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Determination of Mercury Level in *Rana esculenta* (Frog), Sediment and Water from River Guma, Benue State Nigeria

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Abstract
The level of mercury was determined in *R. esculenta* (edible frog), sediment and water from river Guma, Benue State, for three (3) consecutive months using hydride generation atomic absorption spectrophotometer (HG-AAS) technique. The mean concentrations of mercury in the *R. esculenta*, water and sediment were 0.027mg/kg, 0.00mg/kg and 0.001mg/kg, respectively. The absence of mercury in the water signifies its affinity to adsorbed to any surface in the river. Mercury builds up in the tissues of *R. esculenta* and its levels in tissues increase as we go up the food chain. The result of the analysis shows that the level of mercury is always higher in the liver (0.014mg/kg) compared to intestine (0.010mg/kg) and muscle (0.003mg/kg). The mean concentration of mercury obtained in R. esculenta (0.027mg/kg) was below the International Atomic Energy Agency recommendation value (IAEA – 433) of 0.168mg/kg.
Keywords: Mercury, Edible Frog, Sediment, Guma, HG-AAS

1.0 Introduction

Today, *R. esculenta* also known as edible frog has become the main supply of protein besides meat and poultry. Countries like France, Japan, China, Thailand, Indonesia and Nigerian, take edible frog as the main dish of their diet because it provides protein (Dural *et al*., 2007). Therefore, their mode of feeding and environment to these frogs needs investigation. Heavy metals have the tendency to accumulate in the various aquatic animals and the accumulation depends on the intake and elimination from the body (Karadede *et al.,* 2004). Marine fish and edible frog were exposed to these metals that human being consumed as sea foods. Therefore, there is a link for the transfer of toxic metals into human beings as we go up the food chain. However, frog also may contain chromium, mercury and lead that could give negative effects for health. The marine organisms accumulate contaminants such as metals from the environment and have been extensively used in marine pollution monitoring (Mora *et al.,* 2004). These metals accumulate in frog from water, food, sediment and some suspended particulate matter (Agusa *et al.,* 2005). The contamination of water bodies with heavy metals has become a matter of concern over the last two decades (Voegborlo *et al.,* 1999). The natural aquatic systems may extensively be contaminated with heavy metals released from domestic, industries and other man-made activities (Velez *et al.,* 1998). Heavy metals contamination may have devastating effects on the ecological balance of the environment and a diversity of aquatic organisms (Ashraj, 2005). Heavy metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al.,* 2006). Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water (Camusso *et al.,* 1995). Water quality standards should be applied to sediment because of its strong influence on the water quality. However, total metal concentration in sediment is not a good estimation of bioavailability. Different phases of sediment can vary in toxicity with the same concentration (Calmano *et al.*, 1996). Even though, mercury is a naturally occurring metal which has several forms of existence, the most common organic mercury compound is methyl mercury, which is produced mainly by small organisms called bacteria in water and soil. Methyl mercury builds up in the aquatic organisms and its levels in tissues increase as we go up the food chain. Edible frog and other aquatic organisms' intake are the major source of exposure to mercury, mainly in the form of methyl mercury, which accumulates from surrounding waters (Rogers *et al.,* 1992). Studies shows that edible frog accumulate these heavy metals from the surrounding water bodies thereby leaving a health risk if taking as food (US. DPHHS, 2005). EPA drinking water limit is 2ppb and FDA maximum permissible level of methyl mercury in seafood is 1ppm. Therefore, methyl mercury is worse for young children than for adults, because more of it passes into children's brains where it interferes with normal development. In this study, we investigate the distribution of mercury in edible frog, sediment and water from river Guma, Benue state, Nigeria. The observed levels of this metal concentration were compared to the Provisional Tolerable Intake for mercury as set by World Health Organization standard.

2.0 Materials and Methods

2.1 Sampling: Three sampling stations coded **A** (07.80691^{o} North, 008.65763^{o} East), **B** (07.80652^{o} North, 008.65756^{o} East) and **C** (07.76973^{o} North, 008.59413^{o} East) was established based on the anthropogenic activities that are going on around the area. Samples of edible frog, water and sediments were collected from the

River Guma for three consecutive months (between January and March, 2013). A total of 20 mature edible frog samples with mean weight of 150 ± 3g and mean length 26 ± 2cm were obtained from the sampling station (**Figure 1**). The samples were stored in an ice box in order to maintain the freshness and later transported ($1^1/_2$ hours) to the laboratory for dissection to obtain muscles, intestine and liver. The edible frog samples organ (muscles, intestine and liver) were oven dried separately for an hour to constant weight at 105^0C. The organs were pooled separately according to tissue type and milled with a mortar and pestle. They were put in dry labeled plastic containers and stored in desiccators until digestion.

Figure 1: A typical picture of Edible frog showing the side view

Similarly, the sediment samples were taken with hand and transferred into polythene bag and transported to the laboratory. The sediment was placed on a Formica surface ply wood board on a dust-free working bench and spread to air-dry. The sediment was redistributed twice daily for effective drying. When dried, the sediment was crushed in a mortar and sieved through the 2mm sieve into plastic containers and stored for subsequent analysis. A procedure similar to that described by Poldoski (1980) was used to digest the samples. This involves digesting 10g portion of the ground samples with 10mL HNO_3 and 2mL $HClO_4$. The residue was dissolved and diluted with 0.2% v/v HNO_3 to 20mL and made up to 100mL with distilled water. The digest was stored in pre-cleaned polyethylene bottles until analysis using hydride generation atomic absorption spectrophotometer. The KBH_4, carrier liquor and blank sample were connected into their respective sucking tubes. At the start of the hydride generation (connected to the main AAS), the solutions were automatically suck into the system where the mercury hydride was produced and transmitted to the electric quartz absorption tube and was detected and recorded.

3.0 Results and Discussion

The results of analysis shows that the concentration of mercury in all the water samples from the three sampling stations and between the periods of investigation (January, February and March) were below the detection limit. Therefore, any Hg level found in the frog could be as a result of bioaccumulation.

The mean concentrations of mercury measured in the edible frogs are shown in **figures 2 – 4**. The concentration of mercury varied in the organs from 0.001 – 0.006mg/kg in all the periods of investigation. **Figure 2** illustrates the mean concentration of mercury in liver, intestine and muscles of edible frogs from river Guma as obtained in January, 2013. Similarly, **figures 3** and **4** shows the mean concentrations of mercury for February and March, respectively. However, in **figure 4** the concentration of Hg in muscle of frog could not be detected, perhaps it was below the detection limit. Even though, the concentrations of Hg obtained were generally about a factor ten (10) higher than the recommended value of WHO within the period of this investigation.

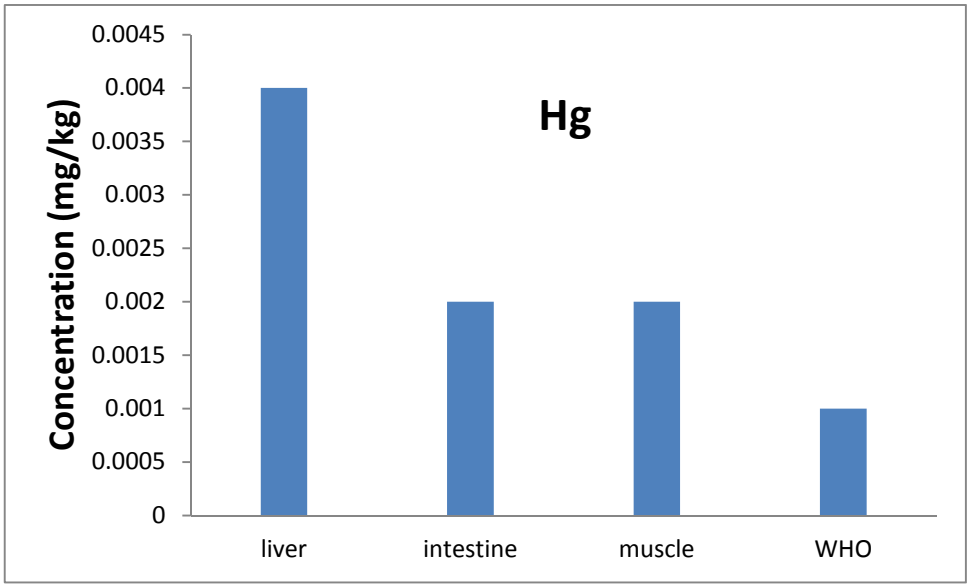

Figure 2: Mean January concentration of mercury in edible Frog organs from river Guma.

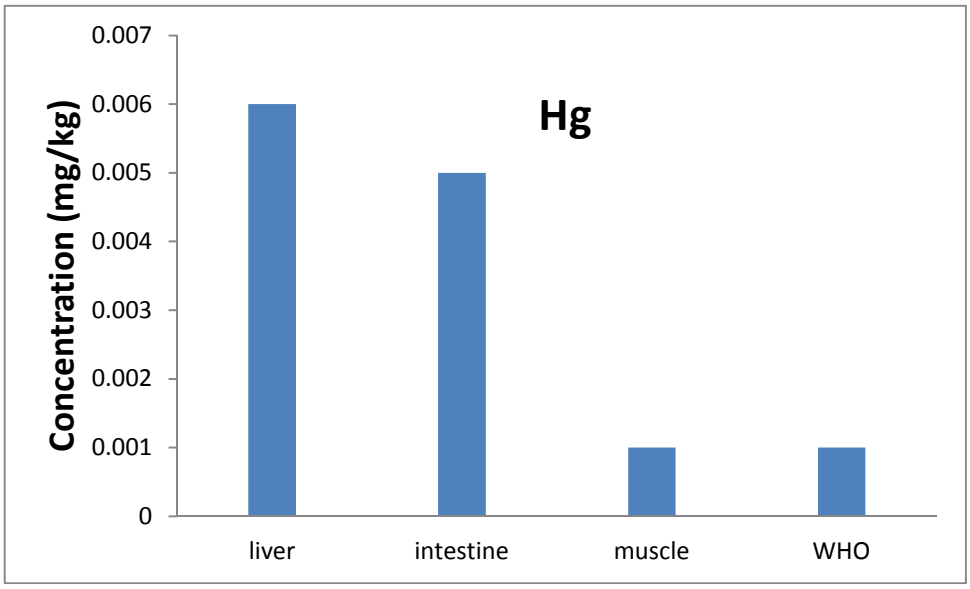

Figure 3: Mean February concentration of Mercury in edible Frog organs from river Guma.

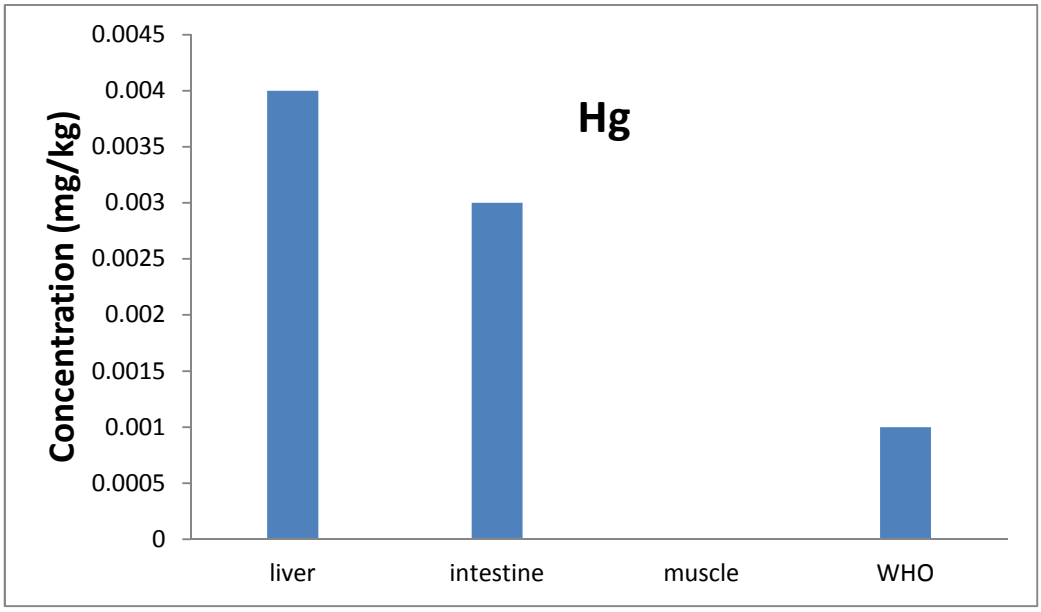

Figure 4: Mean March concentration of Mercury in edible Frog organs from river Guma.

Generally, the result of the HG – AAS analysis shows that the level of Hg is always higher in the liver compared to intestine and muscles. Mercury is rapidly absorbed and distributed by the blood; about 1% is deposited in the brain where it is retained for a long time, and the rest is transported to the liver and kidneys where it is excreted through bile and urine. The mean concentrations of Hg reported in this work are within the range of literature values reported by previous studies. Mukherjee *et al* (2011) reported mercury concentration in *Harpadon nehereus, Daysciaen aalbida, pumpus argentius, Formio niger, Hilsa ilisha and Rastrellige kanagurta* to be 0.91, 0.46 0.70 0.28, 0.37 and 0.93µg/g respectively in fishes from Bag Bergal, India. Voegborlo *et al* (2007) reported mercury concentrations in fish species samples from the coastal waters of Ghana as in *Lagolephalus lagocephalus, Stromatteus fiatrla, Braelydenterus curitus, Pamulinus argus, Calappa rubroguhata, Gerres nigri, Decapterus rhonchus, Braehydentera aurita, Diplodus puntazzo, parapristipomma humile, selene dorsalis, Galeoides decadactylus,* and *Pseudotolithus senegalensis* as 0.066, 0.004, 0.037,0.035, 0.056, 0.043, 0.070, 0.112, 0.034, 0.041 and 0.031µg/g. High value of mercury concentration of 0.32ppm in *Lates nilotcus* has been reported on Kaduna river (Nwaedozie, 1998). Alinnor *et al* (2010) working on Nworier river, reported Hg level of mean in *Liza grandisaquamis* and *Sphyraena sphyraena* to be 0.0083ppm and 0.0083ppm, respectively. Ekpo *et al* (2008) reported mercury concentration in *Metacembelus iconnbergii*, *Clarias lazera, Citarinus cithanus, Tilapia Zilli and Erpetoicithy* from Ikpo river in Benin City to be 0.004mg/kg, 0.003mg/kg, 0.003mg/kg, 0.00mg/kg and 0.002mg/kg respectively. Eneji *et al* (2011) also determined the concentration of these metals in the gills, intestine and muscle tissues of two fish species; *Tilapia Zilli* and *Clarias gariepinus* obtained from up and down streams of the River Benue. They reported the percentage composition of total heavy metals in the fish organs to be 52.2% in the gills, 26.3% in the intestine and 21.5% in the muscle tissue in *Tilapia Zilli* and contain 40.3% in the gills, 31.6% in the intestine and 28.1% in the muscle tissues of *Clarias gariepinus*.

The concentration of mercury in all the sediments samples ranges from 0.000 – 0.001mg/kg in all the periods of investigation. The mean concentration of Hg in the sediment from river Guma is presented in **figure 5**. Similar to the results of water analysis, the concentrations of mercury in most sediment samples were below the detection limit. The result shows that mercury level is at pick of maximum permissible level in the soil and any further addition as a result of anthropogenic activities could leads to contamination.

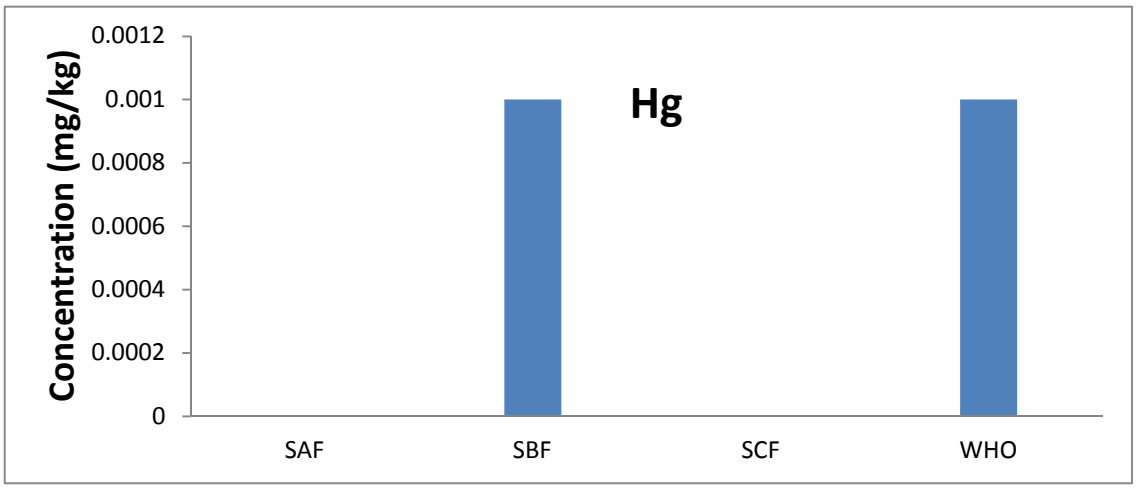

Figure 5: Mean concentration of Mercury in sediment from river Guma,

Norville (2005) reported the spatial distribution of heavy metals in sediments from the Gulf of Paria, Trinidad and recorded mercury concentrations to vary 0.03 – 0.10ppb. Kannan *et al* (1998) study the distribution of total mercury and methyl mercury in water, sediment and fish from South Florida Estuaries. They reported total mercury concentrations in the sediments to range from 1 – 219ng/g dry weight, while methyl mercury accounted for, on average of 0.77% of total mercury in sediment. The relationship of total and methyl mercury concentrations in fish to those of sediments from corresponding locations was fish –species dependent, in addition to several abiotic factors. Kwaansa-Ansah *et al* (2012) investigated the effect of pH, sulphate concentration and total organic carbon on mercury accumulation in sediments in the Volta Lake at Yeji, Ghana. They reported total mercury concentrations ranged from 32.6 – 700ng/g which is below the International Atomic Energy Agency recommended value of 810ng/g (Coquery *et al.,* 2000). Sizmur *et al* (2013) sampled sediments and polychaete worms from mudflats in the Bay of Fundy to investigate the bioaccumulation of mercury and methyl mercury in the coastal invertebrate food web. Their results shows that mercury concentrations in the sediments were low (< 20µg/kg) and worms that were feeding deeper sediments contained the greatest methyl mercury concentrations (69.6µg/kg).

4.0 Conclusion

The mean concentration of mercury obtained in edible frog (0.027mg/kg) was below the International Atomic Energy Agency recommendation value (IAEA – 433) of 0.168mg/kg. Also, the mean concentrations of mercury in the edible frog organs and sediments were found to be statistically significant ($p = 0.50$). This work shows that edible frog could be used as an excellent bio-indicator of mercury in the aquatic ecosystem as the concentration of mercury was too low to be detected in water using routine methods. Nevertheless, the gradual accumulation of mercury within the ecosystem to concentrations of considerable concern was found in edible frog. Generally, the order of mercury concentration in a descending level in edible frog organs was liver > intestine > muscles; while the order in the aquatic ecosystem was edible frog > sediment > water.

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