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Assessment of arsenic and selenium in *Cyprinus carpio* from Alaro stream in Ibadan, Nigeria

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Abstract
An assessment was carried out on the concentration of arsenic (As) and selenium (Se) in the organs of *Cyprinus carpio* from Alaro stream in Ibadan, Nigeria. A total of 32 fish were collected from the sampling of Alaro stream from June to December 2003 and preserved by freezing. Dissections were carried out using dissecting set in order to remove the gills, fins, gut (intestine), liver, bones and muscle. Acid digestion was carried out after drying and pulverization of the fish organs. Inductively coupled plasma-mass spectrometer (ICP-MS) was used for the trace metal analyses while bovine liver standard reference material (SRM) from the National Institute of Standards (NIST) was used for quality assurance of the results. The range of the As in the organs of *C.carpio* was 0.000-0.963ppm, while the following increasing order of mean concentration: fins<liver<gills< muscle < gut< bone was observed. The range of Se in the organs was 0.06-11.80ppm with an increasing order of mean concentration of: bone<gut<fins <muscle <gills<liver. This study also shows that mean concentration of As and Se in the organs *C.carpio* collected from the Alaro stream in Ibadan exceeded the World Health Organization (WHO) guideline limits set the trace metals in food. This shows that Alaro stream is polluted and fish such as *C.carpio* caught from the stream is unhealthy for human consumption due to the public health consequences posed in consuming such contaminated food.

1. Introduction

The pollution of the aquatic environment with trace metals has become a worldwide problem during recent years (Ozturk *et al*, 2009). This is because they are not degradable and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000). Among environmental pollutants, trace metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al*,2006).The input of heavy metals into the aquatic food chain frequently occurs by direct consumption of the contaminated biota (Carvalho and Hartz, 2009). Another potential form of contamination is the uptake by epithelial absorption through the gills which is considered as a non-dietary route of trace metal intake (Burger *et al*., 2002). Fish samples can be considered as one of the most significant bioindicators in freshwater systems for the estimation of trace metal pollution level (Rashed, 2001). The commercial and edible fish species have been widely investigated in order to check for those hazardous heavy metals to human health (Begum *et al*, 2005).Although arsenic (As) has no known use in biological systems, selenium (Se) is an essential trace mineral that is indispensable for cells to function properly. Arsenic (As) and selenium (Se) are unusual metalloids as they both induce and cure cancer. They both cause carcinogenesis, pathology, cytotoxicity, and genotoxicity in humans, with reactive oxygen species playing an important role (Sun *et al*, 2014). At low concentration, Se can decrease As toxicity via excretion of As–Se compound $[(GS_3)_2AsSe]$, but at high concentration, excessive Se can enhance As toxicity by reacting with S–adenosylmethionine and glutathione, and modifying the structure and activity of arsenite methyltransferase. For the normal metabolism of the fish, the essential metals must be taken up from water, food or sediment (Canlı and Atlı, 2003). The essential trace metals like Se can also produce toxic effects when the metal intake is excessively elevated (Tuzen, 2003) while As is ubiquitous in nature and occurence. Both As and Se are toxic and have synergistic effects when acting together in living systems. The objective of this study is to assess the As and Se levels in the organs of the fish *Cyprino carpio*, commonly caught and consumed from Alaro stream in Ibadan and to compare it with World Health Organization guideline limits for human health safety.

2. Materials and Methods

2.1. Study Area

Alaro Stream is located within the hydro-ecological system of the Oluyole Industrial Estate in Ibadan, Nigeria and receives effluents from diverse sources of trace metal pollution as shown in table 1. The Alaro stream flows into Oluyole Estate in a west–south east direction from its source at Agaloke near Apata in Ibadan. It joins River Ona at the south east end of a meat processing factory as its main tributary. The stream receives effluents from diverse industries. Effluents from both natural and anthropogenic sources are discharged into Alaro stream directly or indirectly through run-off, leaching or seepage especially during the rainy season or as windblown materials during the dry season. The Oluyole industrial estate is located between latitude 7° 21’N -7° 22’N and longitude 3° 50’-3° 52’E. Table 1 shows the types of industries that discharge effluents into Alaro Stream and their potential pollutants.

Table 1. *Industrial activities and their potential pollutants in Alaro Stream*

Industry	Number of industries	Potential pollutants
Food processing		
i. carbonated beverages	2	Alkalis, phenols, suspended solids, detergents, fermented starches, pathogens, nitrates, trace metals from oiling machine parts and organic wastes
ii. confectionery and biscuit	2	Organic wastes (solids and suspended), heavy metals, pathogens, total suspended solids(TSS), biochemical oxygen demand (BOD), PH
iii. animal husbandry and meat processing	1	Organic wastes, heavy and trace metals
Iron and fabrication		
i. steel	2	Trace metals, cyanide, fluorides, chromates, thiocyanates, naphthalenes
ii. metal foundry	2	Diverse trace metals
iii. crown corks	1	Metal filings, macro and trace metals
Wood processing	1	Waste lignin, organic sulphur, mercury, magnesium, sulphide, terpenes, arsenates mercaptans, heavy and trace metals

2.2. Sampling Sites

2.2.1. Sampling Site 1

This is located before Oke Alaro Bridge I just before it enters the industrial estate. This is the control site.

2.2.2. Sampling Site 2

Sampling site 2 is downstream of Oke Alaro Bridge II. It is located about 500metres downstream of sampling station 1.It receives run-off water from Alaro settlements and parts of Oluyole residential area. There is a shopping arcade that discharges effluents into the gutter that drains into the stream at this point.

2.2.3. Sampling Site 3

This site receives effluents discharged from the carbonated beverages, crown cork factory and the confectionery and biscuit factories.

2.2.4. Sampling Site 4

This site receives effluents from an animal husbandry factory.

2.2.5. Sampling Site 5

This sampling site was located just before the meeting points of Ona River and Alaro stream behind the south east end of the meat processing factory. It represents the recovery site.

2.3. Fish Collection and Processing

Fish were collected from the entire Alaro stream downstream of the effluent outfall. Fish were collected using the following techniques: Cast nets with mesh sizes ranging between 30-50mm with varying dimensional sizes were used .These nets were left for about three minutes before retrieving with a drawing string to check for any entangled fish. In addition, gill nets with mesh sizes of 30-50mm and varying dimensions were tied to stakes with a lead weight on the stream bed and maintained vertically in water with the aid of floats overnight. Thirty-two (32) *Cyprinus carpio* fish were collected from the sampling of Alaro stream.

Fish were sacrificed by stunning with table salt. The dissections were carried out using dissecting set to remove the gills, fins, gut (intestine), liver, bones and muscle. These tissues were oven dried at 105^{0}C for 6hours .Each organ was pulverized separately by means of a porcelain mortar and pestle. The pulverized samples were kept in sample sachets and sealed prior to analyses.

2.4. Digestion of Fish Organs for Trace Metal Analyses

Fish organ digestion was carried out by adding 2ml trace metal grade HNO_3 to 0.5g of each powdered sample in Teflon digestion tubes which were heated at 105 ^{0}C for 1 hour in a heat block. The clear solution was then allowed to cool down, followed by addition of 1ml H_2O_2 , after the simmering, boiled and left overnight. The digested sample was diluted to the 10ml mark using MilliQ water. These were then transferred into deionized water-rinsed test tubes for the inductively coupled plasma mass spectrometer (ICP-MS) analyses. Standard Reference Materials (SRM) comprising of bovine liver from the National Institute of Standards and Technology (NIST-1577) were used to obtain accurate values for fish tissue. Agilent 7700 ICP-MS was used for the analyses of the samples because it combines a high-temperature ICP (inductively coupled plasma) source with a mass spectrometer, which converts the atoms of the metals in the sample to ions that are separated according to their mass/charge ratios by a quadrupole mass analyzer (MS). The inductively coupled plasma-mass spectrometry (ICP-MS) was preferred to other facilities because it is rapid, precise, accurate, and extremely sensitive multimetal analytical technique for the determination of trace elements in solid sample materials.

3. Results and Discussion

3.1. Standard Reference Materials and Quality Assurance

Percentage recoveries from the reference material were all above 70% with values of 85.9% for (As) and 76.0% for (Se). The results were also corrected for errors using MilliQ water as the blank using the inductively coupled plasma-mass spectrometer (ICP-MS).

3.2. Trace Metal Concentration

Results of the mean As concentration in the organs of *C.carpio* are shown in figure 1.

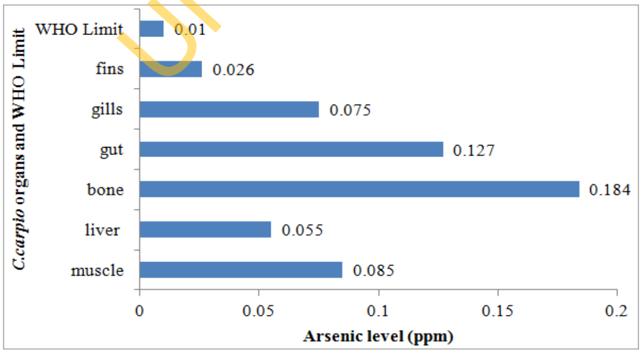

Figure 1. *Mean As in the organs of C.carpio and WHO Guideline limit.*

The range of the As in the organs of *C.carpio* was 0.000-0.963ppm, while the highest mean concentration was in the bone (0.184ppm) and the lowest was in the fins (0.026ppm).The order of As concentration was in the following increasing order: fins<liver<gills<muscle<gut<bone. All the mean concentration of As in the organs exceeded the World Health Organization guideline limit of 0.01ppm. The potential ability of the different organs of *C.carpio* to store, depurate and excrete (As) is responsible for the differences in the levels of the mean concentration of the metalloid in the fish. The bioavailability of As to *C.carpio* is due to the preservatives used in wood processing that are eventually discharged as effluents into the water shown in table 1 as well as geogenic sources (Sun *et al*, 2014).

The results of the mean Se concentration in the organs of *C.carpio* are shown in figure 2.

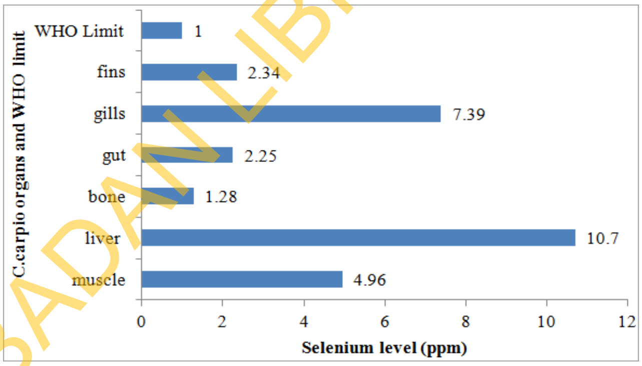

Figure 2. *Mean Se in the organs of C.carpio and WHO Guideline limit.*

The range of Se in the organs of *C.carpio* was 0.06-11.80ppm,while the highest mean concentration was in the liver (10.70ppm) and the lowest was in the bone (1.28ppm).The order of the increasing mean Se concentration in the organs was: bone<gut<fins <muscle <gills<liver. The mean concentration of Se in the organs exceeded the World Health Organization guideline limit of 1.00ppm (WHO, 2003).

4. Conclusion

Results from this study indicate that the mean concentration of As and Se in the organs of *C.carpio* from the Alaro stream in Ibadan exceeded the World Health Organization (WHO) guideline limits set for public consumption. This implies that Alaro stream is polluted and fish (*C.carpio*) caught from the stream is not healthy for human consumption due to the public health consequences posed in consuming such contaminated food.

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