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Dry and Wet Seasonal levels of Heavy Metals in Water, Fish (*Brycinus leuciscus*) and Sediments from Kiri Reservoir in Shelleng Local Government, Adamawa State, Nigeria.

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Abstract

Dry and wet Seasonal variability of heavy metal levels in water, fish (*B. leuciscus*) and sediments was conducted in Kiri reservoir, Adamawa State Nigeria. Water, Fish (B. leuciscus) and Sediments were collected in triplicate from three sampling sites bi-weekly for the period of six (6) months. March, April and May (dry season) and June, July and August (wet season), 2022. Water, fish (*B. leuciscus*) and sediments were digested following the standard methods (APHA, 2005). Heavy metals Pb, Cu, Cd, Zn, and Fe were determined using Atomic Absorption Spectrophotometer (AAS). Data obtained were subjected to descriptive analysis to establish means, standard errors and one way analysis of variance (ANOVA) was used to determine the mean significant at P< 0.05. All the heavy metals investigated were detected in water, fish (B. leuciscus) and sediments in both dry and wet season and were higher in dry season when compared with the wet season. Pb and Cd in water slightly exceeded WHO (2022) recommended permissible limit. Kiri reservoir has higher heavy metals water, fish (*Brycinus leuciscus*) and ediments in dry season when compared to wet season but not beyond the recommended limit suggested by WHO, 2004 except Pb and Cd which were beyond recommended limit in water. Therefore water of Kiri reservoir is moderately polluted with Pb and Cd.

Keywords: Seasonal variability; Heavy metals; Water; Fish; Sediments; Kiri reservoir

Introduction

The provision of water for domestic and other uses in rural and urban centres is one of the most intractable problems in Nigeria today. Access to adequate water of good quality is essential to health, food production and sustainable development. As Open environmental spaces, rivers and reservoirs are more likely to be polluted (Bhuiyan et al., 2015). The domestic untreated water is thrown directly into the water resource and this majorly causes pollution inside the water and harms the ecosystem (Kambe 2014). Fish are relatively situated at the top of the aquatic food chain; therefore, they can accumulate heavy metals from food, water and sediments (Zhao et al., 2012). Uptake of heavy metals by fish from the environment primarily occurs through gills, food, and skin and through water taken with food. River sediments become the storage of heavy metals, which in turn becomes the potential secondary source of metal pollution to the connected aquatic systems (Wang 2017). Agricultural activity like farming takes place both in dry and wet season in Kiri and environ were Fertilizers, Pesticides and herbicides are extensively used to increase yield and to control pests, diseases, weeds and other plant pathogens. Domestic wastes generated flows into the reservoir in the wet season and may contaminate the water with a variety of contaminants especially heavy metals. Three sites

were choosen along the reservoir as sampling sites namely Site A (Babban daba), Site B (at Bobere), and Site C (Dam site) as shown in figure 1.

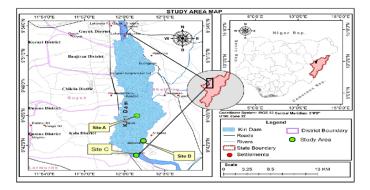


Figure 1: Map of Kiri Reservoir showing the Sampling sites.

Duration of sampling

Water, Fish (*B. leuciscus*) and Sediments were sampled for the period of six months (March to August) 2022. March, April and May, 2022 were regarded as dry season while June, July and August, 2022 were regarded as wet season. The samples were taken fortnightly in triplicate.

Sampling procedures

Sampling was done in both dry and wet season fortnightly in triplicate from the three study sites. Water was sampled according to the procedure described by Robert (2012). The water was collected at the depth of 20cm into 250ml plastic bottle. Prior to sampling, the bottles were washed with 10% nitric acid and rinsed with deionized water. Sample was labelled with sampling site and month then transported to the Nutrition laboratory, Department of Animal production, Adamawa State University Mubi, for analysis.

Fish (*B. leuciscus*) was purchased from fishermen, washed thoroughly and rinsed with deionized water to wash any contaminant present on the fish sample then packaged in a cooler containing ice Blocks and transported to the Nutrition laboratory, Department of Animal production, Adamawa state University Mubi. for analysis.

Sediment was sampled from waterbed using a homemade Auger sampling device as described by U.S EPA (2020). The sample was packed in plastic bag that have been previously soaked in 10%HNO₃ (Nitric acid) and 1:1 HCL (hydrochloric acid) for 24hrs followed by rinsing with distilled water and then allowed to drain to dryness in order to sterilized the plastic bags. Composite of one kilogram

of sediment was then collected at each sampling sites. Sediment was transported to the Nutrition laboratory, Department of Animal production, Adamawa state University Mubi. for analysis.

Sample Digestion

Water sample was prepared following standard methods for examination of water and waste water (APHA, 2005). Each of the unfiltered water sample (100ml) was digested with 5ml HCL (37%) at 90°C until the volume was reduced to 20ml. The digest was cooled, filtered and make up to the mark in 100ml standard flask. The sample solution was kept in a well cleaned analytical bottle with a label until metal analysis (Pandiyan et al., 2020).

The entire fish sample of B. leuciscus in both dry and wet season were dissected with sterile sharp knife and flesh/ muscles sample was cut out and was dried at 105°C for 48hours and grounded to a fine powder using an agate mortar and pestle. Acid digestion of fish samples followed standard methods (APHA, 2005; Daniel and Mathew, 2016). 2.0g of ground fish and that of sediments in both dry and wet season were separately placed into a borosilicate beaker and 12ml of Aqua regia (3:1 HCL/NH0, was added to each. The beaker was covered with watch glass and left for 16 hours at room temperature, the samples were heated for 2 hours on a hot plate at about 80°C, after the first 15 hours, of heating, the watch glass was removed and small amount of 1% v/v HN03 was periodically added to avoid drying of the sample. The sample was allowed to cool and then filtered through whatman 41 filter papers. The sample was made up to the 100ml. The filtrates then was used for metal determination by atomic absorption spectrophotometer (AAS), Pandiyan et al. (2020).

Determination of heavy metals in water and fish (*B. leuciscus*) and sediements.

Determination of heavy metals Copper, Cadmium, Lead, Iron and Zinc concentrations in water and fish (*B. leuciscus*) were done directly on each final solution for both dry season and wet season respectively using Atomic Absorption Spectrophotometer (AAS, Model: VGP 210) equipped with an air acetylene flame (APHA 2005). The values obtained were expressed in milligram per litre in water and milligram per kilogram in Fish (*B. leuciscus*) and Sediments.

Data analysis

Data obtained in this study was analysed using one way Analysis of Variance (ANOVA). LSD± was used to separate means at P>0.05 level of confidence.

Results

All the heavy metals investigated were present in water sample in both dry and wet season. The dry and wet season variation of heavy metal in water is presented on table 1. Dry season recorded the highest value of Lead $(0.034 \pm 0.06^{a} \text{ mg/l})$ in April while wet season recorded the lowest value $(0.016 \pm 0.06^{\circ} \text{ mg/l})$ in August. Dry season recorded the highest value of copper $(0.660 \pm 0.12^{a} \text{ mg/l})$ in April while wet season recorded the lowest value (0.150 ± 0.07^{d} mg/l) in July. Dry season recorded the highest value of Cadmium $(0.034 \pm 0.18^{a} \text{ mg/l})$ in March while wet season recorded the lowest value $(0.018 \pm 0.18^{a} \text{ mg/l})$ in August. The highest value of Zinc $(4.173 \pm 0.07^{a} \text{ mg/l})$ was recorded in dry season (April) while wet season recorded the lowest value $(2.157 \pm 0.12^{\circ} \text{ mg/l})$ in June. Dry season recorded the highest value of Iron (4.420 ± 0.93^{a} mg/l) in April while wet season recorded the lowest value ($2.350 \pm 1.00^{\circ}$ mg/l) in August. There was significant difference between season and levels of heavy metals in water except in Lead and Cadmium in which there was no significant difference in dry and wet season.

Months	Lead (mg/l)	Copper (mg/l)	Cadmium (mg/l)	Zinc (mg/l)	Iron (m g/l)		
Dry Season							
March	0.025 ± 0.06^{a}	0.320 ± 0.10°	0.034 ± 0 .18 ^a	3.243 ± 0.07 ^b	3.493 ± 0.93 ^b		
April	0.034 ± 0.06^{a}	0.660 ± 0.12ª	0.031 ± 0.18 ^a	4.173 ± 0.07 ^a	4.420 ± 0.93 ^a		
Мау	0.021 ± 0.06^{a}	0.153 ± 0.07 ^d	0.030 ± 0.18ª	2.341 ± 0.12 ^c	3.353 ± 0.29 ^c		
Wet Season							
June	0.023 ± 0.06^{a}	0.403 ± 0.09 ^b	0.025 ± 0.18ª	2.157 ± 0.12°	3.017 ± 0.29°		
July	0.018 ± 0.06^{a}	0.150 ± 0.07 ^d	0.023 ± 0.18 ^a	2.177 ± 1.00 ^d	2.360 ± 1.00 ^d		
August	0.016 ± 0.06^{a}	0.173 ± 0.07 ^d	0.018 ± 0.18 ^a	2.293 ± 1.00 ^d	2.350 ± 1.00^{d}		
WHO (2022) (mg/kg)	0.01	2.0	0.003	100	100		

Means with the same superscript in the row are not significantly (P>0.05) different.

Table 1: Dry and wet seasonal variability of heavy metal levels in water from Kiri reservoir.

All the heavy metals investigated were present in fish (*B. Leuciscus*) sample in both dry and wet season. The dry and wet seasonal variation of heavy metal in fish (*B. Leuciscus*) is presented on table 2.

Dry season recorded the highest value of Lead $(0.038 \pm 0.08^{a} \text{ mg/kg})$ in March while wet season recorded the lowest value $(0.018 \pm 0.08a \text{ mg/kg})$ in August. Dry season recorded the highest value of copper $(0.167 \pm 0.26^{a} \text{ mg/kg})$ while wet season recorded the lowest value $(0.040 \pm 0.20^{b} \text{ mg/kg})$ in August. Dry season recorded the highest value of Cadmium $(0.031 \pm 0.06^{a} \text{ mg/kg})$ in March while wet season recorded the lowest value ($0.012 \pm 0.06^{a} \text{ mg/kg}$) in August. The highest value of Zinc $(3.817 \pm 0.14^{a} \text{ mg/kg})$ was recorded in dry season in April while wet season recorded the lowest value ($3.263 \pm 0.08^{d} \text{ mg/kg}$) in August. Dry season recorded the highest value of Iron $(3.047 \pm 0.40^{a} \text{ mg/kg})$ while wet season recorded the lowest value ($1.333 \pm 0.18^{c} \text{ mg/kg}$) in July. There was significant difference between season and levels of heavy metals in water except in Lead and Cadmium in which there was no significant difference in season.

Months	Lead (mg/ kg)	Copper (mg/ kg)	Cadmi- um (mg/ kg)	Zinc (mg/ kg)	Iron (mg/ kg)		
Dry Season							
March	0.038 ± 0.08^{a}	0.157 ± 0.26^{a}	0.031 ± 0.06^{a}	3.363 ± 0.12 ^b	2.540 ± 0.53 ^b		
April	0.034 ± 0.08^{a}	0.167 ± 0.26ª	0.022 ± 0.06^{a}	3.817 ± 0.14 ^a	3.047 ± 0.40^{a}		
May	0.030 ± 0.09^{a}	$0.043 \pm 0.20^{\rm b}$	0.020 ± 0.06^{a}	3.553 ± 0.12 ^b	2.513 ± 0.53 ^b		
Wet Season							
June	0.028 ± 0.08^{a}	0.067 ± 0.20 ^b	0.023 ± 0.06^{a}	3.587 ± 0.12 ^b	2.340 ± 0.53 ^b		
July	0.026 ± 0.08^{a}	0.087 ± 0.20 ^b	0.019 ± 0.06 ^a	3.430 ± 0.10 ^c	1.333 ± 0.18°		
August	0.018 ± 0.08^{a}	0.040 ± 0.20 ^b	0.012 ± 0.06 ^a	3.263 ± 0.08 ^d	1.580 ± 0.18°		
FEPA/WHO 2004 (mg/kg)	0.2	3.0	1.0	100	100		

Means with the same superscript in the row are not significantly (P>0.05) different.

Table 2: Dry and wet seasonal variability of Heavy Metal levels in fish (B. leuciscus) from Kiri reservoir.

All the heavy metals investigated were present in sediments sample in both dry and wet season. The seasonal monthly variation of heavy metal in sediments is presented on table 3. Dry season recorded the highest value of Lead $(0.035 \pm 0.09^{a} \text{ mg/kg})$ in April while wet season recorded the lowest value $(0.021 \pm 0.09^{a} \text{ mg/kg})$

in August. Dry season recorded the highest value of copper (1.880 $\pm 0.12^{a}$ mg/kg) in April while wet season recorded the lowest value (1.417 $\pm 0.16^{c}$ mg/kg) in August. Dry season recorded the highest value of Cadmium (0.051 $\pm 0.11^{a}$ mg/kg) in March while wet season recorded the lowest value (0.032 $\pm 0.11^{a}$ mg/kg) in August. The highest value of Zinc (7.090 $\pm 0.54^{a}$ mg/kg) was recorded in dry season in the month of April while wet season recorded the lowest value (3.453 $\pm 0.48^{d}$ mg/kg) in August. Dry season recorded the highest value of Iron (6.817 $\pm 0.93^{a}$ mg/kg) in April while wet season recorded the lowest value (5.110 $\pm 1.00^{c}$ mg/kg) in July. There was significant difference between season and levels of heavy metals in water except in lead and copper in which there is no significant difference in season.

Months	Lead (mg/ kg)	Copper (mg/ kg)	Cad- mium mg/kg	Zinc (mg/ kg)	Iron (mg/kg)		
Dry Season							
March	0.033 ± 0.09^{a}	1.802 ± 0.14 ^b	0.051 ± 0.11 ^a	6.113 ± 1.00 ^b	6.097 ± 0.29 ^b		
April	0.035 ± 0.09^{a}	1.880 ± 0.12ª	0.047 ± 0.11^{a}	7.090 ± 0.54^{a}	6.817 ± 0.93 ^a		
Мау	0.031 ± 0.09^{a}	1.772 ± 0.14 ^b	0.044 ± 0.11^{a}	5.410 ± 0.37°	5.380 ± 0.29 ^b		
Wet Season							
June	0.025 ± 0.09^{a}	1.757 ± 0.14 ^b	0.041 ± 0.11^{a}	5.553 ± 0.37°	5.408 ± 0.29 ^b		
July	0.028 ± 0.09^{a}	1.758 ± 0.14 ^b	0.035 ± 0.11^{a}	4.453 ± 0.37 ^c	5.383 ± 0.29 ^b		
August	0.021 ± 0.09^{a}	1.417 ± 0.16 ^c	0.032 ± 0.11^{a}	3.453 ± 0.48 ^d	5.110 ± 1.00°		
FEPA/WHO 2004 (mg/kg)	1.5	20-30	0.3-1	100- 300	100-300		

Means with the same superscript in the row are not significantly (P>0.05) different.

Table 3: Dry and wet seasonal variability of heavy metals levels insediments from Kiri reservoir.

Discussion

There was a slight variation in heavy metal levels in water between dry and wet season. Heavy metals Pb, was high in April (dry season), Pb in water (dry season) slightly exceeded the recommended permissible limits 0.01mg/l by World Health Organization (WHO 2022). Cu was high in April (dry season), Cu in water which was high in dry season did not exceed recommended permissible limits

of 2mg/l by World Health Organization (WHO 2022). Cd was high in March (dry season), Cd in water (dry season) exceeded recommended permissible limits of 0.003mg/l by World Health Organization (WHO 2022). Zn was high in April (dry season), Zn in water (dry season) did not exceeded recommended permissible limits of 5mg/l by World Health Organization (WHO 2022). Fe was high in April (dry season), Fe in water (dry season) did not exceeded recommended permissible limits of 5mg/l by World Health Organization (WHO 2022). This results is in line with the study of Alhassan et al. (2016); Edward (2020) from Upper River Benue and Ogungbile et al. (2019) from Ogodi reservoir, Ibadan, who reported that the seasonal metals investigated were higher in dry season when compared with the wet season, this could be attributed to reduce water volume in the dry season, run-off of contaminated water from dry season farming and other anthropogenic activities like use of detergent in washings but different from the report of the study of Adeleke et al. (2022) from Ignosa and Ikopba, Benin city, Edo state who reported heavy metals investigated were higher in the wet season, this could be due to increased water volume and flow as confirmed by Edokpayi et al. (2016).

All the heavy metals investigated were present in fish (B. leuciscus). There was variability of metal distribution from one season to another and from one metal to another in which heavy metal levels investigated were higher in dry season when compared to the wet season, this could be attributed to reduction of water volume in dry season hence increase the levels of heavy metal in water which consequently increase their accumulations and levels in fish (B. leuciscus). Pb was high in March (dry season) this agreed with the study of Igwegbe et al.(2014) from Bargi and catfish of Daban Masara and Doron baga of Borno state; Okerulu and Offor (2019) from Malapteruus electricus of Obii Stream Anambra State, Nigeria who both on separate study reported higher Pb in dry season when compared with the wet season, this could be as a result of reduction in water volume in the dry season but Hashim et al. (2014) reported highest Pb concentration during wet season, this coul be due to differences in species and locations. Cu was high in April (dry season), this is in conformity with the study of Obasohan and Egnavoen (2008) who reported highest Cu in dry season from Erpetoichthys calabaricus of Ogba River Benin city, Nigeria. Cd was high in March (dry season), this agrees with study of Igwegbe et al. (2014) from Bargi and catfish of Daban Masara and Doron baga of Borno state who reported higher Cd during dry season when compared with the wet season. Zn was high in dry season (April),

this is in conformity with the study of Obasohan and Egnavoen (2008) who reported highest Zn in dry season from Erpetoichthys calabaricus of Ogba River Benin city, Nigeria, but Okerulu and Offor (2019) from Malapteruus electricus of Obii Stream Anambra State, Nigeria reported highest Zinc levels in wet season. Fe was high in the dry season (April), this agrees with Olaifa et al. (2004) who reported high Fe level in Clarias gariepinus from Eleiyele Lake in Ibadan, Nigeria. All the heavy metals investigated in Fish (B. leuciscus) did not exceed the recommended permissible limits by FEPA/WHO (2004)

All the heavy metal investigated were present in sediment. Pb in sediments was higher in April (dry season), this agrees with the findings of Adeyemo (2007), from Iddo river sedements in Ibadan, who reported highest Lead in dry season; Nkinda et al. (2021) from Mara River and its tributaries in Tanzania. Cu was higher in dry season (April), this is in conformity with the study of Edokpaij et al. (2017) from Nzhelele River sediments of South Africa, who reported highest Lead in dry season but Ekpechi and Okori (2022) from Esuk Ekpo Eyo Beach Akpabiyo, South-Eastern Nigeria, reported highest Lead in wet season, Cd was high in dry season (March), this is in conformity with the study of Duncan et al. (2018) from sediments of River Pra and its tributaries, but Edokpaij et al. (2017) from Nzhelele River sediments of South Africa, who reported highest Cd in wet season. Zn in sediments was high in dry season (April), this agrees with Duncan et al. (2018) from PS site sediments of River Pra and its tributaries who reported high level of Zn in dry season but Edokpaij et al. (2017) from Nzhelele River sediments of South Africa, reported highest Zn in wet season. Fe was high in dry season (April), this agrees with the report of Wasiu et al. (2016) from Oke-Ora site of South Western Nigeria who reported higher Fe in dry season but Edokpaij et al. (2017) from Nzhelele River sediments of South Africa, reported highest Fe in wet season. All the heavy metals investigated in sediments did not exceed the recommended permissible limits by FEPA/WHO (2004).

Conclusion

In conclusion therefore, Kiri reservoir has higher heavy metals water, fish (Brycinus leuciscus) and ediments in dry season when compared to wet season but not beyond the recommended limit suggested by WHO, 2004 except Pb and Cd which were beyond recommended limit in water. Therefore water of Kiri reservoir is moderately polluted with Pb and Cd.

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