Impact Assessment of Pollution from Metal Concentrations in Water and Fish – A Case Study of Dandaru Reservoir in Ibadan, Nigeria

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Abstract: Hospitals and public offices produce wastewaters that contain various potentially hazardous materials. In this study, concentrations of some metals (Fe, Mn, Co, Zn, Pb and Hg) on the muscles of two fish species (*Oreochromis niloticus* and *Clarias gariepinus*) from Dandaru reservoir as a result of influx of wastewaters from the University College Hospital and Oyo State Secretariat, Ibadan, Nigeria, were investigated. The metals in wastewaters from the hospital, Secretariat and at their confluence en route the reservoir were analyzed; also, water from the Dandaru reservoir and at its exit were analyzed, using Atomic Absorption Spectrophotometer (AAS). The results (mg/L) for the water samples showed that Mn, Co, Fe, Zn, Hg and Pb, respectively, ranged between 0.616-1.169, 0.604–2.160, 0.616–1.272, 0.003–0.005, 0.001–0.002 and 0.001–0.002; the hospital wastewater had the highest concentrations of the metals, whereas Hg and Pb were not detected in the reservoir water. Mn, Co and Fe concentrations in the hospital wastewater were significantly higher ($p>0.05$) than those of the Secretariat and reservoir. Metal concentrations in the muscle of *Oreochromis niloticus* was in the decreasing order of Fe>Mn>Co>Zn>Pb with concentrations (µg/g) of 62.800, 4.390, 4.152, 0.713 and 0.120, respectively. For *Clarias gariepinus,* the decreasing order of the metals was Fe>Co>Mn>Zn>Pb with respective concentration (µg/g) of 56.700, 3.513, 1.060, 0.690, 0.120. There was significant difference at ($p<0.05$) in the concentrations of these metals, except for Zn and Pb. However, mercury was not detected in both fish species. *Oreochromis niloticus* had higher bioaccumulative power for the metals than *Clarias gariepinus.* The increased levels of the metals in the fish muscle than those found in the reservoir water showed their tendency to bioaccumulate the metals which are potentially hazardous if consumed by humans.

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1. Introduction

Water is a natural resource and a basic necessity for all living thing. Water is polluted when its acceptable quality has been altered by man's activities through anthropogenic imputes. Chemical investigation of the water quality of some Nigerian rivers reveals that water, that was once an abundant natural resource, is rapidly becoming scarce in quantity and the quality is deteriorating in many places, owing to population increase, rapid industrialization and rural/urban migration (Ajayi and Osibanjo, 1981; Adeniji and Mbagu, 1983; Asuquo, 1999). The polluted water may have undesirable color, odor, taste, turbidity, organic matter contents, harmful chemical contents, toxic and heavy metals, oily matters, radioactivity, high total dissolved solids (TDS), acid, bacterial, protozoa, worms, etc.

Hospital effluent is referred to as waste water from hospital or health care centre, biological or non biological, that is discarded and not intended for further use. Hospital wastes consist of liquid, solid and gas, which have effect on the element of the environment, altering its natural compositions and rendering it unsafe for human dependence. Hospitals consume an important volume of water a day. Hospitals wastewater has similar quality to municipal wastewater (Ekhaise and Omavwoya, 2008; Onesios, *et al*., 2009). Hospital wastewater contains a great variety of micro-contaminants that are chemicals, heavy metals, disinfectants and specific detergents resulting from diagnosis, laboratory, research activities and medicine excretion by patients. Indeed hospital wastewater may have an adverse impact on environmental and human health (Abd El-Gawad and Aly, 2011). The impact of industrial and hospital wastes on aquatic life including microorganisms, cannot be over-stressed. Consequently, many hospitals, production and manufacturing companies, due to improper waste management techniques, added toxic and hazardous wastes including synthetic compounds into the aquatic environment. The presence of these wastes in the environment causes

extensive damage to the water quality characteristics and the ecology of the environment, especially when microbial degradation activities fail to remove these pollutants fast enough to prevent environmental degradation. The environmental consequences of marine pollution include creating a harsh marine environment which adversely affects activities of marine micro-flora as well as fish and other marine lives (Obire and Okudo, 1997; Obire and Amusan, 2003).

Heavy metals like mercury and cadmium are known to accumulate in marine organisms and cause rapid genetic changes (Nimmo *et al*. 1978, Nevo *et al*. 1986). Other heavy metals include lead, manganese, nickel, selenium, chromium, copper, barium, zinc, etc. These contaminants once assimilated into living plants and animals move quickly through the food chain, affecting the health of animals and humans. According to Olowoyo *et al*. (2011), fish are constantly exposed to chemicals in polluted and contaminated waters. They may accumulate toxic trace metals via their food chains; hence, fish living in a polluted water can be useful tool for determining the level of bioaccumulation of trace metals in fish (Mandil and Uluozlu, 2007; Tariq *et al.*, 1991).

In this study, the effects of contaminations from some metals (trace and heavy), arising from a hospital liquid effluent, inadvertently discharged into a nearby reservoir, were investigated. The effluent from the hospital enters into the pond through a drainage channel en route the Zoological Garden, along the Secretariat road, Ibadan, Nigeria. Metal analyses were conducted on wastewater from University College Hospital (UCH), water and two fish species (*Oreochromis niloticus* and *Clarias gariepinus*) from a nearby reservoir (Dandaru Reservoir) all located at Orita-Mefa, Ibadan, Nigeria.

2. Materials and Methods

2.1 Sample Collection

Five water samples were collected from different points using 1L plastic bottles. The sampling bottles were rinsed with their respective samples before collection, after which they were taken into the laboratory for appropriate analyses. The samples are described in table 1.

Table 1: Sample Locations and Descriptions

Sample	Locations/Coordinates	Sample Description
A	7^{o} 24' 21^{N} latitude; 3^{o} 54' 09^{E} longitude; 206m above the sea level	wastewater from the exit of the hospital
B	7^{o} 24' 23^{N} latitude; 3^{o} 54' 9^{E} longitude; 206m above the sea level	wastewater from the Secretariat drainage
C	7^{o} 24' 22^{N} latitude; 3^{o} 54' 08^{E} longitude; 201m above the sea level	wastewater at the confluence of the hospital and Secretariat effluents inside the Zoological Garden
D	7^{o} 24' 15^{N} latitude; 3^{o} 53' 57^{E} longitude; 207m above the sea level	water from the Dandasu reservoir
E	7^{o} 24' 13^{N} latitude; 3^{o} 53' 56^{E} longitude; 194m above the sea level	water from the exit point of Dandasu reservoir to Ogunpa River

The fish species (*Oreochromis niloticus and Clarias gariepinus*) were collected at two different points in the re"servoir (latitude 7^{o} 24^{1} 16^{N}; longitude 3^{o} 53^{1} 56^{E}; 205m above sea level and latitude 7^{o} 24^{1} 15^{N}; longitude 3^{o} 53^{1} 57^{E}; 207m above sea level) with the help of local fishermen. Control fishes were obtained from a non-polluted river Ayetoro in Osogbo, Nigeria.

2.2 Sample Preparation

The fish samples were gutted and muscle tissue taken. About 100 g tissue of each sample was then homogenized using blender before sub-samples were taken for analysis. Digestion was carried out on the homogenized samples, after which metal concentrations were determined in the digests.

2.2.1 Digestion

One gram each of the homogenate was weighed into the preleased borosilicate 250 ml capacity beaker for digestion and 30 ml of the mixture of concentrated HCl and HNO_3 (3:1) was added for digestion in the fume cupboard. The beaker and its contents after the digestion were allowed to cooled. More 20ml of the digesting solution was added and digested further in the fume cupboard and the mixture was allowed to cool to the room temperature. The mixture was filtered into the 250 ml volumetric capacity borosilicate container. The filtrate was made up to the mark with the de-ionised water. The digested sample was sub-sampled into the pre cleaned borosilicate glass container for atomic absorption spectrophotometric analysis (AAS).

All the water samples were also digested accordingly before analysis by taking 50 ml each, after which analysis for metal concentrations were carried out using the AAS.

2.2.2 Analysis of Metals

Standard solutions of 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L of each metal were prepared. Metal concentrations in each digest were analyzed using Atomic Absorption Spectrophotometer (UNICAM 929, London, powered by the SOLAR software).

2.2.3 Statistical Analysis

Data were analyzed using Analysis of Variance (ANOVA) and means were separated by Duncan's multiple range test at a probability level of < 0.05.

3. Results and Discussion

3.1 Results

Table 2: Concentrations of metals in the water samples

Sample	Metal concentration (mg/L)					
	Mn	**Co**	**Fe**	**Zn**	**Hg**	**Pb**
A	1.169±0.009a	2.160±0.250[a]	1.272±0.009[a]	0.005±0.000[a]	0.002±0.000[a]	0.002±0.00[a]
B	1.051±0.049b	1.826±0.039[b]	0.689±0.007[b]	0.005±0.000[a]	0.001±0.000[a]	0.001±0.00[a]
C	0.796±0.008[c]	1.222±0.045[c]	0.702±0.007[b]	0.004±0.000[a]	0.001±0.000[a]	0.001±0.00[a]
D	0.610±0.057[d]	0.802±0.068[d]	0.516±0.006[c]	0.004±0.000[a]	ND	ND
E	0.616±0.122d	0.604±0.I29[e]	0.616±0.005[b]	0.003±0.000[a]	0.002±0.000[a]	0.001±0.00[a]

Results of the mean of three replicate results ± standard deviation. Values of different superscripts within the column are significantly different at $p<0.05$. ND - Not detectable. Sample A - wastewater from the exit of the hospital; Sample B - wastewater from the Secretariat drainage; Sample C - wastewater inside the zoo at the confluence of the hospital and Secretariat effluents;Sample D - water from the pond; Sample E - water from the exit point of Dandasu pond to Ogunpa River.

Table 3: Concentrations metals in muscle of *Oreochromis niloticus* and *Clarias gariepinus* from Dandasu Reservoir, Ibadan

Fish sample	Metal concentration (µg/g)					
	Mn	**Co**	**Fe**	**Zn**	**Hg**	**Pb**
ON (test)	4.390±0.09[a]	4.152±0.15[a]	62.800±0.59[a]	0.713±0.01[a]	ND	0.120±0.00[a]
ON (control)	0.181±0.00[d]	0.022±0.00[c]	43.201±3.00[c]	0.262±0.00[b]	ND	0.021±0.00[b]
CG (test)	1.060±0.10[b]	3.513±0.10[b]	56.700±1.20[b]	0.690±0.00[a]	ND	0.120±0.00[a]
CG (control)	0.521±0.00[c]	0.011±0.00[c]	41.311±3.40[d]	0.221±0.00[b]	ND	0.020±0.00[b]

Values are the mean of three replicate results. Values of different superscripts within the column are significantly different at $p<0.05$. ON - *Oreochromis niloticus;* CG - *Clarias gariepinus*; ND - Not detectable.

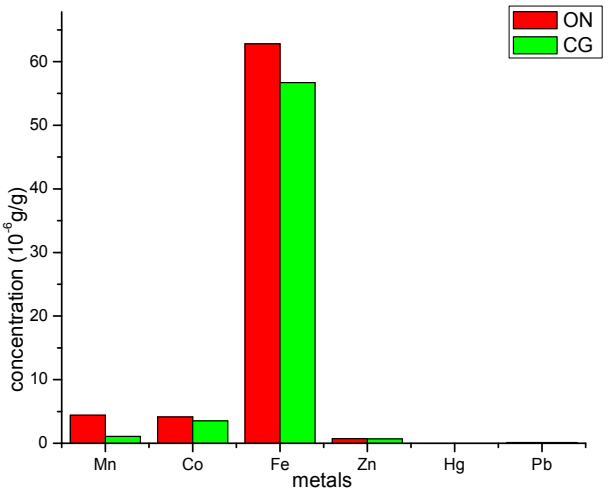

Fig 1: Comparative concentrations of some metals in tissues of *Oreochromis niloticus* (ON) and *Clarias gariepinus* (CG) in Dandasu reservoir, Ibadan, Nigeria

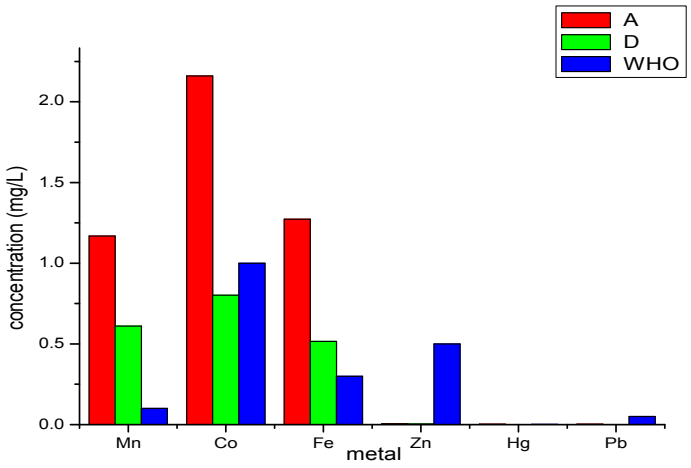

Fig 2: Comparative concentrations of metals present in wastewater from UCH (A), Dandasu reservoir (D), Ibadan (Nigeria) and WHO standards

3.2 Discussions

3.2.1 Water Samples

Manganese (Mn), obtained for all the water samples ranged from 0.610 mg/L to 1.169 mg/L with the hospital waste having the highest concentration and reservoir water having the lowest. The results were found to be significantly different for samples A, B and C at *P>0.05*, while those for D and E were not. Manganese is a mineral that is required in small amounts in the human body to manufacture enzymes necessary for metabolism of proteins and fats. Excessive amount of Mn cause seizure activity, lead to poor bone formation, impair fertility, cause birth defect in human and irreversible brain disease with prominent psychological and neurological disturbances known as manganism (Mergler *et al.*, 1994).

The results for cobalt followed the same trend as that of Mn. Co concentrations in the water samples ranged from 0.604 mg/L to 2.160 mg/L. Cobalt in the hospital effluent is higher than 1.0 mg/L permissible limit of WHO water standard. Cobalt is beneficial to human because it is a part of vitamin B_{12} which is essential for human health. It is used to treat anaemia with pregnant women because it stimulates the production in red blood cell. However, high concentration of cobalt may damage human health.

Iron (Fe) ranged from 0.516 mg/L to 1.272 mg/L with sample A having the highest and sample D with the lowest for all the water samples. All the results were significantly different at *P>0.05*, except for samples B and C. The concentration of Fe in all the water samples is greater than 0.3 mg/L which is the WHO (2004) standard value for Fe in drinking water.

Though Pb and Hg were not detected in the reservoir water, the range of other metals in the samples evaluated are as follows: Zn (0.003-0.005 mg/L), Hg (0.001-0.002 mg/L) and Pb (0.001-0.002). All these concentrations were not significantly different (*p>0.05)* for the samples. The permissible limit of Zn and Pb are 5.0 mg/L and 0.05 mg/L, respectively, according to WHO (2004) which are higher than the values detected in all the water samples. Concentration of mercury in the hospital wastewater and water at the exit of the reservoir is above the permissible limit of WHO (0.001 mg/l), indicating the level of toxicity, as the value was doubled. This shows that the heavy metal is being discharged from the hospital and drained into the reservoir. Mercury can permanently damage the brain, kidneys, and developing fetuses. Increased Hg concentration at the exit of the reservoir could come from wastes dumped into the stream.

Summarily, the selected metals were present in all the water samples, except for sample D, where contaminations from lead and mercury were not detected. Manganese, cobalt, iron, were present in high quantities, while zinc, mercury and lead were present in low concentrations. Cobalt was most present in the hospital effluent, followed by iron and manganese, respectively (figure 2). Both the hospital effluent and reservoir water contained manganese, iron, and mercury in concentrations higher than the limits set by the World Health Organization (figure 2).

3.2.2 Fish Samples

The results of the concentrations of the metals present in the muscle of the two fish species are shown in table 3 and compared in figure 1. These

show that the metals were present in all the fish, except for mercury which was not detected.

Manganese assists in reproduction and normal functioning of the nervous system (Olowoyo *et al.*, 2011). From table 3, *Oreochromis niloticus* contained 4.390 µg/g higher than 1.060 µg/g recorded for *Clarias gariepinus* in the reservoir, while a relatively lower concentrations of 0.18 µg/g, 0.521 µg/g were found, respectively, in their control experiment. The concentrations of the metal in the two fish species for this study were found to be lower than those reported by Olowoyo *et al*. (2011) and Mendil *et al.* (2005), who recorded 13.75 µg/g and a range of 11.1-72.9 µg/g, respectively. There was a significant difference in the metal concentrations found in the test samples (at $p<0.05$).

As low as 0.802 mg/L of cobalt was present in the hospital effluent (table 2), the resident fishes had more than 300% of its increment - *Oreochromis niloticus* (4.152 µg/g) and *Clarias gariepinus* (3.513 µg/g). This values are much higher than that recorded by MAFF (1998). This upsurge of the metal concentration in the fish muscle might not be unconnected with the ability of the two fish species to bioaccumulate the metal in their bodies, even with relatively low concentration of the metal in the resident water, though they might ingest it from their feed too. The control fish species only had between 0.011 µg/g and 0.022 µg/g of the metal.

The muscles of the reservoir fishes bioaccumulated iron than the other selected metals (figure 1). The concentrations of iron in the two fish species from the reservoir were 62.800 µg/g and 56.700 µg/g for *Oreochromis niloticus* and *Clarias gariepinus*, while those for the control experiment were between 41.311 µg/g and 43.201 µg/g with *Oreochromis niloticus* having the higher concentration (table 2). This exceptionally high values for the reservoir fishes could be adduced to pollutions from blood and other medical wastes, rich in iron, that found their ways into them through ingestion and/or bioaccumulation in their muscle, vis-à-vis the proximity of the hospital wastewater to the reservoir. The results confimed that *Oreochromis niloticus* has higher tendency to bioaccummulate the metal (figure 1). Also, the values are ambiguously high when compared with 3.2 µg/g for fish reported by MAFF (1998) and in sharp contrast with other studies by WHO (1993) and UK Ministry of Agriculture, Fisheries and Food (1997). The significant higher concentration of the metal in the two fishes than that found in the reservoir water (table 2) and also in the control fishes underscored bioaccumulation of the metal from their resident water. Iron Provisional Tolerable Daily Intake (PTDI) by JECFA was put at 0.8 mg/Kg body weight per day (WHO, 1983), equivalenght to 48 mg/day for a 60 Kg adult.

Zinc concentrations were 0.713 µg/g for *Oreochromis niloticus* and 0.690 µg/g for *Clarias gariepinus,* while those for control fishes were, respectively, 0.262 µg/g and 0.221 µg/g (table 3). The values are much lower than the general guideline limit of 50 µg/g for zinc in food as recommended by the UK Ministry of Agriculture, Fisheries and Food (1953). Nevertheless, the values are higher than that found in the reservoir water (0.004 mg/L). Zinc is a component of more than fifty enzymes and required in large quantity.

Lead concentrations in the two fish species from the reservoir were the same (0.120 µg/g), while the control samples contained similar lower concentration (approximately, 0.02 µg/g). 0.5 µg/g in fish was the proposed limit for lead by the European Commission (1997). Though lead could not be detected in the reservoir water (table 2), its presence in the fish muscle could be attributed to bioaccumulation over time as the fishes could have ingested the metal ion from their feed or from other source. Higher concentration of lead is known to inhibit active transport mechanisms involving ATP and may also suppress cellular oxidation-reduction reactions and even inhibit protein synthesis.

Mercury was not detectable in the reservoir water and in the fish muscles. Though the metal was present in the hospital wastewater, it could not be leached into the reservoir over distance due to its relatively low concentration.

4. Conclusion

From the results obtained from this study, the concentrations of the metals found in all the water samples are lower than that in the fish species; this may be as a result of bioaccumulation over a long period of time. Except for mercury and lead where the metals were not detected and of same concentration respectively, fish species of *Oreochromis niloticus,* due to their highly scaled body, absorb more of the metals than *Clarias gariepinus* into their muscles. The bioaccumulation of some of the metals in the fish muscles were due to eroded wastewaters from the hospital and Secretariat, containing blood, medical and pharmaceutical materials.

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