{a}	0.026 ± 0.017^{a}	0.320 ± 0.132^{ab}	0.007 ± 0.001^{bc}
WK6	0.460 ± 0.275^{cd}	0.475 ± 0.324^{ab}	0.023 ± 0.009^{a}	0.020 ± 0.014^{a}	0.103 ± 0.103^{a}	0.228 ± 0.101^{ab}	0.008 ± 0.001^{bc}
WK7	0.306 ± 0.060^{abcd}	0.025 ± 0.005^{a}	0.015 ± 0.010^{a}	0.032 ± 0.003^{a}	0.600 ± 0.141^{bc}	0.165 ± 0.038^{ab}	0.008 ± 0.001^{bc}
WK8	0 ± 0^{a}	0.171 ± 0.075^{a}	0.195 ± 0.015^{b}	0.118 ± 0.025^{abc}	0.420 ± 0.036^{b}	0.526 ± 0.121^{bc}	0.005 ± 0.001^{ab}
WK9	0.026 ± 0.006^{a}	0.526 ± 0.210^{ab}	0.044 ± 0.031^{a}	0.068 ± 0.005^{ab}	0.386 ± 0.040^{b}	0.420 ± 0.124^{abc}	0.010 ± 0^{cd}
WK10	0.200 ± 0.073^{abc}	0.130 ± 0.015^{a}	0.038 ± 0.001^{a}	0.256 ± 0.050^{bcd}	0.393 ± 0.112^{b}	0.082 ± 0.005^{ab}	0.005 ± 0^{ab}
WK11	0.146 ± 0.075^{abc}	0.136 ± 0.063^{a}	0.024 ± 0.004^{a}	0.046 ± 0.004^{a}	0.108 ± 0.026^{a}	1.126 ± 0.182^{d}	0.007 ± 0.001^{bc}
WK12	0.050 ± 0.010^{ab}	0.852 ± 0.231^{b}	0.056 ± 0.028^{a}	0.282 ± 0.104^{cd}	0.048 ± 0.017^{a}	0.230 ± 0.148^{ab}	0.008 ± 0.001^{bc}

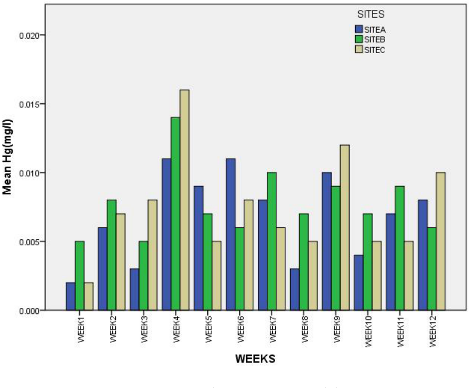

Fig. 3a. Variations in the mean weekly concentration of mercury in Oyun reservoir.

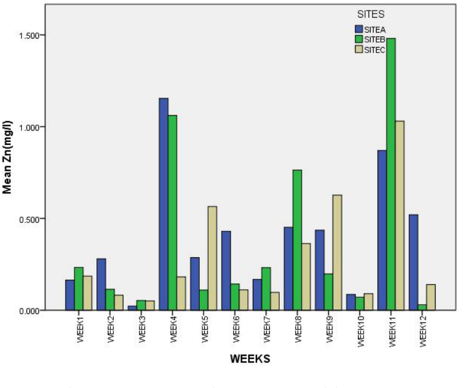

Fig. 3b. Variations in the mean weekly concentration of zinc in Oyun reservoir.

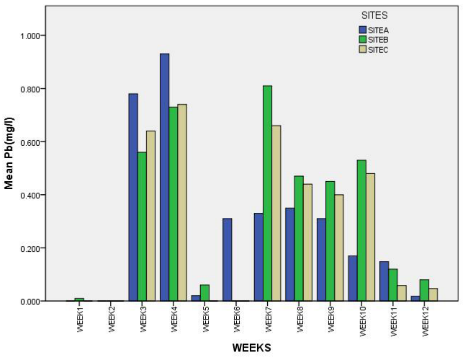

Fig. 3c. Variations in the mean weekly concentration of lead in Oyun reservoir.

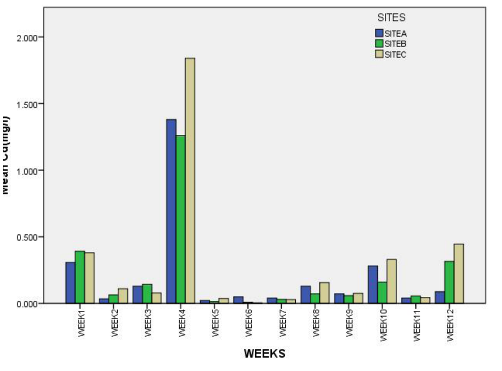

Fig. 3d. Variations in the mean weekly concentration of cadmium Oyun reservoir.

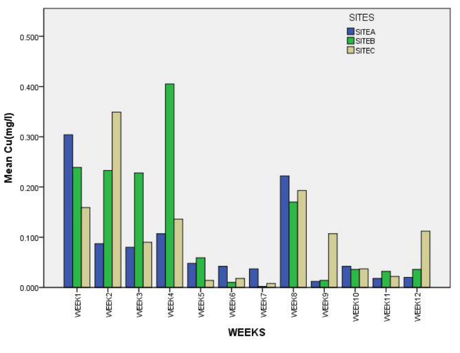

Fig. 3e. Variations in the mean weekly concentration of copper in Oyun reservoir.

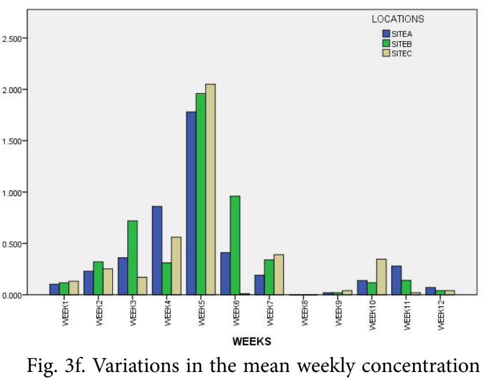

Fig. 3f. Variations in the mean weekly concentration of iron in Oyun reservoir.

Table 6 compares the maximum concentration level of each heavy metal in Oyun reservoir with the WHO (2011) standard.

Discussion

Heavy metals in water are usually not biodegradable but persist in water to bioaccumulate and biomagnify in aquatic organisms, causing different health problems in the organisms and along the food chain.

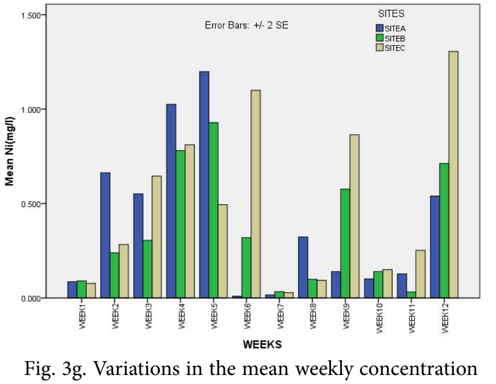

Fig. 3g. Variations in the mean weekly concentration of nickel in Oyun reservoir.

T a b l e 6. Comparison of the concentration levels of heavy metals in Oyun reservoir with WHO (2011) standard.

Heavy metals	**Maximum concentration in Oyun reservoir (mg/l)**	**WHO (2011) standard (mg/l)**
Nickel (Ni)	0.50	0.02
Iron (Fe)	0.42	0.5
Zinc (Zn)	0.40	3
Lead (Pb)	0.21	0.01
Cadmium (Cd)	0.29	0.003
Copper (Cu)	0.12	2
Mercury (Hg)	0.01	0.001

The different health effects of consumption of waters laden with high concentrations of heavy metals have been compiled by different workers, organizations and industries. Thus, reference will only be made to those workers in this paper on the health effects of consumption of water with high concentration levels above WHO (2011) minimum standard and guidelines on heavy metals.

The highest concentration of heavy metals recorded in site C was due to the effects of several human and anthropogenic activities such as washing, bathing, fish smoking, etc. in the site. Several authors have cited anthropogenic activities as a contributing factor to the increasing concentrations of heavy metals in surface waters (Cempel, Nikel, 2006; Adekola, Eletta, 2007; Mohod, Dhote, 2013).

The highest concentration of the heavy metals recorded in week 1 (the beginning of the dry season) was as a result of their high concentrations from the previous rainy season. The reduction in the concentrations of the metals from week 2 was due to accumulation in sediments, uptake by plants and animals and dilution effects. However, the sudden increase in the concentrations of the heavy metals in weeks 4 and 5 could not be easily explained, but could be as a result of intermittent rainfall that occurred during those weeks. The intermittent rainfall for the two weeks could have brought in anthropogenic heavy metal-bearing materials from the watershed into the reservoir.

The highest concentration of nickel recorded in the reservoir could be from watershed runoff of industrial effluents or domestic sewages and agricultural materials into the reservoir. The concentration of nickel in the reservoir was above the WHO (2011) limit of 0.02 mg/l. The effect of high nickel concentration in drinking water reservoir has been comprehensively reviewed by Cempel, Nikel (2006). Because of its toxic effect on humans, the high Ni concentrations in the reservoir could be removed during water purification by active carbon adsorption or coagulation–flocculation processes (Cheremisinoff, 2002).

Iron, which had the second highest concentration in the reservoir, could be expected since iron is a common metal in the earth's crust and has higher retention in sediments. Thus, the iron must have come from the bedrock geology of the reservoir. The Fe concentration in the reservoir is still within the range recommended by WHO (2011) in drinking water, though WHO (2011) did not propose any health-based guideline value for iron. This could be due to the importance of iron in human nutrition; however, concentrations above 200 mg/l, which is rare in the reservoir could pose a health risk. In case the level of iron in the reservoir goes above the minimum permissible limit, the metal can be removed by oxidation-filtration treatment, softening treatment and point of use reverse osmosis.

The low level of zinc concentration in the reservoir, which is below WHO (2011) limit, indicates that there is low leaching of natural zinc in the sediments to the reservoir and as well as low run-off of anthropopenic zinc materials from the watershed. This agrees with WHO (2011) observation that drinking water usually makes a negligible contribution to zinc. Zinc is one of the least toxic heavy metals and which does not bio-accumulate in the organisms. The hazard effect of drinking water with high concentrations of zinc compounds has been highlighted by WHO (2011) and Nriagu (2007). The high level of zinc in the reservoir can be removed during treatment with the use of coagulation, ion exchange, active carbon and sand filtration processes (Degrémont, 2007).

Lead is one of the most documented heavy metals in terms of its anthropogenic sources in water, health effects and its high toxicity even in small concentration. Lead is rarely found occurring naturally in lakes and rivers, thus giving the metal the low concentration in these water bodies. In the event of high concentrations of the metal above the natural background and WHO (2011) permissible limit as it occurred in this reservoir, it is certain that the anthropogenic sources rather than geogenic source were the contributors to the high concentration. Several human activities such as fossil fuel burning, leaching of lead materials, incineration of lead containing sewage and so on occurring in the reservoir and its watershed could have caused the increase in the concentration of lead recorded in the reservoir. Lead does not have any biological function or importance in human nutrition, but its deleterious health effects have been comprehensively compiled by workers such as Järup (2003), Martin and Griswold (2009), among several others. Processes such as coagulation, sand filtration, ion-exchange, active carbon, KDF media-filtration and reverse osmosis may be applied for the treatment and removal of lead in the reservoir.

High amounts of cadmium in water could pose serious health hazards. The sources of the Cd concentration, which was above the WHO (2011) limit in the reservoir, could be from run-off of nitro-phosphate fertilizers from nearby farm lands, sewage and by air diffusion of the metal. This scenario has already been reported in water bodies by Järup et al. (1998), Martin and Griswold (2009), and WHO (2011). The high concentration of Cd in the reservoir can be removed during treatment by the following processes coagulation/filtration, ion exchange, lime softening and reverse osmosis.

The level of copper concentration in the reservoir is below the 2 mg/l WHO (2011) limit. This shows that anthropogenic contribution of copper materials into the reservoir is minimal. According to Nolte (1988), in the absence of anthropogenic source of copper into a water body, copper elevation is from run-off. With low copper concentration in the reservoir, possible health hazard of copper is minimal. The effect of short- and long-term exposure to water-copper toxicity has been reviewed by WHO (2011). High level of copper in reservoirs can be removed by processes such as activated sludge, chemical precipitation, reverse osmosis and ion exchange, all of which can be effective in removing copper from aqueous systems (Akpor, Munchie, 2010).

Among the heavy metals in water, mercury has been recognized as a pollutant with serious effects on human health. Lakes and reservoirs are known to contain very low mercury concentration coming from natural sources from the rock and soil. WHO (2011) recommended that the concentration of total mercury in raw drinking water should not exceed 0.001 mg/L at any time. The concentration of mercury in the reservoir is also low but slightly higher than the WHO (2011) guideline. The higher concentration coming from human activities such as coal combustion, waste incineration, etc., which often releases mercury into the atmosphere and this then enter the water body. The heath effect of elevated mercury consumption in water has been highlighted by Järup (2003) Martin and Griswold (2009) and WHO (2011). Approved methods of removing mercury from the drinking water supply include coagulation/filtration, granular activated carbon, lime softening and reverse osmosis processes.

For treatment and removal of heavy metals to be successful in a reservoir, the physico-chemistry and general limnology of the reservoir should be related to the treatment and removal options.

Apart from chemical processes used in the treatment and removal of heavy metals in drinking water reservoirs, which are often expensive, several other cheaper methods have been developed and tested in water bodies for the treatment and removal of heavy metals in lakes and reservoirs.

Among those methods that have being developed and tested include phytoremediation (Paz-Alberto, Sigua, 2013), Rhizofiltration (Krishna et al., 2012) bisorption (Volesky, 1992) bioremediation (Le Cloirec, Andres, 2005)

Conclusion

Since run-off of anthropogenic materials stemming from human activities on the watershed of Oyun reservoir, Offa, Nigeria, has been identified as the leading cause of elevated heavy metal concentrations, which was above the normal background levels and the WHO (2011) recommended guidelines in the reservoir, the best way of reducing the intrusion of these heavy metals from the watershed into the reservoir is to adopt watershed best management practices (BMP). The adoption, enforcement and use of these practices will not only ensure that heavy metals run-off into the reservoir is reduced, but will also make the water to be free from high heavy metal concentration and of good quality. This will lessen the cost of treatment for these heavy metals and reduce health hazards associated with consumption of heavy metal laden water.

Ethical statement

The authors declare that there is no conflict of interest in this research.

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