ISSN: 0976-3031

Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 10, Issue, 09(A), pp. 34537-34541, September, 2019

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

ASSESSMENT OF HEAVY METALS ON SEDIMENTS AND TILAPIA SPECIES FROM UREJE RESERVOIR, ADO EKITI, EKITI STATE NIGERIA

Odeyemi Dolapo Funmi*[1, 2], Idowu Eunice Opeyemi[2] and Akinbinuade Akinyemi[3]

[1]Department of Science Laboratory Technology, (Biotechnology Option), Faculty of Science, Ekiti State University, Ado Ekiti, Ekiti State, Nigeria
[2]Department of Zoology and Environmental Biology, Faculty of Science, Ekiti State University, Ado Ekiti, Ekiti State, Nigeria
[3]Department of Science Laboratory Technology, (Biotechnology Option), Faculty of Science, Ekiti State University, Ado Ekiti, Ekiti State, Nigeria

DOI: http://dx.doi.org/10.24327/ijrsr.2019.1009.3917

ARTICLE INFO

Article History:

Received 10th June, 2019
Received in revised form 2nd July, 2019
Accepted 26th July, 2019
Published online 28th September, 2019

Key Words:

Heavy Metals, Fish, Sediments, Reservoir, Pollution

ABSTRACT

An investigation into the accumulation of Lead, Arsenic, Zinc, Cadmium and Iron, in the sediment and the organs (gills, liver and flesh) of Tilapia species from Ureje Reservoir was undertaken. The sediment and fish parts were digested and analysed for the metals using Atomic Absorption Spectrophotometer.. The level of metal accumulation in the sediment followed this order Fe> Zn> Pb >As> Cd. Iron (Fe) was the most abundant metal present in the gills of the fish with the value (3.168± 0.03) for the month of June with a similar trend for the subsequent month which are July, August and September. The accumulation of metals were significantly higher ($P<0.05$) in gills than the liver and Muscle. The levels of metals accumulation in the gills, liver and muscle followed the order: Fe>Zn>Pb>As>Cd. The most concentrated metal in the organs of the fish samples was iron. Fe, Zn and Pb were the three most abundant metals in the organs of these fishes and the same trend was also seen in the sediment. Cadmium and Arsenic were detected at low levels in the fish organs and the sediment samples. The heavy metals assessed were a little above WHO/FEPA standard limit which suggests that the reservoir could be polluted with heavy metals.

INTRODUCTION

Heavy metals are natural trace components of the aquatic environment but when present at certain levels is known to result in pollution of the environment; this can be a result of discharges and effluents from industries, change in geochemical structure, agricultural and mining activities. Aquatic environments are known to serve as deposits for pollutants including heavy metals, which through one way or the other are linked into food chains through bioaccumulation in plankton, invertebrates, fishes and finally biomagnified in man[1]. The buildup and elevation of heavy metals can potentially become toxic to aquatic biota like fish at very low exposure contact[2]. Several anthropogenic activities and geologic processes such as disposal of waste effluents and utility waste from industries and agrochemicals influence the introduction of heavy metal contaminants into aquatic systems[3].

Fish have been considered as one of the most significant indicators in water systems for the estimation of metal pollution level[4, 5].Tilapia fish have the ability to persist in poor water quality and grow rapidly[6]. Heavy metal concentrations in aquatic ecosystems are also monitored by measuring their concentrations in sediments, water and plants, During normal metabolism of the aquatic life, metals are taken up from water, food or sediment[7,8,9,10]. Sediments are important sinks for various pollutants such as pesticides and heavy metals and play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions[11]. Sediments are considered as good indicator for water pollution as they serve as traps for materials in aquatic environment[12], so contaminants which escape detection of water analysis can be detected via sediment analysis. Metals have a wide range of adverse effects on reproductive function, young stages of fish and amphibian are highly sensitive to metals; it can result in decrease in hatchability of eggs. Iron (Fe), Lead (Pb), Zinc (Zn), Cadmium

Corresponding author:* **Odeyemi Dolapo Funmi
Department of Science Laboratory Technology, (Biotechnology Option), Faculty of Science, Ekiti State University, Ado Ekiti, Ekiti State, Nigeria

(Cd), and Arsenic (As) all play an important role in the disruption of the endocrine system possible with the mechanism of action with consequent health effects both on human and wildlife[13].

Notably in Ekiti state, reservoir water and fish risk exposure to heavy metals from untreated agricultural runoff from farm settlement where agrochemicals such as pesticides and fertilizers are being used to improve yields. This may results in bio-accumulation of heavy metals in man using water and eating fish from this reservoir since its tributaries pass through populated residential areas, towns, and agricultural sites. Although quite a number of report has shown Ureje Reservoir to contain heavy metals at optimal limits [3,11, 14,] It is expedient to get updates on the quality of water as well the well being of aquatic life in the reservoir because the environment is always at risk of pollution from several anthropogenic activities. Sediments and fish samples have proven to be good indicator of aquatic pollution as reported in several studies [3,15,16]. The analysis of heavy metals that include lead, iron, zinc, cadmium, and arsenic was therefore studied in sediments and fish to provide precautionary use of the water, as well as provide a basis to sensitize government authorities such as National Environmental Management Authority (NEMA) as well as the communities towards management of discharge into the reservoir.

METHODOLOGY

Study Area

Ado- Ekiti Reservoir was constructed by damming the Ureje River in Ado-Ekiti in 1958 for the supply of water for domestic uses and production of fish for Ado-Ekiti community and the environs[17]. It is situated on an undulating plane of an average height of about 440m above sea level and surrounded by highlands. The reservoir lies between latitude 7^0 33' north and longitude 5^0 14' east of the equator as shown in figure 1 and it is a major source of water supply in Ado-Ekiti.

Sampling stations

Sediments were taken from three different stations within the reservoir as described below and illustrated in figure 1

Station A- is at end of reservoir close to areas where farming activities takes place in ado community.

Station B- is at the centre of the damn, no visible activity here except fishing.

Station C- is at the edge of the reservoir close to the pump house where water is being pumped and dispensed through pipes to the community.

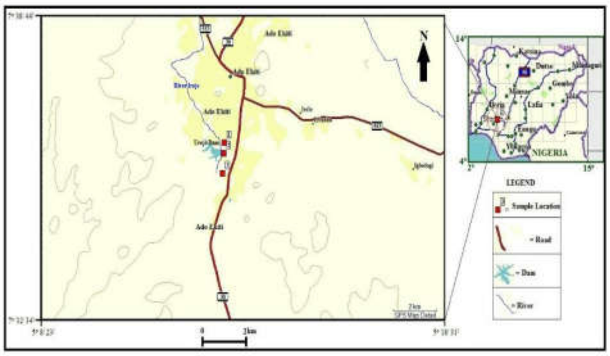

Figure 1 Map showing Ado Reservoir and sampling stations.

Note: 1, 2, 3 in figure are stations A, B and C

Sample collection

Sediment samples were collected from the three stations using Ekman grab. It was dispensed into appropriately labeled polythene bag as A, B and C. The samples were conveyed to the laboratory for heavy metal analysis. Fish samples were collected with help of a fisherman at the reservoir and were taken to laboratory for analysis. The fish was dissected and the gills, liver and muscle were excised.

Digestion of Samples

Fish samples

The fish samples were homogenized and oven dried at 45^0C-50^0C prior to digestion. One gram of sample was weighed in a platinum crucible and placed in a muffle furnace at 450^OC-550^OC until all carbon content was removed as evidence by a white ash. The ash was dissolved in 10ml Nitric acid (5%) and gently warmed on a water bath to speed up dissolution of the ash. The dissolved ash solution was filtered and brought to 50ml and presented for metal analysis.

Sediment samples

One gram of pulverized and oven dried (50^0C) soil sample was weighed into a 100ml conical flask and moistened with distilled water, 10 ml HNO_3: HCl (3:1) was added then boiled with steady heat to almost dryness. It was allowed to cool and leached with 5ml of 6M H_2SO_4. 5ml of distilled water was added and allowed to boil for 10mins. It was cooled and filtered; the filtrate was made up to 100ml and was subjected to metal analysis.

Heavy metal analysis

The analytical method used for the analysis of metal concentration was spectrometry and the equipment used is Atomic Absorption Spectrophotometer (AAS) Buck Scientific model 210 VGP using the calibration plot method. Three processes were involved; standard preparation, equipment calibration and sample analysis. For each element, the instrument was auto-zeroed using the blank (distilled water) after which the standard was aspirated into the flame from the lowest to the highest concentration. The corresponding absorbance was obtained by the instrument and the graph of absorbance against concentration was plotted. The samples were analyzed with the concentration of the metals present being displayed in parts per million (ppm) after extrapolation from the standard curve.

Statistical Analysis

The data values were subjected to analysis of variance (ANOVA) and the mean difference was compared using new Duncan multiple range test using spss version 21. Results are expressed as mean ± standard error of mean (SEM). Statistical significance will be accepted at the $p < 0.05$ level. Microsoft excel was used to derive histogram chart.

RESULTS

Table 1 shows the accumulation of heavy metals: lead (Pb), Arsenic (As), Zinc (Zn), Cadmium (Cd) and Iron (Fe) in sediments collected from three stations in Ado (Ureje) Reservoir for the period of four months. The table presents the mean values of the samplings done in each month and were measured in parts per million (ppm). Iron (Fe) was the most abundant metal present in the sediments from each stations A (170.396±0.57ppm), B(203.659±0.23) and C(200.375±0.35) for the month of June with a similar trend in the months of July, August and September. There was no significant difference ($P<0.05$) in the accumulation of iron (Fe) in the three sampling stations for the period of June and August; Similarly, there was no significant difference ($P<0.05$) for the period of July and September. The results for June and July as well as August and September were significantly different ($P>0.05$). Zn (0.946) was relatively abundant in the sediments compared to Pb (0.284) , As (0.019) and Cd (0.015) as shown in table 2.0: Arsenic(As) and Cadmium (Cd) were the least abundant metal found in sediments all through the period of the study as shown in table 1.0. The level of metal accumulation in the sediment followed this order Fe> Zn> Pb >As> Cd.

The concentration of each metal in the different stations A, B and C are significantly different ($P>0.05$) from one another as presented in table 1.0. the mean values of the metal concentration across the period of study as shown in table 2.0 shows that station B has the highest concentration of Pb (0.319) following this order station B>station A>station C; similarly, station B has the highest value for As (0.022) and Zn (1.15) but follows the order station B>station C> station A; While station A has the highest concentration for Cd (0.018) and follows this order: station A>Station B>Station C; lastly station C has the highest value of Fe (224.386) in this order Station C>Station B>Station A.

A total of 24 fish samples were collected and identified as *Tilapia sp.* The accumulation of Fe in the different organs (gill, liver and flesh) also follow the same pattern as sediment with the highest values in gills (3.168), liver (1.462), Flesh (0.947) as presented in table 3.0 following the same order Fe>Zn>Pb>As>Cd. The accumulation of metals in gills, liver and flesh are significantly different ($P>0.05$) from one another following the order gill>liver>flesh as shown in table 3.0 for the month of June. Similar results were obtained for the month of July and August as presented in table 4. and table 5. respectively. A similar result was obtained for September with the exception of lead having the highest concentration in liver in the order: Liver>Gill>Flesh as shown in table 6.

Iron has the highest accumulation in all the fish parts that was sampled throughout the four months of sampling but the accumulation of iron was seen to be higher in the gills of the fish sample compared with the liver and flesh. Zinc also showed high accumulation in the fish parts but relatively lower to iron. There was no substantial difference in the accumulation of zinc in the fish parts throughout the whole months of sampling. Lead showed a low accumulation compared with iron and zinc in the fish part. Also no substantial difference between the accumulations of lead in the fish parts throughout the period of sampling. Arsenic and cadmium has a very low accumulation in the fish parts throughout the period of sampling. There was no substantial difference between the accumulation of arsenic and cadmium in the fish parts that was sampled throughout the four months sampling.

Comparative analysis of heavy metal on sediment and fish sample using the average accumulation of metals in sediment and fish for four month spanning from June to September. The mean values of heavy metals as presented in figure 2 shows a substantial difference between accumulations of iron in sediment as compared to fish sampled in the four month considered in the study. However, the figure shows that there is no much difference in the level of accumulation of heavy metals such as lead, in sediment and fish sampled from Ado-Ekiti Reservoir. Result also revealed that the accumulation of zinc was higher in the gills of the fish sample compared to the sediment, but the level of zinc in the sediment was higher than that of the liver and flesh. The histochart also revealed that there was no substantial difference in the accumulation of arsenic and cadmium in the fish samples and the sediments throughout the whole month of sampling.

Table 1 Heavy metal accumulation in sediments

Month	Sediment Stations	Mineral composition				
		Pb	As	Zn	Cd	Fe
June	A	0.322 ± 0.00^{c}	0.022 ± 0.00^{b}	0.611 ± 0.00^{a}	0.027 ± 0.00^{c}	170.396 ± 0.57^{a}
	B	0.248 ± 0.01^{b}	0.014 ± 0.00^{a}	0.937 ± 0.01^{b}	0.023 ± 0.00^{b}	203.659 ± 0.23^{c}
	C	0.212 ± 0.00^{a}	0.014 ± 0.00^{a}	1.006 ± 0.00^{c}	0.015 ± 0.00^{a}	200.375 ± 0.35^{b}
July	A	0.340 ± 0.00^{c}	0.020 ± 0.00^{c}	0.721 ± 0.00^{a}	0.034 ± 0.00^{c}	181.901 ± 0.12^{a}
	B	0.265 ± 0.00^{b}	0.013 ± 0.00^{a}	1.254 ± 0.00^{b}	0.013 ± 0.00^{a}	217.741 ± 0.04^{b}
	C	0.215 ± 0.00^{a}	0.015 ± 0.00^{b}	1.515 ± 0.00^{c}	0.023 ± 0.00^{b}	225.919 ± 0.13^{c}
August	A	0.232 ± 0.00^{a}	0.009 ± 0.00^{a}	0.472 ± 0.00^{a}	0.008 ± 0.00^{a}	157.045 ± 0.09^{a}
	B	0.335 ± 0.00^{c}	0.019 ± 0.00^{b}	1.395 ± 0.00^{c}	0.013 ± 0.00^{c}	219.278 ± 0.45^{c}
	C	0.284 ± 0.00^{b}	0.033 ± 0.00^{c}	1.247 ± 0.00^{b}	0.010 ± 0.00^{b}	198.393 ± 0.10^{b}
September	A	0.213 ± 0.00^{a}	0.011 ± 0.00^{a}	0.468 ± 0.00^{a}	0.006 ± 0.00^{b}	181.175 ± 0.20^{a}
	B	0.427 ± 0.00^{c}	0.041 ± 0.00^{c}	1.013 ± 0.01^{c}	0.011 ± 0.00^{c}	196.670 ± 0.15^{b}
	C	0.313 ± 0.00^{b}	0.019 ± 0.00^{b}	0.718 ± 0.00^{b}	0.001 ± 0.00^{a}	272.857 ± 0.10^{c}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different ($P<0.05$).

Table 2 Mean values of heavy metal accumulation in sediments from the different stations

	Pb	As	Zn	Cd	Fe
Station A	0.277	0.016	0.568	0.019	172.629
Station B	0.319	0.022	1.150	0.015	209.337
Station C	0.256	0.020	1.122	0.012	224.386
Mean	0.297	0.023	0.904	0.011	207.196

Table 3 Fish samples collected in June

Fish organs	Mineral composition				
	Pb	As	Zn	Cd	Fe
Gill	0.058 ± 0.01^{b}	0.006 ± 0.00^{a}	0.425 ± 0.00^{c}	0.001 ± 0.00^{a}	3.168 ± 0.03^{c}
Liver	0.002 ± 0.00^{a}	0.002 ± 0.00^{a}	0.261 ± 0.00^{b}	0.000 ± 0.00^{b}	1.462 ± 0.01^{b}
Flesh	0.001 ± 0.00^{a}	0.001 ± 0.00^{a}	0.223 ± 0.00^{b}	0.000 ± 0.00^{a}	0.947 ± 0.01^{a}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different ($P<0.05$)

Table 4 Fish samples collected in July

Fish organs	Mineral composition				
	Pb	As	Zn	Cd	Fe
Gill	0.143 ± 0.01^{c}	0.009 ± 0.00^{c}	0.438 ± 0.00^{b}	0.003 ± 0.00^{a}	2.421 ± 0.00^{c}
Liver	0.004 ± 0.00^{b}	0.004 ± 0.00^{b}	0.265 ± 0.00^{a}	0.002 ± 0.00^{a}	1.377 ± 0.03^{a}
Flesh	0.002 ± 0.00^{a}	0.002 ± 0.00^{a}	0.262 ± 0.00^{a}	0.001 ± 0.00^{a}	1.719 ± 0.04^{b}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different ($P<0.05$)

Table 5 Fish sample collected in August

Fish organs	Mineral composition				
	Pb	As	Zn	Cd	Fe
Gill	0.186 ± 0.01^{c}	0.010 ± 0.00^{c}	0.294 ± 0.00^{c}	0.010 ± 0.00^{c}	2.149 ± 0.03^{c}
Liver	0.085 ± 0.00^{b}	0.004 ± 0.00^{b}	0.199 ± 0.00^{b}	0.003 ± 0.00^{b}	0.777 ± 0.01^{b}
Flesh	0.005 ± 0.00^{a}	0.001 ± 0.00^{a}	0.135 ± 0.00^{a}	0.000 ± 0.00^{a}	0.541 ± 0.01^{a}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different ($P<0.05$)

Table 6 Fish samples collected in September

Fish organs	Mineral composition				
	Pb	As	Zn	Cd	Fe
Gill	0.055 ± 0.00^{b}	0.006 ± 0.00^{b}	0.335 ± 0.00^{c}	0.002 ± 0.00^{a}	1.737 ± 0.02^{c}
Liver	0.062 ± 0.00^{b}	0.003 ± 0.00^{a}	0.220 ± 0.00^{b}	0.002 ± 0.00^{a}	1.091 ± 0.01^{b}
Flesh	0.009 ± 0.00^{a}	0.005 ± 0.00^{b}	0.173 ± 0.00^{a}	0.001 ± 0.00^{a}	0.839 ± 0.01^{a}

Data are presented as Mean±S.E (n=3). Values with the same superscript letter(s) along the same column are not significantly different (P<0.05)

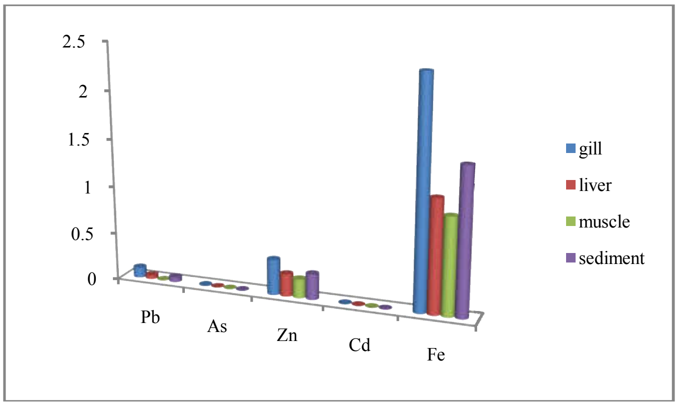

Figure 2 Heavy metals accumulation in fish parts and sediments

DISCUSSION

Iron (Fe), Zinc (Zn), Lead (Pb), Arsenic (As) and Cadmium (Cd) were all detected in the sediments. The accumulation of iron was higher in the sediments compared to the other heavy metals which support the report of [11] that iron and zinc were higher in concentration than other metals examined. The high content of iron may be due to clayey materials that may form the riverbed; it may also be due to human activities such as discharge of untreated sewage that contains iron as well as the ability of the sediments to act as a sink [18]. Low concentration of cadmium and arsenic were detected in sediment although lower than the reported value of [3] on heavy metal analysis of Ureje Reservoir but against the report of [11] where cadmium was not detected during his study. Furthermore, it has been reported that iron occurs in high concentration in Nigeria soils. In the sediments, zinc was detected to have a high accumulation but not as high as the concentration of iron. High concentration in the sediments is in agreement with previous reports that sediments is the sink for aquatic pollutants [3.15.16,19]

Heavy metals in Fish

In the parts of the fish and for all the fishes analyzed, the concentration of iron was the highest in all samples throughout the period of study. The low concentration of cadmium and arsenic recorded is in line with the report of [16]. All the heavy metals analyzed were detectable in the flesh of the fishes assayed. The skin serves as a point of contact and exposure as well the point of excretion. The gills of the fishes had the highest concentration of heavy metals compared to that seen in the liver and flesh of the fishes. The gills are more exposed to water and its pollutants than any other organ of the fish due to their anatomical and physiological properties that allows more absorption from water. Furthermore, the accumulation of chemicals in fish occurs through the membrane and by ingestion, during this process; metals could be retained by the gills. The gills perform the function of respiration and are directly in contact with water and pollutants that may be present in water[15]. Thus, the concentrations of heavy metals in gills reflect the concentration of trace metals in the waters where the fish lives[20]. This suggests that the concentration of metals accumulated in the gills is a measure of the concentration of heavy metals in the aquatic environment.

The concentration of Fe was also relatively high in the liver as shown in table 2 this can be as a result of the liver being the organ for detoxification in fish[15], thus heavy metals tends to accumulate more in the liver than the muscle due to the fact that the liver is site of detoxification, it is thus expected to accumulate more than the flesh. The muscle has the least accumulation of metals which is in support of the report of [15]

Figure 2. shows the accumulation of metals in sediment and fish parts, although both accumulated a considerable amount of metals but the gill showed higher concentration of metals than the sediment, this could be because the gill has a direct access to the contaminated water which is its habitat.

Generally, the heavy metals accumulation assessed in this study were above WHO/FEPA limit for sediments and fish which is in line with the study of [21,22]. This suggests that the Ado Reservoir may be polluted with heavy metals which could be as a result of indiscriminate discharge of wastes and run off from farms where agrochemicals such as pesticides and fertilizers are being used.

CONCLUSION AND RECOMMENDATION

Based on the findings of the study, Ureje Reservoir, Ado Ekiti is polluted with heavy metals assessed (Pb, Zn, Cd, As and Fe) as the level observed were above the optimum standards of WHO/FEPA of heavy metals on sediments and fish. It is therefore recommended that further studies be carried out on the assessment of the quality of the reservoir. Also the community should be sensitized on proper disposal of waste and also the use of biological control of pest to avoid the use of pesticides in the farm and subsequently possible run off of harmful chemicals into the water bodies.

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How to cite this article:

Odeyemi Dolapo Funmi *et al*.2019, Assessment of Heavy Metals on Sediments and Tilapia Species from Ureje Reservoir, Ado Ekiti, Ekiti State Nigeria. *Int J Recent Sci Res.* 10(09), pp. 34537-34541. DOI: http://dx.doi.org/10.24327/ijrsr.2019.1009.3917

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