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Assessment of Levels of Some Metals in Water and Fish from Jos, Plateau State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Authors JDD and LJD designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author AGJ managed the analyses of the study. Author EAA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aim: This study was designed to assess the levels of chromium (Cr), manganese (Mn), cobalt (Co) and nickel (Ni) in water and fish to monitor the toxicity risk of consuming these fish.
Place and Duration of Studies: The water and fish samples were obtained from Farin gada river, Liberty Dam, Dahwol-Tohort and Diye-Tohort mining ponds, all within Jos Metropolis, Plateau State, Nigeria, between March and April, 2018.
Methodology: Water and six fish species samples were collected from four different locations, digested and analysed using Buck Scientific Atomic Absorption Spectrophotometer, model 210VGP.
Results: Farin gada river had all the four metals studied in varying concentrations in the following order Mn>Ni>Co>Cr with Mn having the highest mean concentration of 0.4133±0.0100 mg/L. The concentrations of the metals in the other three sources were in the order of Ni>Co>Cr with Mn not detected. Cr also was not detected in Lamingo Dam. The concentrations of Mn and Ni in all the water sources were higher than the World Health Organisation (WHO) maximum permissible limits of 0.05 mg/L and 0.06 mg/L respectively. *Petrocephalus bovei* recorded the highest mean concentrations of Mn and Ni, while Co was highest in *Clarias gariepinus* species. The

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concentrations of these metals in the head, body and gills of the fish species showed that the head of *Petrocephalus bovei* species had the highest concentrations of all the metals except chromium. Fish species from other water sources exhibited the same general pattern of Head>gill>body except Co which was found to accumulate more in the body than in other parts of the fish.
Conclusion: The results showed that there was biomagnification of these metals from water to the fish as the concentration of the metals in the fish far exceeded those of the water sources from which they were obtained and *Petrocephalus bovei* species has the highest potential to biomagnified all the metals.

Keywords: Assessment; environment; carry-over; heavy metals; water; fish; bioaccumulation.

1. INTRODUCTION

Pollution of different environments in Jos, Plateau State, Nigeria, is due to increased human activities in recent decades as a result of mining and smelting operations which are important causes of heavy metal contamination in the environment. Mining activities such as mineral excavation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines [1] lead to pollution by metals. Automobile mechanic village in Farin Gada also have added a new dimension to metals pollution in Jos and its environs. Environmental pollution is a worldwide problem as heavy metals belong to the most important pollutants [2]. The development of industries has also resulted in increased emission of pollutants into the ecosystem [3]. Environmental degradation therefore results to poisoning, diseases and even death for fish and humans through the food chain [2].

There are ample literatures on the adverse environmental impact of excessive heavy metals dispersed from mine and smelter sites and contamination of water and soil, phytotoxicity, soil erosion, and potential risks to human health [4]. The metals of concern in this work are Mn, Cr, Co and Ni. At low concentrations, Cr is used for medical purposes; it is also involved in natural human lipid and protein metabolism. Conversely, at high concentrations, hexavalent Cr is toxic and carcinogenic [5]. Exposure to Mn causes clinical signs and symptoms resembling, but not identical to, Parkinson's disease. Mn-induced neurodegenerative, cardiovascular and hepatotoxicities are other signs in which excess Mn exposure presents itself in humans [6]. Excessive exposure to Co has been reported to be linked to neurotoxicity and cardiomyopathy among other symptoms [7]. Exposure to Ni may lead to various adverse health effects, such as Ni allergy, contact dermatitis and organ-system toxicity. Findings confirmed that Ni can cause respiratory problems and is carcinogenic [3].

Studies on the mining sites of Plateau State, Nigeria, show that in the recent past decades, the natural environmental concentrations of Mn, Cr, Co and Ni have largely increased on the Jos Plateau, mostly as a result of anthropogenic activities [8]. These metals are toxic, persistent and can accumulate in aquatic habitats leading to increased concentrations through bio-magnification [9]. This is made possible because of the long half-life of these metals which range from 20-30 years in organisms. Fish and other aquatic organisms in elevated heavy metals concentrations may have negative effects on their health, reproduction and survival and indirectly negatively impacting on human health through the food chain [10].

Studies have established that fish are good indicators of chemical pollution and have long been used to monitor heavy metal pollution in coastal and marine environments [11]. Fish is a bio indicator organism; it is easy to be obtained in large quantity; has the potential to bioaccumulate heavy metals and has a long lifespan as compared to other aquatic organisms [12]. Heavy metal intake by fish in polluted aquatic environments depends on the physico-chemical properties of the environment such as pH, temperature and redox potential [11]. Accumulation of heavy metals in the aquatic environment has direct consequences on the ecosystem and Man [11]. This impact is pronounced because of the non-biodegradability of the heavy metals that can result to bioaccumulation and is transported along the successive food chain [13].

The health concerns of these metals on the food chain necessitate this work. Therefore, monitoring bioaccumulation of these heavy metals in different fish species commonly consumed in Jos, Plateau State, Nigeria, will give us data on the bioaccumulation potential of the different fish species consumed in Jos, which will serve as an early warning indicator for the government and the populace to take appropriate action to protect public health and the environment.

2. MATERIALS AND METHODS

2.1 Study Area

All the water and fish samples for this research were collected from Jos, the Plateau state capital city. Plateau State, is located in the North Central part of Nigeria; it lies between latitude 90 55'45.56N and longitude 80 53'31.63E as shown in Fig. 1. According to the 2006 census, Jos Plateau was said to have a population of 900,000. Jos is a famous city in Nigeria known for its tin mining activities and the corresponding steel rolling mills which has attracted Nigerians of almost all tribes into the city. Agricultural activities, both irrigation and seasonal farming in the city outskirts, as well as automobile workshops are some of the common human activities in Jos.

2.2 Water Sampling

Random sampling technique was used in the collection of water samples from the four water sources within the month of March, 2018. The water samples were collected into 120 ml High Density Polyethylene (HDPE) bottles and labelled appropriately. The water samples were transported immediately to the Department of Chemistry Laboratory, Abubakar Tafawa Balewa University (ATBU) Bauchi, Nigeria, and stored in a refrigerator at 3.3°C for digestion the next day.

2.3 Fish Sample Collection

Fish samples were collected from the same water sources through the services of fishermen in the month of March, 2018 and taken to The Department of Fisheries and Hydrology, University of Jos for identification. The fish were transported in a picnic box, with some quantity of water, to the laboratory. Each fish was properly cleaned by rinsing with distilled water to remove debris, plankton and other external adherents. It was then drained under folds of Whatman No. 1 filter paper, weighed, wrapped in aluminum foil and then frozen at –10°C prior to dissection to harvest the fish parts of interest. Six (6) fish species were used for this research. Catfish (*Clarias gariepinus*), Tilapia fish (*Oreochromis niloticus*), *Petrocephalus bovei, Hyperopisus bebe occidentalis, Lates niloticus* and *Cyprinus carpio* (carp fish) were collected from each of the water sources and labelled appropriately.

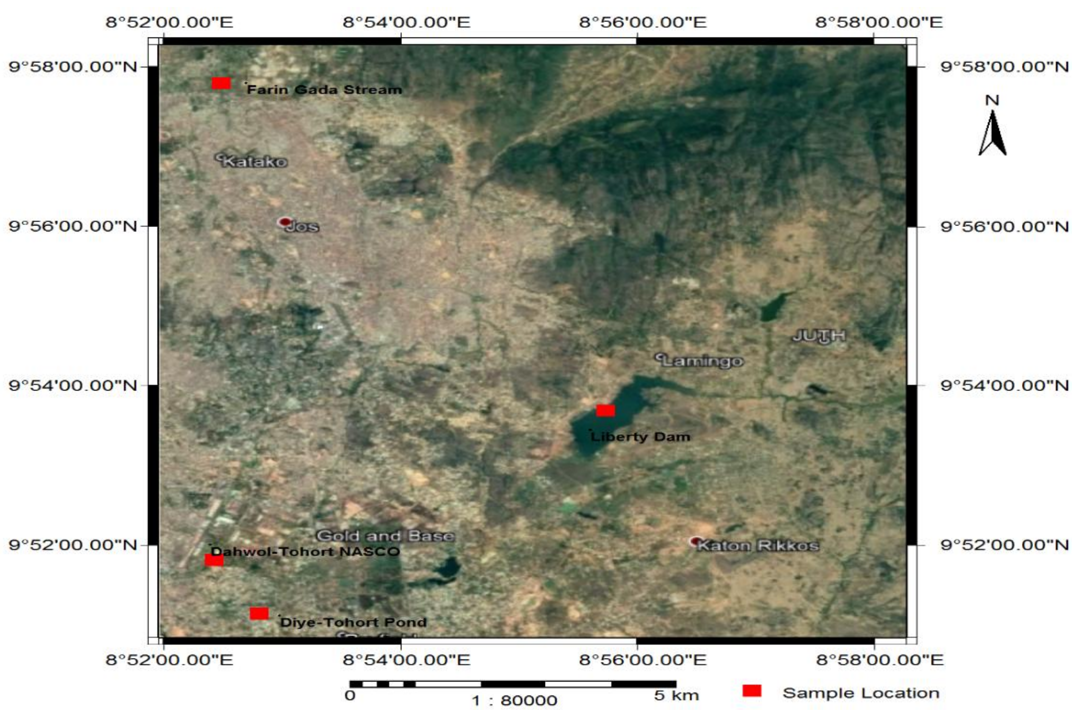

Fig. 1. Satellite image showing water and fish sample locations within the study area

2.4 Water Sample Digestion

The water sample was digested using the Aqua Regia (King's water) method. Concentrated nitric acid (reagent grade 69%) and Hydrogen chloride acid in 1:3 ratio was mixed together to form the aqua regia solution, a yellowish-brown solution was formed. Some 100 ml of each water sample was taken into a labelled beaker and 40 ml of the aqua regia solution was added. The mixture was heated on a hot plate in a fume cupboard until the solution became colourless. The solutions were then removed and allowed to cool at room temperature. Each solution was then filtered using Watmann No.1 filter paper into a volumetric flask and made up to the mark of 100 ml using distilled water. They were transferred into rinsed and labelled HDPE bottles and stored in a refrigerator at 3.3°C prior to Atomic Absorption Spectrophotometer analysis.

2.5 Fish Sample Preparation, Digestion and Atomic Absorption Spectrophotometric (AAS) Analysis

The fish samples were rinsed with deionised water; scales were removed (where necessary). The head, body and gills of each fish sample were oven dried at 105°C until they reached a constant weight. Each dried tissue of the species was homogenized and ground into powder, using a porcelain mortar and pestle. They were put in dry labelled plastic containers and stored in desiccators until digestion. One gram (1.000 g) of the powdered fish sample was weighed in each case, transferred into a 100cm^3 beaker, 40ml aqua regia (King's water) solution was added and the mixture placed on a hot plate and heated inside a fume cupboard until the solution became colourless. The residue was allowed to cool, filtered using Whatman No1, filtrate transferred to 100ml volumetric flask and made up to mark with distilled water [13]. The blank experiment was carried out involving all the reagents and procedure used for the actual digestion, but without the sample [13]. The digests were kept in labelled plastic bottles and later the heavy metal concentrations were determined using a Buck Scientific Atomic Absorption Spectrophotometer (AAS), model number 210VGP.

2.6 Analytical Method

Metals analysis of both digested water and fish samples were carried out using Line Source Atomic Absorption Spectrometry (LS AAS). Samples were analyzed by AAS Buck Scientific Model 210VGP in the Energy Commission Centre Laboratory, ATBU Bauchi-Nigeria.

2.7 Statistical Analysis

Statistical analysis was performed using the Instat software, version 3.01 (Graphpad, San Diego, CA, USA). One-way analysis of variance (ANOVA) followed by Turkey-Kramar multiple comparisons test was used to test for the significant difference between the concentrations of metals in water sources, fishes, different fish sources, and different parts of the fish species. The results are presented as mean ± SEM. Statistical significance was considered at 95% ($p< .05$).

3. RESULTS AND DISCUSSION

3.1 Results

3.1.1 Mean concentrations of the metals in the four water sources

Results show that Mn was detected only in Farin gada stream water and in very high concentration (0.4133±0.01). Ni was detected in all the water sources at varying concentrations with the highest in Liberty dam, Lamingo (0.1801±0.01) followed by Diye-Tohort mining pond, Farin gada and lowest Dahwol-Tohort mining pond (0.0711±0.01) in that order. Co was also detected in all the water sources at different concentrations; Diye-Tohort mining pond (Pond) recorded the highest concentration (0.052±0.000) followed by Dahwol-Tohort mining pond; Farin gada had the least level (0.020±0.000). Cr was detected in Farin gada, Diye-Tohort and Dahwol-Tohort each at the same mean level of (0.01±0.00). The metal levels in the water sources were in the order Ni>Co>Cr except in Farin gada stream with Mn> Ni>Co>Cr. Mn in Farin gada, Ni and Co in all the water sources were above the WHO maximum permissible limits. Analysis of variance showed significant difference between the concentrations of Mn in Farin gada and other water sources. The results are presented in Fig. 2.

3.1.2 Mean concentrations of metals in fishes obtained from the four locations in Jos

The fish species from the different water sources bioaccumulated the metals in varying concentrations. *P. bovei* recorded the highest mean concentrations of Ni, Mn and Co, while *C. gariepinus* and *C. carpio* follow in that order. On the other hand, *L. niloticus* has the lowest Mn. Four fish species (*P. bovei, C. gariepinus*, O. niloticus and *C. carpio)* bioaccumulated relatively the same level of Mn which, statistically, was not significantly different (p>0.05). The results revealed that all fish accumulated Co, but at varying concentrations. *P. bovei* had the highest mean concentration, followed by *L. niloticus* and then *O. niloticus*. *C. gariepinus* recorded the lowest Co concentration. Cr was detected at different concentrations in all fish species studied. *L. niloticus* recorded the highest level of Cr followed by *O. niloticus*. Lowest Cr level was detected in *C. gariepinus*. All fish were found to accumulate Ni at different levels. *P. bovei* recorded the highest Ni concentration followed by *C. gariepinus* and *C. Carpio* in that order. The lowest Ni concentration was detected in *O. niloticus*. Ni, Co and Mn levels were high in *P. bovei*. Comparing the levels of Ni in the different fish species revealed that there was significant difference ($p<0.05$) between that in *P. bovei* and other fish species. The results are summarized in Fig. 3.

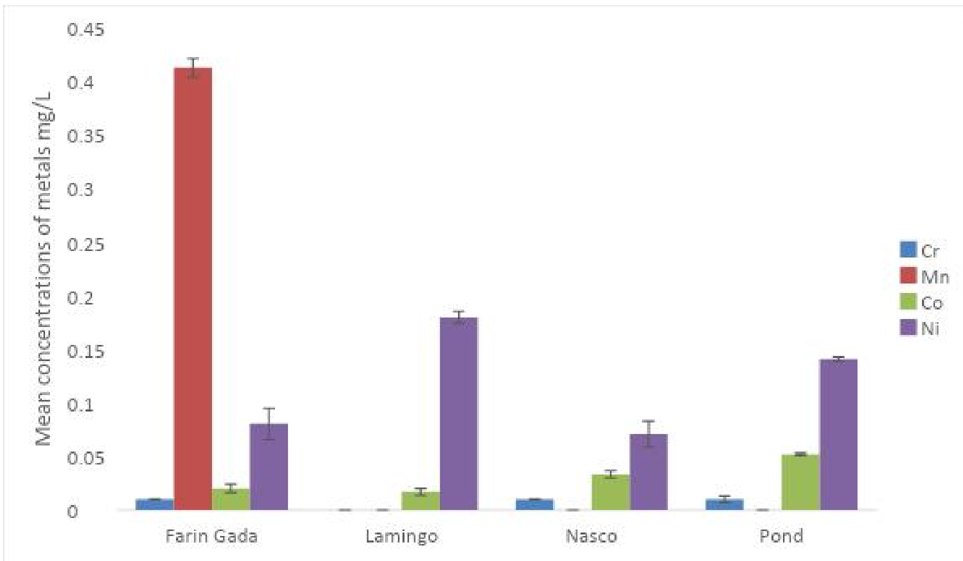

Fig. 2. Mean concentrations (mg/L) of Cr, Mn, Co and Ni in four water sources

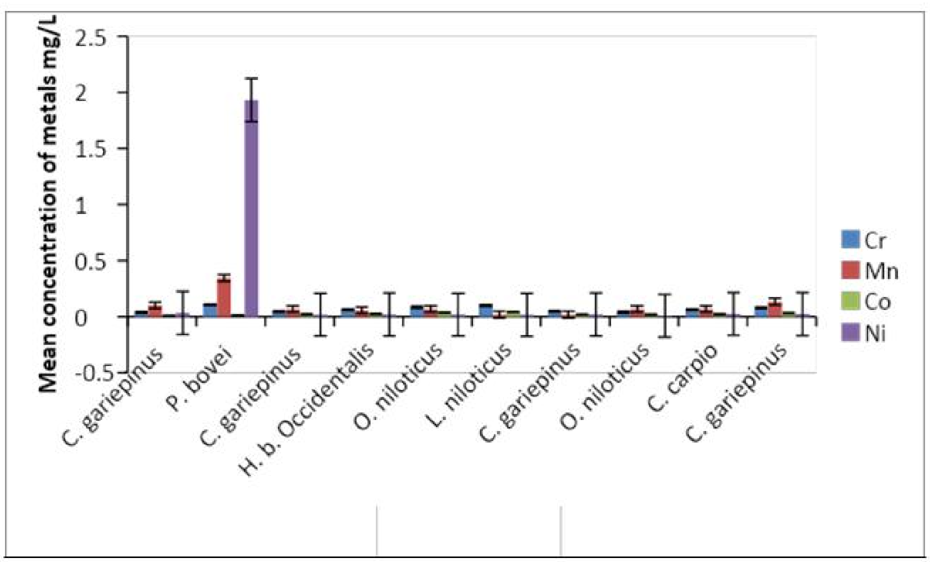

Fig. 3. Mean concentrations (mg/L) of Cr, Mn, Co and Ni in fishes sampled from the four water sources

3.1.3 Mean concentrations of chromium (Cr) in the head, gills and body of the fishes obtained from the four locations

Cr was detected in all the parts of the fishes. *C. gariepinus* recorded the highest concentration of Cr in the body part, followed by *L. niloticus*, *O. niloticus* and *C. gariepinus*. *C. gariepinus* recorded the least mean Cr level in the body. The head of *L. niloticus* recorded the highest mean concentration of Cr followed by *C. gariepinus, O. niloticus* and *H. b. occidentalis*. *C. gariepinus* recorded the least Cr concentration in the head, and gills, while *L. niloticus* recorded the highest concentration of Cr in the gills followed by *O. niloticus* and *C. gariepinus*. *C. gariepinus* recorded the least Cr level and the highest level of Cr was detected in the body of *C. gariepinus* and head of *L. niloticus* both at levels within the permissible limits. Analysis of variance showed significant difference between the levels of Cr bioaccumulation in the different parts of the fish ($p<0.05$) for some fish species as shown in Fig. 4.

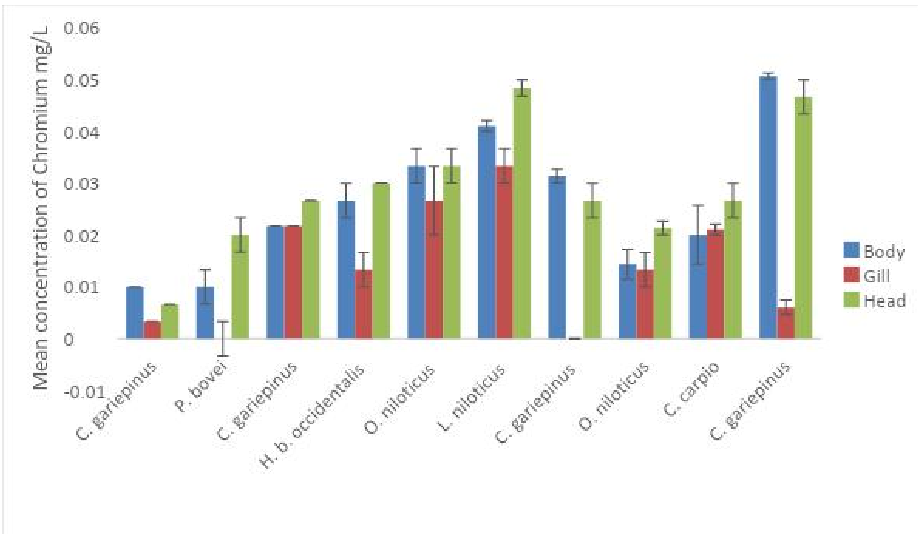

Fig. 4. Mean concentrations (mg/L) of chromium (Cr) in the body parts of fishes sampled from the four water sources

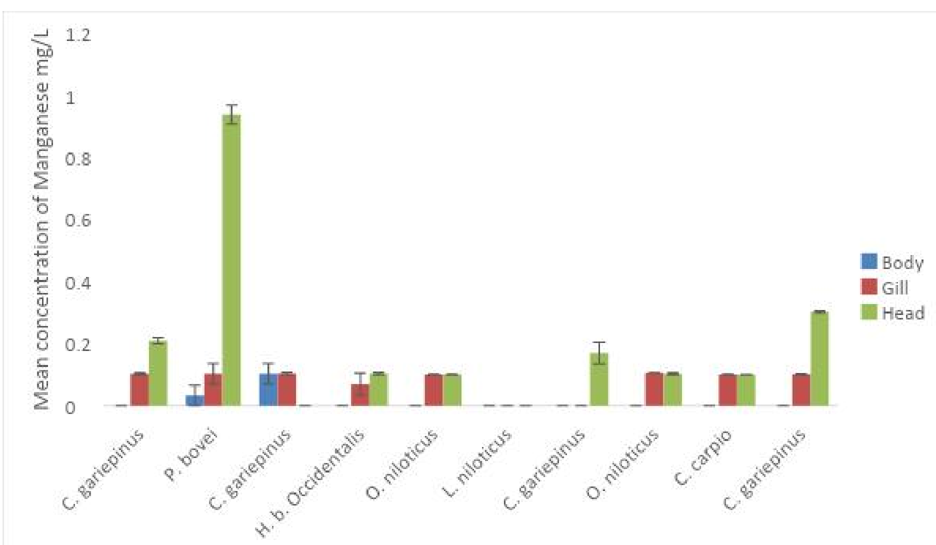

Fig. 5. Mean concentrations (mg/L) of manganese (Mn) in the body parts of fish species sampled from the four water sources

3.1.4 Mean concentrations (mg/L) of manganese (Mn) in the body parts of fishes sampled from the four Water sources in Jos

All the parts of the fish species investigated bioaccumulated Mn at varying concentrations except *L. niloticus*, which had none of the metals under study. *P. bovei* recorded the highest mean level of Mn in the head, followed by *C. gariepinus and O. niloticus* respectively. Only two fish species (*C. gariepinus* and *P. bovei)* showed bioaccumulation of Mn in the head and in the body. Mn was detected in the gills of all, but two species; *L. niloticus* and *C. gariepinus*. The remaining fish species recorded almost the same Mn levels in the body parts, with *H. b. occidentalis* recording the least concentration. The head and body of *P. bovei* and the heads of *C. gariepinuses* bioaccumulated high levels of Mn. Analysis of variance showed that there is significant difference ($p<0.05$) in Mn bioaccumulation in the head of *P. bovei* and other body parts of fish species, except gills. The results are presented in Fig. 5.

3.1.5 Mean concentrations of cobalt (Co) in the body, gills and head of the different fish investigated

Co was found to bioaccumulate in all the fish at varying concentrations in the body. *C. gariepinus* had the highest mean concentration of Co in the body followed by *L. niloticus*, *O. niloticus,* and *C. gariepinus* in that order. *P. bovei* recorded the least Co in the body. Co was detected in the gills of all the fish species at varying concentrations, except in *P. bovei* and *C. gariepinus*. *L. niloticus* had the highest concentration of Co in the gills followed by *O. niloticus* and then *C. carpio*. *C. gariepinus* recorded the least concentration of Co in the gills. Only *P. bovei* recorded high concentration of Co in the head than in the body and gills. The remaining fish parts recorded Co bioaccumulation in the following order: body>gills>head. The heads of *O. niloticus* and *C. gariepinus* recorded the least concentrations respectively. The levels of Co in the head of *P. bovei*, and in the body of all the fishes were very high. Comparison of the concentrations of the metal in the parts of the fish species shows significant difference ($p<0.05$) between Co concentrations in the head of *P. bovei* and other fish species. The results are presented in Fig. 6.

3.1.6 Mean concentrations of nickel (Ni) in the body, gills and head of fishes

The mean Ni concentrations in the fish parts were generally low except for *P. bovei*, which recorded high concentration of the metal. This was followed by the head of *C. gariepinus,* and *O. niloticus* respectively. The remaining fish species recorded very little or no Ni in the body, head and gills. The concentration of Ni in the head of *P. bovei* was found to be significantly different ($p<0.05$) from the levels of the metal in the head of other fish species. The results are presented in Fig. 7.

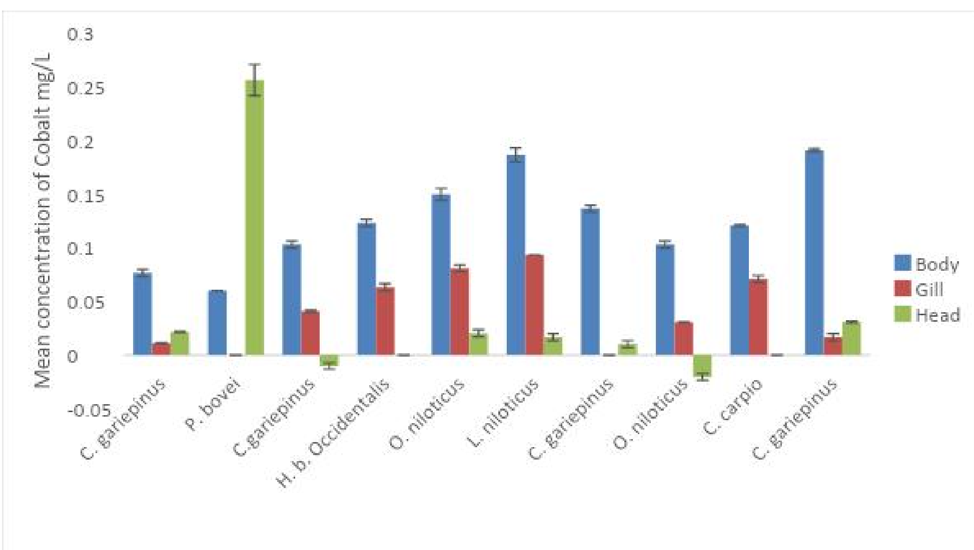

Fig. 6. Mean Concentrations (mg/L) of cobalt (Co) in the body parts of Fishes sampled from the four water sources

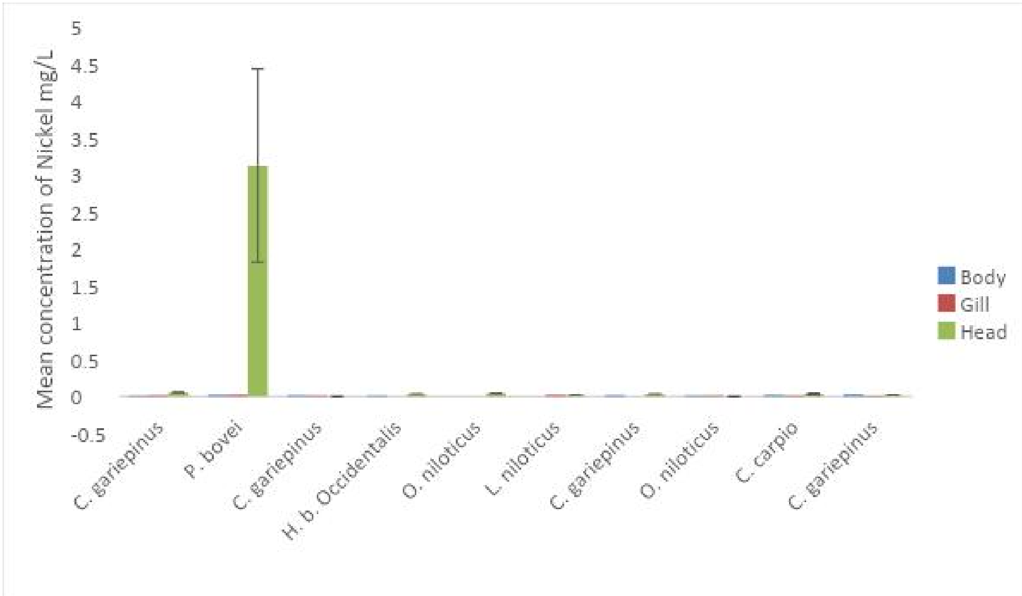

Fig. 7. Mean concentrations (mg/L) of nickel (Ni) in the body parts of fishes sampled from the four water sources

4. DISCUSSION

The result of the concentrations of Cr, Mn, Co and Ni in water showed that Farin gada had high concentrations of Mn which was undetected in Diye-Tohort mining pond, Dahwol-Tohort mining pond and Liberty Dam, Lamingo waters. The absence of Mn in these water sources could be as a result of the low sensitivity of the AAS used, as high concentrations of these metals were detected in high concentration in *P. bovei* and *C. gariepinus*. Mn level in Farin Gada was far above the World Health Organisation [14] permissible limit of 0.05 mg/L. The presence of all the four metals in Farin gada stream could be attributed to anthropogenic activities. The human activities around this area include discharge of metal wastes from the many automobile mechanic workshops, batteries, domestic wastes from residences, local tin mining and the use of inorganic fertilizer on irrigation farms around the stream. The concentrations of Ni in all the water sources were found to be higher than the permissible limit of 0.05 mg/L. This is a potential health hazard to man as the fish, which are in the food chain, could bio-accumulate high concentrations of this metal as the results show. The fishermen go fishing in this stream for their domestic consumption as well as selling to the public. Consumption of these fishes by the inhabitants could lead to Ni chronic toxicity in the long run as small quantities of the metal are bio-accumulated as their half-life is in years. Dahwol-Tohort and Diye-Tohort mining ponds recorded Cr concentrations within the permissible limits specified by the World Health Organisation of 0.06 mg/L, which contradicts the findings of Ahmed *et al*, [15] who found that Cr was present in Naraguta stream in Jos above WHO/FEPA permissible limit. Ni and Co were in agreement with the finding of Halliru *et al,* who found that the levels of Mn, Co, Cr and Ni were above the WHO permissible limits [16]. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic ground however, Ni is bound to become more mobile and it will often rinse out to the groundwater [17]. Ni concentrations in surface waters can diminish the growth rates of algae which is also on the food chain. It is an essential element in humans but it can be dangerous when the maximum tolerable amounts are exceeded. It can cause various kinds of cancer on different sites within the bodies of animals, especially those inhabiting areas near refineries. Co levels in all the water sources were above the permissible limit of 0.005 mg/L. Farin gada water recorded the lowest concentration of Cr and Co. The high levels of these heavy metals in Dahwol-Tohort, Liberty Dam, Lamingo and Pond waters could be due to the relatively low pH of the waters; in acidic ground water, heavy metals go into solution and become more mobile making them readily available for uptake by aquatic organisms [17], and human activities [18].

The results of the concentrations of the metals in different fish species show that *Petrocephalus bovei* recorded the highest concentration of Mn 0.344 mg/L. This level is remarkably higher than the maximum permissible limit of 0.05 mg/L for Mn in food [14]. Co concentration in the same fish species was also found to be higher (0.106 mg/L) than the recommended value of 0.005 mg/L in food and fish. From the results, this fish species will pose a big health risk as the same fish biomagnified high concentrations of all the metals despite the fact that some of the metals were in low concentrations in the water sources. *C. gariepinus* on the other hand had a mean concentration value of 0.0796 mg/L, which was also above the permissible limit but Cr and Ni concentrations were within the permissible limit. Mn concentration in Farin gada stream water was very high and that led to the concentrations of the metal being high in the fish obtained from that source. This means that there was a clear case of carryover of the metals to the fish from water to the fish species. This is in agreement with the findings of Sabo et al. [19] who found that there was a positive correlation between the concentration of heavy metals in water and in the muscle of *C. gariepinus* from River Gongola in Nigeria. The fact that the results of this work showed that Co was not detected in Liberty Dam, Lamingo water, but *P. bovei* accumulated it even above the WHO permissible limits. This suggests that the fish species has high tolerance to this metal and hence could biomagnify it in its tissues. This also means that there is high health risk to the consumers of this fish species, as it has been reported that the systemic health effects are characterized by a complex clinical syndrome, mainly including neurological (e.g. hearing and visual impairment), cardiovascular and endocrine deficits. The health effects could be associated with a decrease in Co bound to serum proteins and an increase in free ionic Co^{2+} which is believed to be the primary toxic form [20].

The results of Cr levels in body parts of fish show that the mean concentrations of Cr in the body of *C. gariepinus* and *L. niloticus* were high, whereas *C. gariepinus* and *P. bovei* recorded low mean concentrations. The head of *L. niloticus* recorded the highest concentration of Cr while *C. gariepinus* had the lowest. This would mean that persons who eat fish heads could be exposed to high concentrations of this metal. Cr was detected in high concentrations in *L. niloticus* in the head and body. This result is consistent with the report of Habib and Dayyab [21] who reported that *C. gariepinus* recorded the lowest accumulation of Cr. The gills recorded the lowest Cr concentration with *L. niloticus* and *O. niloticus* having the highest concentrations. In general, the data has revealed the bioaccumulation pattern of Cr in the fish parts thus; head>body>gills except in a few fish species. This order agrees with a finding of Gijs et al. [22] who reported that the blood ordinarily is not a usable indicator of Cr nutritional status, as it is excreted or transported out from the blood to its storage sites. The mean concentrations of Cr in all the fish parts were within the permissible limits of 0.06 mg/L in food [23]. Cr is an essential trace mineral which, in its trivalent form (Cr^{3+}) plays a vital role in glucose metabolism. Human exposure to Cr above safe concentration limits is a recognized health risk. Significant health risk is associated with hexavalent Cr (VI) that is more easily transported through the cellular membranes, which could lead to damage of lipids, proteins and DNA [24].

The mean concentrations of Mn in fish showed that the head of *P. bovei* recorded the highest mean concentration of 0.903 mg/L, which is higher than the maximum permissible limit of Mn in food [21]. *C. gariepinus* recorded high Mn concentration in the head and Mn was not detected in *L. niloticus*. The gills were the next in Mn bioaccumulation while the body recorded the lowest. Few exceptions exist in other fish parts. In all the fish parts in which Mn was detected, the concentrations were above the permissible limit. The fact that Mn accumulated more in the head is in agreement with the findings of Wolfgang [25] that Mn is an essential element involved in bone formation as well as neuronal functions [26].

Co concentrations in fish parts showed that *P. bovei* recorded the highest concentration of the metal in the head. Other fish species recorded low Co concentrations in the head, with *O. niloticus* having the lowest. The mean concentrations of Co in the body of the fish species were generally high. All the fish species recorded Co levels in the body and gills higher than the maximum permissible limit of 0.005 mg/L. The general bioaccumulation pattern of Co in the fish species is body>gill>head except in *P. bovei*. This is consistent with earlier findings of Rinaldo et al. [25], who reported that Co is not an essential element required for bone formation, rather it is an essential component of the metalloprotein called cobalamin, also known as vit-B12, required for red blood production, DNA synthesis as well as nerve (myelin sheath) maintenance.

The head of *P. bovei* recorded the highest mean concentration of Ni 3.130 mg/L. This concentration value of Ni is far above the maximum permissible limit of 0.05 mg/L [19]. The very high concentration of Ni accumulated by *P. bovei* is consistent with the findings of Wolfgang [27] who found that fish species from Ogun State Rivers in Nigeria had Ni and Cr concentrations above the permissible limits. The high concentration of Ni in liberty Dam, Lamingo could have resulted in its carry-over from the water into the head of *P. bovei*. Excessive intake of Ni has been linked to lung and nasal cancer in workers of Ni smelters [17]. All other parts of the fish species recorded very low Ni in the head, body and gills. This could be due to the fact that Ni is essential in the metabolism of bones.

5. CONCLUSION

The results of this study show that Mn in Farin gada and Ni in all the water sources were above the WHO maximum permissible limits. *Petrocephalus bovei, C. gariepinus* and *Lates niloticus* were found to bioaccumulate almost all the heavy metals investigated more than other fish species. There was carry-over of the metals from the water sources to the fishes as results show that some fish species biomagnified the concentrations of the metals in their tissues as some of the metals were within the WHO maximum permissible limits in the water sources. The inhabitants of the community who rely on these fish as their sole protein source stand the risk of being exposed to different diseases associated with these heavy metal toxicities.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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