Heavy Metals Accumulation and Enzymatic Biomarker in Commercially Important Fish Species (*Hemichromis fasciatus* and *Chrysichthys nigrodigitatus*) at the Landing Site, Bariga, Lagos Lagoon

S.O. Ayoola, A.A. Idowu, O.E. Babalola and M.K. Ademoye

1Department of Marine Sciences, University of Lagos, Lagos State, Nigeria

2Federal University of Agriculture, Abeokuta, Ogun State, Nigeria

Submitted: Dec 1, 2013; Accepted: Jan 4, 2014; Published: Jan 8, 2014

Abstract: Pollution of the aquatic environment is a serious and growing problem. Increasing number and amount of industrial, agricultural and commercial chemicals discharged into the aquatic environment have led to various deleterious effects on the aquatic organisms. Aquatic pollution is a major contributor to oxidative stress in fish resulting from the redox cycling of pollution. Heavy metals level of lead (Pb), cadmium (Cd), iron (Fe), mercury (Hg), chromium (Cr), zinc (Zn) and copper (Cu) were determined in two commercially important fishes (*Hemichromis fasciatus* and *Chrysichthys nigrodigitatus*) from the Bariga landing site, using Atomic Absorption spectrophotometer. Physicochemical parameters were investigated by determining the level of dissolve oxygen (DO), biological oxygen demand (BOD), pH, temperature among others for the water samples. The activities of superoxide dismutase (SOD), Glutathione (GSH) and malondialdehyde (MDA) were also determined. Heavy metals were accumulated in the flesh of the fishes to varying extent. The trend of accumulation of the metals in each fish is as follows: *Hemichromis fasciatus* - Zn>Fe>Cu>Cr>Pb. Hg and Cd were not detected; *Chrysichthys nigrodigitatus* - Zn>Cu>Fe>Cr>Pb. Hg and Cd were not detected. SOD activities in the liver of *Chrysichthys nigrodigitatus*, with the highest concentration of 69.73% and SOD activities in the gill of *Chrysichthys nigrodigitatus*, with highest value of 45.83%. SOD activities in liver of *Hemichromis fasciatus*, with highest concentration of 53.77%. MDA concentration in liver of *Chrysichthys nigrodigitatus*, with highest concentration of 43.7%. While in gill, the highest concentration recorded 36.82%. Concentration of MDA in liver of *Hemichromis fasciatus*, with highest concentration of 37.91%. Furthermore, GSH concentration in the liver of *Chrysichthys nigrodigitatus* with highest concentration of 0.54%. Also in gill, with the highest concentration recorded 0.35%. The result demonstrates that alteration in the antioxidant enzymes and induction of lipid peroxidation reflects the presence of heavy metals which may cause oxidative stress in *Hemichromis fasciatus* and *Chrysichthys nigrodigitatus* from the Lagos Bariga landing site of the Lagos Lagoon. The study therefore, provides a rational use of biomarkers of oxidative stress in biomonitoring of aquatic pollution.

Key words: Heavy Metals - Enzymatic Biomarker Fish - Lagos Lagoon

INTRODUCTION

Over the past few decades, heavy metal contamination of aquatic system has attracted the attention of several investigators both in the developed and developing countries of the world. Many industrial and agricultural processes have contributed to the contamination of fresh water systems thereby causing adverse effects on aquatic biota and human health [1, 2]. Aquatic pollution is a major contributor to oxidative stress in fish resulting from the redox cycling of pollution. In addition, it is known that xenobiotic metabolism causes continuous production of reactive oxygen species (ROS) even without pollution [3]. To cope with the continuous
The generation of ROS from normal aerobic metabolism, cells and tissues contain a series of cellular antioxidants with both enzymatic and non-enzymatic activities [4]. To neutralize toxic effects of ROS on fish, like mammals, possess well-developed antioxidant defense systems [5, 6].

The fact that aquatic organisms can accumulate pollutants such as metals and organic compounds from water are well documented [7]. Bioaccumulation measurements refer to studies or methods monitoring the uptake and retention of pollutants like metals or biocides by organisms such as fish [8]. The accumulation of metals in an organism’s body can take place, if the rate of uptake by the organism exceeds the rate of elimination [9].

Industrial development in the developing and developed countries has resulted in heavy metal contamination of local waters. Metal pollution may damage marine organisms at the cellular level and possibly affect the ecological balance. Exposure and ingestion of polluted marine organisms as sea foods can cause health problems in people and animals including neurological and reproductive problems [10].

Pollutants enter fish through a number of routes: via skin, gills, oral consumption of water, food and non-food particles. On absorption, pollutants are transported in the blood stream to either a storage point (i.e. bone) or to the liver for transformation and/or storage [8].

The tremendous increase in the use of heavy metals in cosmetic, detergent and textile industries located near the river over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment [11]. The metals are of special concern because of their diversified effect and the range of concentration stimulated toxic ill effect to the aquatic life forms. Industrial wastes constitute the major source of metal pollution in natural water [12]. Aquatic systems are exposed to a number of pollutants that are mainly released from effluents discharged from industries, sewage treatment plants and drainage from urban and agricultural areas. These pollutants cause serious damage to aquatic life [13, 14].

Metals, especially heavy metals, are important contaminants of aquatic environments worldwide. Metal pollution has increased with the technological progress of human society. Industry, mining, advanced agriculture, household waste and motor traffic is all among the activities considered to be major sources of metal pollution. Metals can accumulate in aquatic organisms, including fish and persist in water and sediments [15]. Metals are natural components of the aquatic environment, but their levels have increased due to anthropogenic activities [13]. Essential trace elements that exist naturally at background levels in the environment include chromium, cobalt, copper, iron, manganese, molybdenum, vanadium, strontium and zinc. However, non-essential heavy metals such as mercury, cadmium, arsenic, thallium and lead are toxic and tend to accumulate in living organisms [16].

Cellular antioxidant defense systems in biological systems are impaired when exposed to environmental pollutants, but the levels of antioxidants in living organisms can increase in order to restore the imbalance caused by oxidative damage. Levels of antioxidant enzymes can be used as an indicator of the antioxidant status of the organism and can serve as biomarkers of oxidative stress [12]. When antioxidant defences are impaired or overcome, oxidative stress may produce DNA damage, enzymatic inactivation and peroxidation of cell constituents, especially lipid peroxidation [17]. Toxicity biomarkers, such as malondialdehyde (MDA), have been also proposed to reflect the oxidative status of exposed species [18]. MDA is used as marker of oxidation of membrane phospholipids through lipid peroxidation. An increase in MDA levels in organisms can be related to degradation of an environmental site by decreasing the water quality [19]. The level of antioxidant enzymes have been extensively used as an early warning indicator of lake pollution [20]. Fish have been proposed as indicators for monitoring land-based pollution because they may concentrate indicative pollutants in their tissue, directly from water through respiration and also through their diet. Fish are frequently subjected to peroxidant effects of different pollutants often present in the aquatic environment [21].

The fact that heavy metals cannot be destroyed through biological degradation and have the ability to accumulate in the environment make these toxicants deleterious to the aquatic environment and consequently to humans who depend on aquatic products as sources of food. Heavy metals can accumulate in the tissues of aquatic animals and as such tissue concentrations of heavy metals can be of public health concern to both animals and humans [22, 23].

Fish are largely being used for the assessment of the quality of aquatic environment and as such can serve as bioindicators of environmental pollution [2, 24]. Heavy metals accumulated in the tissues of fish may catalyze reactions that generate reactive oxygen species (ROS) which may lead to environmental oxidative stress. Arabatizis and Kokkinakis [25] observed that lagoon systems are places of great biological importance where fishery is the main economic activity but intensive
agriculture, industry and tourism have degraded their sensitive environmental structure.

Research over time has focused on various species and various biomarkers to determine the amount of heavy metal toxicity in aquatic environments without also ascertaining the enzymatic biomarkers. There has been paucity of information of heavy metal accumulations and enzymatic biomarker in Lagos lagoon.

Therefore this project is focused on estimating the heavy metal accumulation and enzymatic biomarker in two commercial fishes at the Bariga landing site of the Lagos lagoon.

MATERIAL AND METHODS

Description of Study Site: The Bariga Landing site of the Lagos lagoon is a well commercialized environment known for its fishing activities and sales. The GPS coordinate of the sampling site is 6° 31'29"E and 3° 23'58"N aligned with the Lagos lagoon. The Lagos lagoon is part of the continuous system of lagoons and creeks that are found along the coast of Nigeria from the border with the Republic of Benin to Niger-Delta. This lagoon bordering the Lagos Island is located between longitude 3°10' and 3°45' E and 6°15’N and 6°36’.N. It stretches for about 257 km from Cotonon in the Republic of Benin to the Western edge of the Niger-Delta. The lagoon boarders the forest belt and receives input from a number of important large rivers draining more than 103,626 km of the country [26].

Experimental Set-up: Adult commercially important fishes with mean weight (163.70 ± 3.71) g and mean total lengths (27.23 ± 0.19 cm) were purchased from Bariga landing site of the Lagos lagoon Nigeria. They were transported in a well ventilated container containing the same water obtained from the landing site where the fishes were caught and transported to the laboratory. The fishes were caught in different month of May-July.

Heavy Metals

The Measurement of Heavy Metals: The determination of the heavy metals in the fish tissue was with the aid of using the Atomic Absorption Spectrometer (AAS). (Lead (Pb), Cadmium (Cd), Iron (Fe), Mercury (Hg), Chromium (Cr), Zinc (Zn) and Copper (Cu)). 5g of dried fish tissue sample is to be digested with Nitric acid (10ml), the sample is then heated until the brown fumes disappear. Allow the sample to cool, add distilled water and make up to 50ml in a standard volumetric flask. Filter off the filtrate and analyze the filtrate using the Atomic Absorption spectrometer. Analyze 200 Perkin Elmer AAS.

Biochemical Parameters

Malondialdehyde (MDA): Lipid peroxidation as evidence by the formation of Thiobarbituric acid reactive substances (TBARS) were measured by the method of Jiang et al., (1992). 0.1ml of tissue homogenate was treated with 2ml of (1:1:1 ratio) TBA-TCA-HCL reagent (thiobarbituric acid 0.37%, 0.25N HCl and 15% TCA) and placed in water bath for 15min, cooled and centrifuged at room temperature for 10min at 3,000 rmp. The absorbance of clear supernatant was measured against reference blank at 535nm.

Enzymes Activity Assays

Superoxide Dismutase (SOD): Superoxide dismutase activity was determined by measuring the inhibition of auto-oxidation of epinephrine at pH 10.2 at 30°C. One unit of SOD activity is the amount of SOD necessary to cause 50% inhibition of epinephrine auto-oxidation. The assay was performed in 3.0ml of 50m NaCO3 buffer to which 0.02ml of the sample was added and 0.03ml of the epinephrine stock solution was then added to the above before taking absorbance readings at 480nm for 3-5min.

Estimation of Reduced Glutathione: Glutathione peroxidase (GSH reduced) was determined by the method of Ellman, (1959). To the homogenate 10% TCA was added, Centrifuged. 1.0ml of the supernatant was treated with 0.5ml of Ellman’s reagent (19.8mg of 5,5-dithiobismitrobenzoic acid (DTNB) in 100ml of 0.1% Sodium nitrate) and 3.0ml of phosphate buffer (2.0m pH 8.0). The absorbance was read at 412nm.

Statistical Analysis: The means and standard error of means as well as one-way analysis of variance (ANOVA) for statistical significance (P < 0.05) was determined using Duncan Multiple Range Test while error bars were created using Microsoft® Office Excel programme and SPSS 18 windows.

RESULT

The Physico-chemical parameters at the Bariga landing site used for this study are represented in figure 1. The Bariga landing site water for pH has a mean range of 7.0±0.1 to 7.2±0.1 and this result was observed to be within FEPA limit of 6-9. The temperature values ranged from 24.0 to 25°C which falls within the guideline of FEPA limits.
Table 1: Heavy metal in the fish tissue caught at the Bariga landing site of the Lagos lagoon

<table>
<thead>
<tr>
<th>FISH SAMPLE</th>
<th>Pb</th>
<th>Cd</th>
<th>Fe</th>
<th>Hg</th>
<th>Cr</th>
<th>Zn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrysichthys nigrodigitatus</td>
<td>0.003±0.0</td>
<td>0</td>
<td>0.07±0.01</td>
<td>0</td>
<td>0.04±0.03</td>
<td>42.37±0.12</td>
<td>0.17±0.13</td>
</tr>
<tr>
<td>Hemichromis fasciatus</td>
<td>0</td>
<td>17.92±0.89</td>
<td>0.06±0.00</td>
<td>0.003±0.0</td>
<td>0.17±0.14</td>
<td>0.09±0.00</td>
<td>0.03±0.025</td>
</tr>
</tbody>
</table>

Footnote: The Mean of superscript on the same row are significantly different (p<0.05)

Table 2: Enzymatic biomarker of fish species caught at the Bariga landing site

<table>
<thead>
<tr>
<th>Hemicromis fasciatus (ENZYMATIC BIOMARKER IN LIVER) PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSH</td>
</tr>
<tr>
<td>CONTROL</td>
</tr>
<tr>
<td>MAY</td>
</tr>
<tr>
<td>JUNE</td>
</tr>
<tr>
<td>JULY</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hemicromis fasciatus (ENZYMATIC BIOMARKER IN GILL) PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSH</td>
</tr>
<tr>
<td>CONTROL</td>
</tr>
<tr>
<td>MAY</td>
</tr>
<tr>
<td>JUNE</td>
</tr>
<tr>
<td>JULY</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chrysichthys nigrodigitatus (ENZYMATIC BIOMARKER IN LIVER) PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSH</td>
</tr>
<tr>
<td>MAY</td>
</tr>
<tr>
<td>JUNE</td>
</tr>
<tr>
<td>JULY</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chrysichthys nigrodigitatus (ENZYMATIC BIOMARKER IN GILL) PARAMETER</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSH</td>
</tr>
<tr>
<td>MAY</td>
</tr>
<tr>
<td>JUNE</td>
</tr>
<tr>
<td>JULY</td>
</tr>
</tbody>
</table>
The mean value range of Dissolved oxygen ranged from 1.60 to 1.70mg/L and BOD with a mean range of 89 to 123mg/l. There is no significant difference (P > 0.05) between temperature, pH, DO and BOD.

**Heavy Metals:** The determination of the heavy metals in the fish tissue was with the aid of Atomic Absorption Spectrometer (AAS) and are presented in Table 1.

Mean range value for *Hemichromis fasciatus* was 0mg/L to 0.28mg/L for Iron and 0mg/l to 0.20mg/L for *Chrysichthys nigrodigitatus*. Copper recorded a mean range value of 0.01 to 0.19mg/L in *H. fasciatus* and 0.02 to 0.43mg/L in *C. nigrodigitatus*. While Zinc recorded highest among the heavy metals with a mean range value of 0.08 to 53.70mg/L in *H. fasciatus* and 0.05 to 126.60mg/L in *C. nigrodigitatus*.

The correlation coefficient value of the heavy metals showed a significant difference (P<0.05) between Copper (Cu) in the tissues of *Hemichromis fasciatus* and Chromium (Cr) in the tissues of *Hemichromis fasciatus* with 0.998*. While Copper (Cu) in the tissues of *Chrysichthys nigrodigitatus* and Chromium (Cr) in the tissues of *Hemichromis fasciatus* with 0.999* showed a significant difference (P<0.05).

The general heavy metal of both *Hemichromis fasciatus* and *Chrysichthys nigrodigitatus* showed that there is no significant difference (P>0.05) using ANOVA (DMRT).

**Enzymatic Biomarker:** The results of enzymatic biomarker in gill and liver of two commercially important fish species in Lagos lagoon, Bariga landing site are presented in Table 2.

**Biochemical Parameters**

**Malondialdehyde-(MDA) (nmol/mg):** The mean MDA in the liver of *Hemichromis fasciatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 13.99 to 43.70nmol/mg (Table 2). The analysis of variance (ANOVA) results of the lipid peroxidation assay indicates that the level of MDA in the liver of the fish at the landing site shows a significant difference (P < 0.05).

The mean MDA in the liver of *Chrysichthys nigrodigitatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 32.38 to 43.97nmol/mg (Table 2). The analysis of variance (ANOVA) results of the lipid peroxidation assay indicates that the level of MDA in the gill of the fish at the landing site shows a significant difference (P < 0.05).

**Superoxide Dismutase-(SOD) (U/mg):** The mean superoxide dismutase SOD in the liver of *Hemichromis fasciatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 8.63 to 29.18 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the superoxide dismutase content of *Hemichromis fasciatus* liver at different months (May-July).

The mean superoxide dismutase SOD in the gill of *Hemichromis fasciatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 11.84 to 53.77 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the superoxide dismutase content of *Hemichromis fasciatus* gill at different months (May-July).

The mean superoxide dismutase SOD in the liver of *Chrysichthys nigrodigitatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 15.83 to 69.73 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the superoxide dismutase content of *Hemichromis fasciatus* liver to all different months.

The mean superoxide dismutase SOD in the gill of *Chrysichthys nigrodigitatus* caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 13.94 to 45.83 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the superoxide dismutase content of *Hemichromis fasciatus* gill at different months (May-July).
Estimation of Reduced Glutathione (GSH): The mean Estimation of Reduced Glutathione (GSH) in the liver of Hemichromis fasciatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.10 to 0.54 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the Estimation of Reduced Glutathione content of Hemichromis fasciatus liver at all different months(May-July).

The mean Estimation of Glutathione (GSH) in the gill of Hemichromis fasciatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.10 to 0.54 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the Estimation of Reduced Glutathione content of Hemichromis fasciatus gill at different months (May-July).

The mean Estimation of Reduced Glutathione (GSH) in the liver of Chrysichthys nigrodigitatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.06 to 0.34 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the Estimation of Reduced Glutathione content of Chrysichthys nigrodigitatus liver at different months(May-July).

The mean Estimation of Reduced Glutathione (GSH) in the gill of Chrysichthys nigrodigitatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.06 to 0.34 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the Estimation of Reduced Glutathione content of Chrysichthys nigrodigitatus gill at different months (May-July).

Total Protein: The mean total protein in the liver of Hemichromis fasciatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.06 to 0.34 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the total protein content of Hemichromis fasciatus liver at different months (May-July).

The mean total protein in the gill of Hemichromis fasciatus caught at the Bariga landing site of the Lagos lagoon at different months (May-July) ranged from 0.06 to 0.34 U/mg (Table 2). Furthermore, Post hoc using (Duncan Multiple Ranged Test) DMRT revealed that there is a significant difference (P < 0.05) observed in the total protein content of Hemichromis fasciatus gill at different months (May-July).

DISCUSSION

As rain increases from May to July concentration of heavy metals become reduced this is a result of dilution of the Lagoon water by gradual increase in trend of heavy down pour from May to July 2012. This can be noted by low tide in early May and gradual increase in level of water till high tide in July.

As trend of rain increases it dilute the polluted Lagoon water which reflect in the concentration of the heavy metals in Chrysichthys nigrodigitatus and Hemichromis fasciatus at Bariga landing site, Lagos Lagoon indicate that the Lagoon is polluted.

The levels of heavy metals as biomarkers of oxidative stress were evaluated in, Chrysichthys nigrodigitatus and Hemichromis fasciatus from the Bariga landing site of the Lagos lagoon. From this result, copper and chromium and zinc were highly accumulated in the flesh of Chrysichthys nigrodigitatus and Hemichromis fasciatus from the Lagoon, the high level of accumulation for copper in Chrysichthys nigrodigitatus suggest that the Lagoon has high concentration of these metals or the fish species have poor digestive mechanism for digesting and eliminating this metal and may provide good monitoring levels of copper pollution and it is in accordance with the findings of [27]. Chrysichthys nigrodigitatus has higher concentration of all the metals in all the month compared to Hemichromis fasciatus except for Fe in the month of July as indicated in the result which shows that...
chrysichthys has lower digestibility of heavy metals or means of eliminating this metal compared to *Hemichromis fasciatus*.

The water quality parameters measured were Temperature which has a mean of 24.5±0.5, Dissolved oxygen 1.65±0.05; Biological oxygen demand 106±17.0 and pH 7.1±0.1. The BOD increases while DO decreases and temperature increases. The water was slightly alkaline.

Metal are reported to be well concentrated in the water [28] and sediments. Bioaccumulation of these metals in many fish species and their organs have been variously reported by [29,30,31,32]. These metals in trace amount may play important role in the biochemical life process of the fish, some as enzyme co-factor. However, their sublethal concentrations become lethal to fish or other aquatic organisms when the duration of exposure to these metals is prolonged [33].

There was a strong correlation of the heavy metals observed in the tissues of the fishes using a paired T-test analysis which indicates that there is a significant difference (P<0.05) between Pb in *Hemichromis fasciatus* and Pb in *Chrysichthyes nigrodigitatus*; Zn in *Hemichromis fasciatus* and Zn in *Chrysichthyes nigrodigitatus*; Fe in Hemichromis fascitus and Fe in *Chrysichthyes nigrodigitatus*; Cr in *Hemichromis fascitus* and Cr in chrysichthies nigrodigitatus except Cu in *Hemichromis fasciatus* and Cu in *Chrysichthies nigrodigitatus* were there is no significant difference (P>0.05) but was strongly correlated (r = 0.993*).

Iron (Fe) is an important metal in both plants and animals, especially in the cellular processes. The insoluble Fe³⁺ is reduced to soluble Fe²⁺ water by bacterial action. Fe is found in natural fresh- and groundwater, but have no health-based guideline value, although high concentrations give rise to consumer complaints due to its ability to discoulour aerobic waters at concentrations above 0.3 mg/l [34].

Zinc(Zn) is present in large amount in Lagos lagoon water and followed by Cu in terms of concentrations as it was revealed in my result. The relatively high Zn level is suggestive of the influence of refuse dump and domestic sewage sources. It could also be attributed to industrial effluents. The level of concentrations of Zn in this study is not significantly different across the stations (Table 1). This suggests the intense anthropogenic influence due to industrialization and urbanization within the catchments of the lagoon.

Zinc(Zn) is an enzyme co-factor in several enzyme systems including carbonic anhydrase found in red blood cells. Chance of being poisoned with Zn is rare because salts of alkaline earth element reduce toxicity of Zn. High temperature and low dissolved oxygen concentration lead to increase in toxicity of Zn. Its toxicity to fish according to Everall et al., [33] can be greatly influenced by both water hardness and pH. It is one of the earliest known trace metals and a common environmental pollutant, which is widely distributed in the aquatic environment. Studies have also shown that it could be toxic to some aquatic organisms such as fish.

Chromium(Cr) oxidizes easily from trivalent to hexavalent. Cr⁶⁺ ion and is not toxic, but an essential nutrient, but Cr⁴⁺ ion is very toxic and damages adrenals, livers and lungs. Exposure of man to high concentration of Cr⁶⁺ may cause dermatitis, ulcer, destruction of mucus of nose and cancer of the stomachs. The major source of Cr in water is via industrial effluents.

A probable source of Pb to aquatic environment could be from used dry-cell batteries and tyres from dump sites. Absence of dry cell battery manufacturing industry from catchment areas of the lagoon might probably be responsible for non-detectable level of Pb in water from Lagos lagoon.

Significant decrease in total protein content indicates that, stress due to effluent treatment induces proteolysis. Stress has been reported to accelerate protein metabolism in man and animals. Protein decrease may be due to stress in fish as protein is likely to undergo hydrolysis and oxidation through TCA cycle to meet the increased demand for energy caused by the stress [18]. Toxicants at lower levels given for a prolonged time cause severe damage to the branchial system of fish than short term treatment [35].

The mean of MDA showed that there is no significant difference (P > 0.05) but has variability in values through different concentrations exposed to test organisms. The activity of antioxidant enzymes may be enhanced or inhibited under chemical stress depending on the intensity and the duration of the stress applied, as well as, the susceptibility of the exposed species.

The GSH, MDA, SOD and TP showed a significant difference (P<0.05) in the liver of both fishes alongside the gills. This is an indication that the Bariga landing site of the Lagos lagoon is polluted.

The activities of SOD and the redox sensitive compound GSH were elevated in the liver and for SOD; it was reduced in the gills. The accumulation of heavy metals might have led to the production of superoxide radical of H₂O₂. SOD catalytically scavenges superoxide radical, toxicity of oxygen and this provides a defense against this aspect of oxygen toxicity [36]. GSH is known
to be a substrate for the activity of GST. The apparent increase in GSH levels in the organs suggests an adaptive and protective role of this biomolecule against oxidative stress induced by the heavy metals. This result is in agreement with the findings of [6] on wallago attu fish from the Panipal River in India.

CONCLUSION

The average concentrations of metals in the tissues of the fishes (Hemichromis fasciatus and Chrysichthys nigrodigitatus) according to [33,7] Cu 1-3.0, Cd 2.0, Pb 2.0, Zn 1000, Fe 0.2-0.3 were within limits except Iron (Fe) which was higher in Hemichromis fasciatus. While, the enzymatic biomarkers in both liver and gills indicated that the water body is polluted because there was a significant difference which existed amongst all parameters. Therefore, the Bariga landing site of the Lagos lagoon is found to be polluted from this study.

REFERENCES


