

Full Length Research Paper

# Mercury contamination in artisanal gold mining area of Manyera river, niger state Nigeria

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The study was conducted on Manyera River, Niger State Nigeria due to the mining activities in the area as the river is mainly used as the source of livelihood of people around it. Samples of water, fishes and sediments were collected along the river course in March, 2013. Samples were persevered and taken to the laboratory for analysis by Cold Vapor Atomic Absorption Spectrometer. The water collected at SBW5 downstream had the highest concentration of 0.025mg/L and lowest value was recorded from upstream where there's little or no mining activity with concentration of 0.014mg/L. The concentration of fish obtained from the river (*Heterotis niloticus*) is 0.008mg/L, although no fishing activity where the mined soil is been washed. Sediment collected downstream also had the highest concentration of mercury of 0.021mg/L while at point where the mined soil is washed showed lower concentration of 0.015mg/L. These values were high compared to 0.001ppm standard limit for environmental matrices by WHO. There is need to continually monitor this activity to prevent the outbreak of problems associated with Mercury poisoning as the water is the only source of livelihood for domestic activities in the communities around it.

**Keywords:** mining, contamination, water, mercury

## INTRODUCTION

Since the occurrence of the Minamata incidence in Japan in 1957, where an outbreak of the Minamata disease occurred due to contamination of the fish in the Minamata bay water with mercury from untreated effluence of a plastic factory discharged into the bay, interest has increased over the years in studying mercury contamination in the environment. This is because mercury is a heavy metal which is toxic and cannot be eliminated from the earth. It does not occur naturally in living organisms as it is undesirable and potentially hazardous (Eisler, 2006).

Mercury is found naturally in small quantities throughout the environment. It is released by the breakdown of minerals in rocks and soil and as a byproduct of fossil fuel combustion and waste incineration. It is inhaled with the air that we breathe, absorbed through the skin, and ingested with food. The tiny amounts to which the vast majority of people are

exposed do not generally cause health concerns, but exposure to excessive amounts of mercury can be toxic. The amount of mercury absorbed by an individual and its effects on his or her health depend on the type of mercury weather elemental, inorganic or organic metallic, its concentration, and the exposure time. According to the Agency for Toxic Substances and Disease Registry (ATSDR), very little metallic mercury (less than 0.01%) is absorbed by the body, even if it is swallowed. However, if the same mercury is inhaled as a vapor, about 80% is absorbed into the bloodstream (ATSDR, 2011) when mercury is absorbed into the body, it can be deposited in a variety of body organs, including the kidneys and brain, Naturally the body slowly rids itself of mercury through the urine and stool, but if an excessive amount accumulates, it can result in permanent damage to the kidneys, nervous system, and brain. Also pregnant women with elevated levels of mercury can pass it on to their unborn babies, affecting development, especially the baby's brain; kidney, and nerves, mercury can also be passed from mother to baby through breast milk during nursing (ATSDR, 2011).

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It is globally recognized that mercury is one of the global hazardous pollutants due to the anthropogenic mercury emission and many international agencies such as United Nations Environment Programme (UNEP), World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations have listed it as one of the priority pollutants (Jiang *et al.*, 2006). Once released into the environment mercury is never broken down to a harmless form and exists in the atmosphere, soil and aquatic phase. It transform into very stable organic compounds such as methyl mercury which has a strong bioaccumulation and can be finally taken by humans (Basel, 2010).

Mercury a toxic metal is widely used in chemical production and small scale mining, particularly gold. It is naturally occurring element that is found in the air water and soil and it cannot be created or destroyed. Mercury emission comes from sources such as coal burning and the use of mercury to separate metal from ore in small scale mining, and mercury pollution also comes from discarded electronics and other consumer products. Mercury in the air settles into soil from where it can then seep into the water. United Nation report found out that mercury emission from artisanal gold mining had doubled since 2005 due to factors such as rising gold prices and better reporting on emission (John, 2013). Africa, Asia and South America could see increasing emission of mercury into the environment mainly due to small scale gold mining and through cold burning for electricity. Asia accounts for just under half of all global releases of mercury (John, 2013). Efforts are being made by countries and various institutions to minimize the use of mercury and to develop efficient means of handling, treating and disposing of mercury waste.

Artisanal mining release 1,000 tones of mercury into the environment every year, which accounts for 30% to 40% of the world's mercury pollution (Clarke, 2011). Mercury vapors are released when mercury gold amalgam is heated to separate the gold; most of these vapors end up being inhaled by miners and their families. The vapor can also spread from the amalgamation heating site through the air to distant communities. Excess liquid mercury used in the gold amalgamation process is often dumped with mine tailing and enter waterways, mercury enter stream as inorganic mercury, where it is converted to the more toxic methyl mercury by organisms. The methyl mercury, bioaccumulation in fish, moving up the food chain to species eaten by humans. Though mercury accumulation is most commonly associated with large, predatory fish, traces have also been found in birds, reptile, and mammals, all of which can spread mercury to humans if consumed (UNEP, 2002).

Mercury, found in virtually every environment media is of the six most poisonous metals known to humans. It is toxic and capable of biomagnifying and bioaccumulating as it moves along the food chain. From ancient times to

this present moment, there have been cases and incidents of individuals and animals being adversely affected by mercury poisoning with some cases leading to death. While its presence in the environment cannot be eliminated, a good knowledge of the amount released into the environment by various activities in different locations; would help in taking adequate measure to prevent poisoning and mitigate its effects by adopting appropriate technology. Some research has been carried out on mercury and its impact on the environment (majorly aquatic) in Nigeria (Odunlami, 2002), but there is lack of comprehensive data on the amount of mercury released due to artisanal mining activities in the country. Various research works have been carried out to assess the level of mercury in the environment in Nigeria. In carrying out the determination of heavy metals concentration in whole as well as different parts of Tilapia species from Lagos Lagoon in 1997, Fodeke concluded that measured values were high. The gut contained 0.03 – 0.19ppm Hg while in whole minced fish 0.01 - 0.04 ppm Hg (Odunlami, 2002). Kakulu and Osibanjo (1986) found the level of Hg in fish from Niger Delta area of Nigeria to be less than 10ug/kg-410ug/kg wet weight and 0.024µg/g-1.54µg/g dry weight. These levels were low in comparison with the 0.5ug/g Hg level recommended for human consumption by WHO. Omgbu and kokogbo (1993) carried out the determination of Zn, Pb, Cu and Hg in soils of Ekpan, Nigeria to assess the impact of petroleum refining activities on the soil. Results obtained showed the concentration of Hg to be between 4.00ug/g-6.33ug/g. Oyewo *et al.* (2003) found mercury to be toxic to test species (*Tilapia guineensis*, *Mugil* and *T. Fuscatus*) by bringing about reduced weight increase or weight loss when exposed to sub-lethal concentration of mercury over a period of 28 days.

Kakulu (2002) carried out analysis on the mercury content of fresh fish of the federal capital territory of Nigeria and the levels of mercury in the samples were low with over 78% of the sample recording a total Hg level of then 200ug/g wet weight in the muscle tissue. Osibona and Kusemiju (2006) evaluated the total mercury concentration in the tissue and whole body of *sphryna couardi* collected off Lagos coast. The mercury content of hammer head shark, *sphryna couardi* was determined by means of atomic absorption spectroscopy and was found to be higher than the European Union's legal limits of 0.5mg/kg mercury in sea food. Total mercury values obtained were between 9.2 and 35.1 µg/g wet weight, with a mean value of 18.78±7.26 mg/kg indicating that regular consumption of fish could be hazardous to health. Achudume (2007) also conducted a study to evaluate ten heavy metals in dry sediment samples used to assess the contamination of farm land in Niger Delta after a protracted flooding. Eighteen samples in six locations were collected. These sediments were subjected to analysis using standard methods for the examination of the soil samples. Results showed a trend

toward induction of environmental contamination with Zn, Cu, Fe, Hg, and Pb on the farmland. This is a result of activities of petrochemical industries in the area. Mercury and lead concentrations were disproportionately higher than other sediment elements and above compliance limit for Nigeria. A research work carried out by Mahre et al. (2007) to obtain pollution indicators in River Kaduna, observed that mercury has a range of 1.72 to 2.50mg/L for drinking water, fisheries and aquatic life had a range of 0.0001-0.001mg/L Hg.

Ekpo *et al.* (2008) also investigated the health metal concentration in some fish species (*Metacembelus Ikonbergis*, *Clarias lazera*, *Citarinus Citharus*, *Tilapia Zilli* and *Erpetoichithy*) from Ikpoba River, Benin city. The muscle was found to be in the range 0.001-0.002mg/kg, kidney and the liver are in the ranges of 0.004-0.006mg/kg and 0.002-0.004mg/kg respectively. These were within the World Health Organization (WHO) and Food and agricultural Organization (FAO) limits for food. Ipeaiyeda and Dawodu (2008) carried out a research on heavy metal contamination of topsoil and dispersion in the vicinities of reclaimed auto-repair workshop in Iwo, Nigeria. Their result showed that the topsoil in the area have an average Hg concentration of Hg  $9.4 \pm 4.6$ mg/kg which exceeded the international threshold agriculture use. Oribhabor and Ogbeibu (2009) investigated the concentration of heavy metals in a Niger Delta Man groove creek, Nigeria. Mercury concentration was found to be extremely low (0.01mg/L) throughout the study period.

In Nigeria over 90% of solid mineral production in Nigeria is done by artisanal and small scale miners, who are frequently challenged by lack of appropriate mining exploitation methods and limited knowledge of mineral processing techniques. The study is justified as it will help in providing some of the much needed data on mercury emission into the environment by identifying the source of mercury emission into the environment in Nigeria, quantifying them and determine their environmental impact. The objective of this study is to assess the level of pollution caused by artisanal mining in the study area. The study will be conducted on Manyera River in Sabo / Nasarawa community Niger state, Nigeria due to the continuous use of mercury in the washing of gold mined along the river course.

## METHODOLOGY

### Description of study area

The study area is Manyera River between Sabo and Nassarawa in Borgu Local government, Niger State Nigeria. The river lies between latitude  $09^{\circ} 71'N$  and longitude  $004^{\circ} 29'E$  and is the major river where all activities is conducted, washing, drinking, bathing, fishing and major area for mining of gold, a process which is

capable of emitting mercury into the environment.

### Sample preparation

The samples were collected in March, 2013. 3 Sediment samples were taken from depths of 0-15cm (top soil) with the aid of a depth calibrated soil auger as sampling tool randomly in three different locations. Sediments were obtained by sampling at the location closest to the point of disposal of the waste water. Each sediment sample collected was immediately placed in clean black polythene bags, tightly sealed and labeled. The samples were preserved by storing at  $4^{\circ}C$  in an ice chest to preserve sample integrity and then transported to the laboratory. Mercury determination in sediment has a holding time of 28 days (OMAAOAC, 1970). Water samples was collected in 5 different sample location along the river and 3 samples are collected randomly in each location in a 500ml plastic container and preserved with concentrated nitric acid. 3 fishes (*Heterotis niloticus*) were bought from fisherman while fishing on the river for analysis. The sediment and fish sample was air dried and then grounded to fine powder using an agate mortar and sieved. A composite sample was taken after mixing the sample obtained in a sample location. An aliquot of the sample was subjected to hot refluxing  $HNO_3/H_2SO_4$  digestion for 4hours followed by bromine monochloride (BrCl) oxidation for total mercury analysis. The water sample was also refluxed using the same method. The pH, conductivity and temperature of the water were also determined.

### Detection of mercury

The content of total mercury in the sediment, fish and water was determined using the USEPA method 1631 (USEPA 2001). Total mercury was analyzed by BrCl oxidation and immediately prior to analysis, excess bromine in all samples was neutralized with 10% hydroxylamine hydrochloride. All samples were then reduced with stannous chloride, purged with nitrogen gas and trapped on columns packed with gold coated sand. The gold trap was heated and the desorped mercury detected with Cold-Vapor Atomic Fluorescence Spectrophotometer- CVAFS.

## RESULT

Sediments samples collected from artisanal mining areas of Manyera River for total mercury analysis showed a maximum total mercury concentration of 0.021mg/L for the sample collected at point 3 and the minimum of 0.015mg/L for sample collected at point 5. The mean total mercury content of sediment in the area is

**Table 1:** Concentration of Hg in water, sediment and fish of Manyera River, Nigeria

Sample points	Water Hg concentration (mg/L)	Sediment Hg concentration (mg/L)	Fish Hg concentration (mg/L)
1	0.024	0.017	-
2	0.014	-	-
3	0.023	0.021	-
4	0.019	-	-
5	0.025	0.015	0.008
Total	0.105	0.053	0.008
Mean concentration	0.021±0.004	0.018±0.003	0.008±0.000

**Table 2:** Physicochemical parameters of the water

Sample point	pH	Temperature (°C)	Conductivity (µs)
1	5.3	26	60
2	5.2	25	80
3	6.1	26.5	65

**Table 3:** Mercury in sediments of AGM area of other part of the world

Location	Sample	Total Hg	References
Amazon	Soil	0.26-5.53 6 times above local background	Requelme et al, 2003
Pra river	Sediment	0.7-9.3 Background 0.5	Donkor et al, 2005
Indonesia	Sediment	0.265 avrg	Lasut et al, 2010
Thailand	Sediment	0.010-0.017	Pataranawata et al, 2007
Nilambur, Kerala, India	Sediment	0.096-0.402	Mohan et al., 2012
Shaanxi Province, PR China	Soil	0.103-0.468	Feng, 2006
	Sediment	0.90-160	
Mayera river, Nigeria	Sediment	0.3-0.9	
	Sediment	0.018	Present study

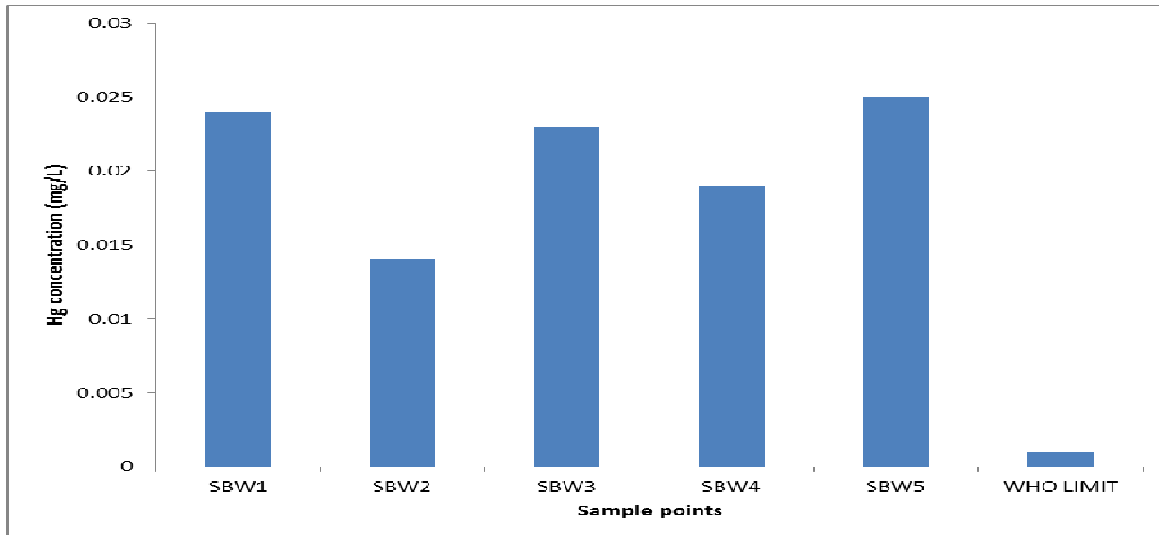
0.018±0.003mg/L. The water samples collected from the study site was analyzed for total mercury and other geochemical parameters. The concentration of mercury was detected for all samples analyzed. The maximum total mercury concentration observed was 0.025mg/L at point 5 and the minimum of 0.014mg/L for sample collected at point 2. The mean total mercury content of water in the area is 0.021±0.004mg/L. The pH of the water varied from 5.2-6.1. The result indicates that the water is slightly acidic. The result obtained for electrical conductivity ranged between 60-80µs. Values of temperature ranged between 25-26.5°C. The results are shown in Table 1 and Table 2. Only a fish species was collected for this experiment from the river which is *Heterotis niloticus*, and the mean total mercury content of the fish is 0.008mg/Kg (Table 1).

## DISCUSSION

The result of the study indicated that all water samples collected were slightly acidic. This condition may enhance the mobility and bioavailability of mercury in the

sediments. High pH favors adsorption of mercury with minerals (Gabriel and Williams, 2004). This explains why the concentration of mercury in the sediment is also high in relation to the water. This can also be attributed to the fact that higher acidity enhance the mobility of mercury in the environment likewise its adsorption to clay and mineral oxides of iron, aluminum and silicon as explained by Kim *et al.* (2004). The mercury concentration in the were higher than the environmental limit of 0.001mg/L set by WHO, although lower than EPA limit of 0.105mg/Kg as shown in Figure 1. Recent evidence suggest that mercury is responsible for the microbiological activity vital to terrestrial food chain in soil over large part of Europe and potentially in many other places in the world with similar soil characteristics (Pirrone *et al.*, 2001). The microbial activity in soil is vital to the processing of carbon and nutrients in the soil and the health of microbiological community has a great effect of the living condition of trees and soil organisms which forms basis of terrestrial food chain. Although the values were within the range of preliminary critical limits to prevent ecological effect due to mercury in organic soils which is set at 0.07-0.3mg/Kg for the total mercury content in soil as stated by Pirrone *et al.* (2001).

Table 3 shows the level of mercury in the sediment. It was discovered that sediment collected downstream has



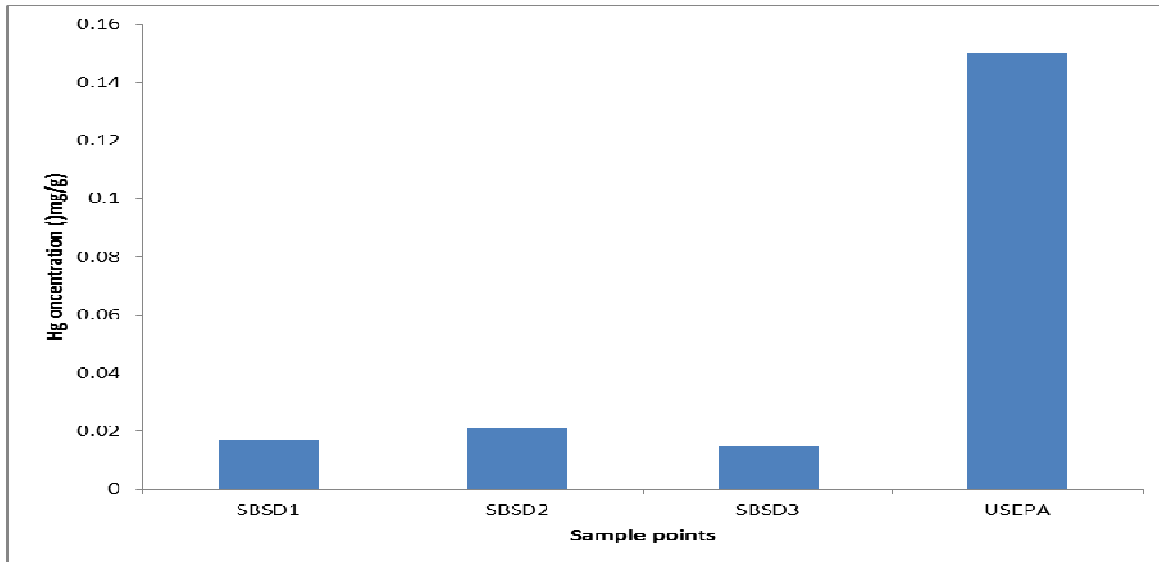
**Figure 1:** Comparison of Hg concentration with WHO limit

the highest concentration of 0.021mg/Kg, although lower value was observed where the washing is done with concentration of 0.015mg/Kg. Omgbu and Kokogho (1993) carried out the determination of Zn, Pb, Cu and Hg in soils of Ekpan, Nigeria to assess the impact of petroleum-refining activities on the soil. Results obtained showed the concentration of Hg to be between 4.00 $\mu$ g/g-6.33 $\mu$ g/g. Achudume (2007) conducted a study to evaluate ten heavy metals in dry sediment samples used to assess the contamination of farmland in Niger Delta after a protracted flooding. Eighteen sediment samples in six locations were collected. These sediments were subjected to analysis using standard methods for the examination of the soil samples. Results showed a trend toward induction of environmental contamination with Zn, Cu, Fe, Hg and Pb on the farmland. This is a result of activities of petrochemical industries in the area. Mercury and Lead concentrations were disproportionately higher than other sediment elements and above compliance limit for Nigeria. Dawodu (2008) carried out a research on heavy metals contamination of topsoil and dispersion in the vicinities of reclaimed auto-repair workshops in Iwo, Nigeria. Their result showed that the top soils in the area had an average Hg concentration of Hg 4.6-9.4 mg/kg which exceeded the international threshold agricultural use. All the values obtained in these studies were higher than that obtained in the present study except for that of Omgbu and Kokogho (1993) for soil collected in Epan. Table 3 also revealed the concentrations of mercury from different part of the world; the values were higher compared to the present study but for that obtained in Indonesia (Lasut *et al.*, 2010).

Low concentration of mercury in fish might be attributed to high turbidity of water around the area where washing of soil for gold is high. This could also have resulted to

why there is low population of fish in the study area due to longer hours of waiting before they are caught. Mean concentration of total mercury recorded in fish was 0.008mg/Kg which is relatively low compared to that obtained in water and sediments. The amount of mercury in fish depends on a number of factors including the amount of mercury deposited from the atmosphere, local, non-air release of mercury, naturally occurring mercury in soil, the physical, biological and chemical properties of the water body as well as the age, size and type of food the fish eats. Although, the fishes obtained for the analysis were small in size. The effects of mercury on wildlife can include mortality (death), reduced fertility, slower growth and development and abnormal behavior that affect survival, depending on the level of exposure (EPA, 2013). In addition, research indicate that the endocrine system of fish, which plays an important role in fish development and reproduction may be altered by the levels of methyl mercury found in the environment (EPA, 2013).

The commonly eaten fish species *Heterotis niloticus* from the river were to contain mean mercury level of 0.008mg/kg. This can be attributed to the fact that the high turbidity of the water has not allowed fishes to dwell in the area as the fishes caught for the experiment was downstream away from where mined soil is washed. Ekpo (2008) also investigated the heavy metal concentration in some fish species (*Metacombelus Iconnbergii*, *Clarias lazera*, *Citarinus citharus*, *Tilapia zilli* and *Erpetoichthy*) from Ikpoba River, Benin city. The amount of mercury in the muscle was found to be in the range of 0.001 - 0.002 mg/kg, kidney and the liver are in the ranges of 0.004- 0.006 mg/kg and 0.002 - 0.004mg/kg respectively. Determination of heavy metals concentration in whole as well as different parts of *Tilapia*



**Figure 2:** Comparison of Hg concentration of sediments and USEPA standard

species from Lagos Lagoon in 1979, Fodeke concluded that measured values were high. The gut contained 0.03 - 0.19ppm Hg while in whole minced fish 0.10 - 0.40mg/kg Hg (Odunlami, 2002). Kakulu and Osibanjo (1986) found the level of Hg in fish from Niger Delta area of Nigeria to be less than 10 µg/kg - 410 µg/kg wet weights and 0.024 µg/g - 1.54 µg/g dry weight. These levels were low in comparison with the 0.5 µg/g Hg level recommended for human consumption by WHO. Kakulu (2002) carried out analysis on the mercury content of fresh fish of the Federal capital territory of Nigeria and the levels of mercury in the samples were low with over 78% of the samples recording a total Hg level of less than 200ng/g wet weight in the muscle tissue. Osibona and Kusemiju (2005) evaluated the total mercury concentrations in the tissues and whole body of *Sphryna couardi* collected off Lagos Coast. The mercury content of hammerhead shark, *Sphryna couardi* was determined by means of atomic absorption spectroscopy and was found to be higher than the European Union's legal limits of 0.5 mg/kg mercury in sea food,

Total mercury values obtained were between 9.2 and 35.1ng/g wet weight, with a mean value of  $18.78 \pm 7.26$  mg/kg indicating that regular consumption of fish could be hazardous to health. There are heavy metals considered by WHO as priority metals and their health effect. The value obtained in this study as shown in Figure 2 was a bit higher than the WHO standard limit for drinking water and that of sediment shown in Figure 2, was lower than European Union legal limits. Thus, there could be an increased risk of the neurological damage and foetal deformities commonly associated with mercury poisoning as most notably exemplified in the fish village population of Minamata, Japan in the 1950s when a chemical

manufacturing plant discharged mercury salts and  $\text{CH}_3\text{Hg}^+$  into the bay to be taken up by fish and shell fish. Other effects include gastrointestinal disorders, respiratory tract irritations and renal failure.

The value was lower to that obtained in Lagos Lagoon but high compared to that obtained in the other areas (Kakulu and Osibanjo, 1986; Ekpo *et al.*, 2008; Kakulu, 2002). This is attributed to high industrial activity in the area discharging waste in the Lagos lagoon. Most fishes available in the river were found in the extreme part of the river where there is no washing of mined soil. Typically revealed is such activity happened in the past with the price of gold boarding in the late 1970 and early 1980s, where there is a modern day gold rush in southern America. The effect of the activity is seen in increased turbidity with clear water turning a muddy brown colour and it is obvious that there is been increased fish mortality. A survey conducted by Spencer A. Peterson in 2007 of 2707 fish randomly collected from 626 rivers in 12 states in the West revealed fishes with elevated mercury levels and attributed to a local source such as an old mercury site (Jeff, 2013). Monash University also researched into heavy metal contamination levels in Dolphins from Port Phillip Bay and the Grippsland lakes revealed high mercury within range (dead, 3.45mg/Kg; living, 1.32mg/Kg) considered to cause negative health and mental effect and the value were higher than mercury level found around the world. This is attributed to historical gold mining sites where mercury was used in gold processing as well as other industrial sources (Thompson, 2013).

Table 1 shows the range of concentration of mercury in water between 0.014-0.025mg/L. The concentration of mercury in the water sample was high compared to

0.001mg/L limit recommended by WHO. This could be detrimental to the communities around the river who depend solely on the water from the river for their livelihood like for drinking, washing, bathing etc. EPA report has revealed that elevated mercury levels has been linked to learning disabilities and developmental delays in children and to heart nervous system and kidney damage in adults. A research work carried out by Mahre *et al.* (2007) to obtain Pollution Indicators in River Kaduna, observed that Mercury has a range of 1.72 to 2.50 mg/L for drinking water, fisheries and aquatic life had a range of 0.0001-0.001 mg/L Hg.

## CONCLUSION AND RECOMMENDATION

The result showed that the release of mercury into the aquatic environment have resulted in elevated concentration of mercury in sediments, although the concentration in fish is very low compared to that obtained for sediments and water. The practice of artisanal gold mining, where mercury is used for amalgamation of gold after washing the mined soil in the river where the study is conducted has led to the release of mercury into the stream. Majority of THg in aquatic system is always found in the sediment due to relative binding with organic carbon bearing particles.

The mean concentration of mercury in the sediment is 0.018mg/L. this value is low compared to the 0.105mg/Kg limit of USEPA. Mercury is a toxic metal capable of bioaccumulation and biomagnification in the food chain and can cause a lot of health hazards in humans consuming them either directly or indirectly. Exposure to mercury has been confirmed to cause disease such as cancer, neurological disorder, autism, and in some cases has resulted into death.

The result of chemical analysis carried out on sediment, and water in the present study ranged between 0.014-0.021mg/L and 0.015-0.021mg/L respectively. Mean concentration of 0.008mg/L was detected in fish samples collected. These values were higher compared to the regulatory limit of 0.0001ppm for its presence in environmental samples. There is need to continually monitor this activity in the study area and probably be stopped in order to avoid possible health problems associated with Hg poisoning. There is therefore need to assess the level of contamination on the people living around the study area and who make use of water from the river for their domestic purpose and as well consume the fishes in the river.

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