Ethiopian Journal of Environmental Studies & Management 15(4): 474 – 485, 2022
ISSN:1998-0507 doi: https://ejesm.org/doi/v15i4.6
Submitted: May 11, 2022 Accepted: August 4, 2022

HEAVY METALS CONCENTRATION AND ENZYMATIC BIOMARKER OF TWO COMMERCIALLY IMPORTANT CICHLID SPECIES (*Sarotherodon melanotheron* AND *Tilapia guineensis*) FROM THE MAHIN LAGOON, SOUTH WESTERN, NIGERIA

***LOTO, O.O.,[1] SAMUEL, O.B.[2] AND CHUKWU, L.O.[2]**
[1]Department of Fisheries and Aquaculture Technology, Olusegun Agagu University of Science and Technology Okitipupa, Nigeria
[2] Department of Marine Sciences, Faculty of Science, University of Lagos, Nigeria
*Corresponding author: jide.loto@gmail.com

Abstract
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. This study aimed to evaluate heavy metal concentrations and enzymatic biomarker of two fish species (Sarotherodon melanotheron and Tilapia guineensis) from the Mahin Lagoon, Ondo State, Nigeria. Heavy metals (Zinc, Lead, Cupper, Chromium, Cadmium, Nickel and Cobalt) in fish tissues were analysed with GBC Savant AA Sigma flame atomic Absorption Spectrometer (AAS). Antioxidant enzyme (catalase (CAT), superoxide dismutase (SOD), glutathione (GSH), Glutathione-S-Transferase (GST)) activities were evaluated in the livers of both fish species using standard methods. Observed mean level of heavy metals was in the order Zn > Fe > Cu > Ni > Cr > Cd > Co > Pb. When compared with the World Health organization (WHO) limit, the heavy metals were higher in all tested fish samples. There was significant difference ($p>0.05$) in the activities of the antioxidant enzymes across stations and seasons. Elevation in the activities of SOD and GST were observed. While the activities of CAT and GSH were observed to be inhibited. This study provides evidence that enzymatic biomarkers of oxidative stress can be sensitive indicators and biomarker of aquatic pollution.

Key Words: *Pollution, health risk, Food safety and security, Biomarker, Heavy metals*

Introduction

Aquatic environment is subject to different types of pollutants which enter into the water bodies via industrial, domestic and agricultural waste waters and severely affect the aquatic biota (Cappella, 2018). The major sources of pollution of lagoon are land-based. These land–based sources of pollution may reach the lagoon through creeks, rivers, drainages, ditches, shallow pits, as run-off and the direct dumping of wastes (Onyema *et al.,* 2003). The series of contamination may vary between organic pollutants such as polycyclic aromatic hydrocarbons from oil explorative

activities, resin acids, and heavy metals from industries and also akylphenols deriving from domestic activities (Chindah, 2004).

Heavy metals are non-biodegradable, they persist and accumulate in the environment and become deleterious to the aquatic ecosystem and consequently to humans who depend on aquatic products as sources of food (Kalay *et al*., 1999). Heavy metals can accumulate in the tissues of aquatic biota and as such tissue concentrations of heavy metals can be of public health concern to both animals and humans (Farombi *et al*., 2007; Loto *et al*., 2021).

The release of chemicals into the aquatic environment also brings about some changes, which may pose a great threat to the functional attributes, the integrity and existence of aquatic organisms, especially fish (Chindah and Hart, 2000). Enzymatic biomarkers have become promising biomarkers in measuring the effects of chemical pollutants in fish. They are good sensitive biochemical indicators of pollution, as they give early warning signal before hazardous effects occur in fish. Changes in Enzymes activities in fish have been used frequently as indicators of water pollution and intoxication (Kim *et al.,* 2008; Ayoola *et al*., 2014).

The accumulation of heavy metals can result in the rapid elevation of reactive oxygen species (ROS) in fish by producing free radicals such as the hydroxyl radical (OH^-), proxy radical (RO_2^-) and superoxide (O_2^-) and some non-radical such as hydrogen peroxide (H_2O_2), which could lead to the induction of enzymatic antioxidants (superoxide dismutase (SOD), catalase (CAT) and Glutathione-S-Transferase (GST)) and non-enzymatic antioxidant glutathione (GSH) (Khalil *et al*., 2017). These antioxidants scavenge free radicals and provide protection against this aspect of oxygen toxicity (Kadar *et al.*, 2005).

Fish are used to monitor land-based pollution in water. They serve as indicators because through their diet as well as respiration, they may bio-concentrate pollutants directly from water. Velkova-Jordanoska *et al.* (2008) reported that fish are often under the influence of pro-oxidant effects of different pollutants being present in the aquatic environment. *Sarotherodon melanotheron* and *Tilapia guineensis* were chosen in this present study due to their all year availability and sensitivity to environmental changes. Therefore, this study aimed to investigate the level of heavy metal concentration and activities of antioxidative enzymes in fish as biochemical indicator of aquatic pollution,

Materials and Method

Study Area

The Mahin Lagoon is one of the Lagos lagoon complex or system. It is located within the Ilaje Local Government Area of Ondo state, Nigeria. It lies between Latitude 6.175989 °N – 6.206869 °N and Longitude 4.810944 °E – 4.823770 °E (Figure 1). It is approximately 2.3 km, and at a distance of 9 km from the Atlantic Ocean (Akinrinade *et al*., 2016). The lagoon is famous as a fishing hub. Communities are sited around it for economic purposes, and a section of it serve as transportation route from Igbokoda to communities on the coastline.

Mahin Lagoon represents a mixed and dynamic ecosystem, considering its proximity to the ocean and associated tidal influences. It is fed by the adjoining creeks

connected to a 29 km long river channel which drains to the sea. The western flank of the lagoon used to be the major transportation route from Igbokoda to the coastal communities (Akinrinade *et al*., 2016). Due to oil exploration activities and urbanization as well as continuous industrial and agricultural growth in Ondo State, Nigeria, the coastal water has been heavily impacted by a number of pollutants originating from different sources including oil exploitation, direct discharges of domestic and industrial wastes, urban and agricultural runoff, discharges from ships or hydrological, and atmospheric process (Abdus-Salam *et al*., 2010). In the course of the research, Four (4) sampling stations were taken within the lagoon. The sampling stations were selected to incorporate sites with fishing activities, anthropogenic impacts, and accessibility.

Collection and Identification of Samples

Two commercially important fish species (*Sarotherodon melanotheron* and *Tilapia guineensis*) were used for this study. Fishes were collected bimonthly (once in every two months) from each study area for four (4) seasons (24 months), between June 2019 and May 2021. The fishes were caught using cast net. They were identified *in situ* according to Olaosebikan and Raji (2013), and transported to the laboratory in an ice-chest for necessary analysis.

Determination of Heavy Metals

Concentrations of Cu, Hg, Pb and Zn in the fish tissues were determined using a standard scientific model of flame atomic absorption spectrophotometer (FAAS) according to Zhang *et al.* (2007).

Enzymes Activity Assays

Fish were carefully dissected on ice, to remove the liver. After dissection, the fish livers were washed with isotonic saline, dried using filter paper and quickly homogenized in ice-cold 50 mM phosphate buffer, 1% Triton X100 (pH 7.4) to give a 10% homogenate. Then centrifuged at 6,000 xg in cooling centrifuge at 4°C for 15 min, the supernatant was saved for immediate assay of enzymes activity in the liver.

Catalase Activity (CAT)

CAT activity was assayed by a UV spectrophotometer according to Xu et al. (1997). 10 mL of sample was added to 3.0 mL of H_2O_2 phosphate buffer, pH 7.0 (0.16 mL of 30% H_2O_2 to 100 mL of 0.067 M phosphate buffer), at 25C, and the change in H_2O_2 absorbance in 60s was measured with a UV-220 spectrophotometer at 250 nm. One unit of enzyme activity was defined as the amount of enzyme per protein milligram which resolved half of the concentration of H_2O_2 in 100s.

Superoxide Dismutase (SOD)

SOD activity was determined by measuring the inhibition of the auto-oxidant of pyrogallol using a modification of the method of Magwere *et al*. (1997). 30 µL of sample was assayed in a solution of 8.7 mL of 50 mM phosphate buffer, and 0.3 mL of 3 mM pyrogallol (dissolved in 10 mM HCl), pH 8.24, at 25C. The rate of pyrogallol auto-oxidation was measured with a UV-220 spectrophotometer at 325 nm. One unit of enzyme activity was defined as the amount of the enzyme which gave 50% inhibition of the auto – oxidation rate of 0.1 mM pyrogallol in 1 mL of solution.

Glutathione-S-Transferase (GST)

GST activity was measured according to Habig *et al*. (1974). Assays were performed in a reaction mixture containing 100 mM tris buffer (pH 7.4), 1

mM GSH and tissue homogenate. Before use, GSH was dissolved in tris buffer and 1-chloro-2,4-dinitrobenzene (CDNB) dissolved in ethanol. In all cases, the final concentration of ethanol in the assay mixture did not exceed 5% (vyv). Blanks were achieved under the same conditions, but replacing the sample with tris buffer. Enzyme activity was determined by monitoring changes in absorbency at 340 nm for 2 min at constant temperature and expressed as μmol min $^{-1}$ mg $^{-1}$ protein at 25^{o}C.

Glutathione (GSH)

The reduced glutathione content of the liver was estimated according to the method described by Jollow *et al.* (1974). To the tissue homogenate, 10% TCA was added, centrifuged. 1.0ml of supernatant was treated with 0.5ml of Ellman's reagent (19.8mg of 5, 5-dithiobisnitro benzoic acid (DTNB) in 100ml of 0.1% sodium nitrate) and 3.0ml of phosphate buffer (0.2M, pH 8.0). The absorbance was read at 412nm.

Data Analysis

The concentration of heavy metals obtained in this study was subjected to descriptive statistics to determine the means and standard deviations using SPSS 20.0. The significant difference in concentration of different parameters were evaluated with the use of Multi-vitiate Analysis of Variance (MANOVA), Duncan Multiple range test (DMRT) and T-test, using Excel and Statistical Package for Social Science (SPSS) 20.0 software. A probability level of less than 0.05 was considered significant. Standard deviations were also estimated. Descriptive analysis was used to present table and figures.

Results

The mean concentrations of the selected heavy metals in the liver of *S. melanotheron* and *T. guineensis* are presented in table (1). In dry season, the mean concentration of Zn, Pb, Fe, Cu, Cr, Cd, Ni and Co in *S. melanotheron* were Zn (12.47mg/kg), Pb (0.30 mg/kg), Fe (12.53 mg/kg), Cu (1.50mg/kg), Cr (0.21mg/l), Cd (0.23mg/kg) Ni (0.34mg/kg) and Co (0.39mg/kg) while in wet season, and ranged between Zn (17.91mg/kg), Pb(0.21mg/kg), Fe (17.01mg/kg), Cu (2.36mg/kg), Cr (0.24mg/kg), Cd (0.22mg/kg) Ni (0.58mg/kg) and Co (0.68mg/kg) in dry season respectively. For *T. guineensis*, the mean concentration of heavy metals are Zn (12.57mg/kg), Pb (0.40 mg/kg), Fe (12.63 mg/kg), Cu (1.60mg/kg), Cr (0.31mg/kg), Cd (0.33mg/kg) Ni (0.44mg/kg) and Co (0.49mg/kg) in wet season, and dry season the concentration are: Zn (18.11mg/kg), Pb(0.41mg/kg), Fe (17.21mg/kg), Cu (2.56mg/kg), Cr (0.44mg/kg), Cd (0.42mg/kg) Ni (0.77mg/kg) and Co (0.88mg/kg) All the observed concentrations were above the Federal Environmental Protection Agency (FEPA, 2003) and World Health Organization (WHO, 2003) permissible limits for fish in the aquatic medium and as food respectively.

Table 1: Mean concentration of heavy metals in *S. melanotheron* and *T. guineensis* from Mahin lagoon

Parameters	*S. melanotheron*		*T. guineensis*	
	Dry	Wet	Dry	Wet
Zn	12.47±6.29 [a]	17.91±5.57 [b]	12.57±6.29 [a]	18.11±5.57 [b]
Pb	0.30±0.20 [b]	0.21±0.09 [a]	0.40±0.20 [a]	0.41±0.09 [a]
Fe	12.53±5.47 [a]	17.01±5.48 [b]	12.63±5.47 [a]	17.21±5.48 [b]
Cu	1.50±1.12 [a]	2.36±1.37 [b]	1.60±1.12 [a]	2.56±1.37 [b]
Cr	0.21±0.10 [a]	0.24±0.18 [a]	0.31±0.10 [a]	0.44±0.18 [b]
Cd	0.23±0.10 [a]	0.22±0.08 [a]	0.33±0.10 [a]	0.42±0.08 [b]
Ni	0.34±0,17 [a]	0.58±0.28 [b]	0.44±0.17 [a]	0.77±0.28 [b]
Co	0.39±0.20 [a]	0.68±0.30 [b]	0.49±0.20 [a]	0.88±0.30 [b]

Mean value with same superscripts along the rows were not significantly different (p>0.05).

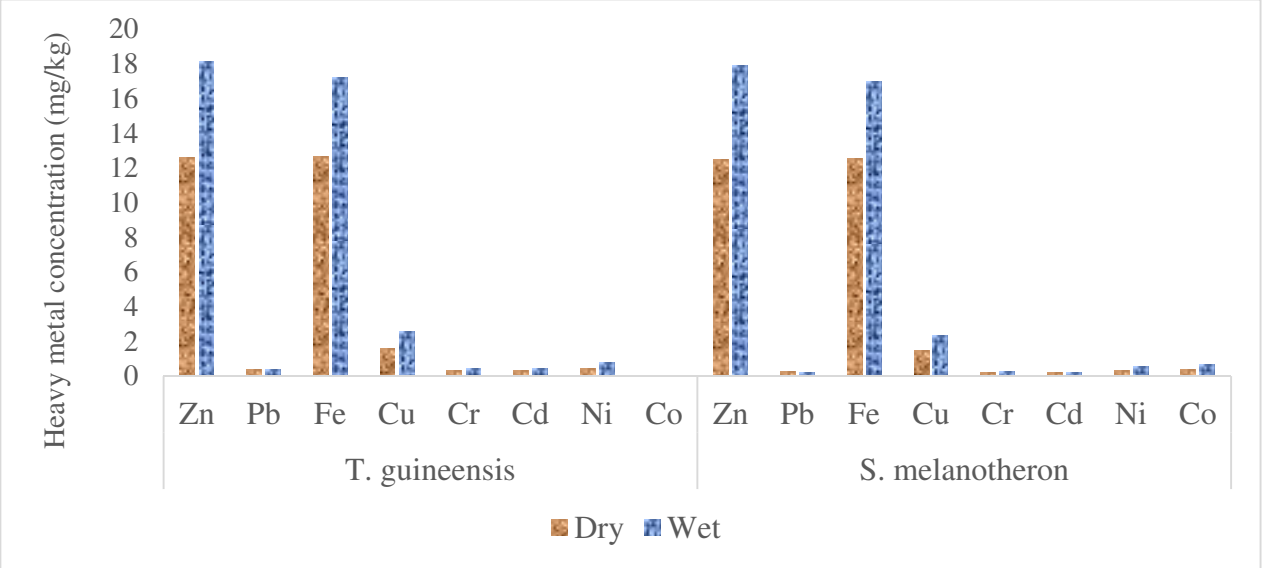

Fig. 1: Mean variation of heavy metal concentrations in S. melanotheron and T. guineensis from Mahin lagoon.

Enzymatic Biomarker

The results of enzymatic biomarker in the liver of two commercially important fish species (*Sarotherodon melanotheron* and *Tilapia guinensis*) in Mahin lagoon, are presented in tables 2 and 3 respectively.

Catalase

The mean values of Catalase (CAT) level in *Sarotherodon melanotheron* and *Tilapia guinensis* collected from Mahin lagoon for this study were presented in tables 2 and 3 respectively. In wet season, the mean value of CAT in *S. melanotheron* ranged from 2.34±1.79µmol/mg to 3.34±1.93µmol/mg and that *T. guinensis* ranged from 2.77±2.00µmol/mg to 3.21±1.90µmol/mg. In dry season the mean value of CAT in *S. melanotheron* ranged from 3.03±2010µmol/mg to

3.58±1.97µmol/mg and that of *T. guinensis* ranged from 3.51±1.88µmol/mg to 3.84±2.18µmol/mg. Analysis of variance (ANOVA) showed that there was no significant difference (p>0.05) in CAT activities in the livers of *S. melanotheron and T. guinensis* between stations and seasons in Mahin lagoon.

Superoxide Dismutase

The mean values of Superoxide Dismutase (SOD) level in *Sarotherodon melanotheron* and *Tilapia guinensis* collected from Mahin lagoon for this study were presented in tables 22 and 23 respectively. In wet season, the mean value of SOD in *S. melanotheron* ranged from 179±38.45µmol/mg to 201.66±14.4µmol/mg and that *T. guinensis* ranged from 158.14±25.57µmol/mg to 238.99±53.02µmol/mg. In dry season the mean value of SOD in *S. melanotheron* ranged from 180.83±38.73µmol/mg to 225.38±8.36µmol/mg and that of *T. guinensis ranged* from 169.86±29.01µmol/mg to 226.20±61.50 µmol/mg. Analysis of variance (ANOVA) showed that there was no significant difference (p>0.05) in SOD activities in the livers of *S. melanotheron and T. guinensis* between stations and seasons in Mahin lagoon.

Glutathione

The mean values of Glutathione (GSH) level in *Sarotherodon melanotheron* and *Tilapia guinensis* collected from Mahin lagoon for this study were presented in table 22 and 23 respectively. In wet season, the mean value of GSH in *S. melanotheron* ranged from 2.09±1.69µmol/mg to 2.54±1.73µmol/mg and that *T. guinensis* ranged from 2.49.±2.25µmol/mg to 2.87±2.15µmol/mg. In dry season the mean value of GSH in *S. melanotheron* ranged from 2.58±1.75µmol/mg to 2.98±1.89µmol/mg and that of *T. guinensis ranged* from 3.05±1.84 µmol/mg to 3.82±2.21 µmol/mg. Analysis of variance (ANOVA) showed that there was no significant difference (p>0.05) in GSH activities in the livers of *S. melanotheron and T. guinensis* between stations and seasons in Mahin lagoon.

Glutathione-S-Transferase

The mean value of Glutathione-S-Transferase (GST) level in *Sarotherodon melanotheron* and *Tilapia guinensis* collected from Mahin lagoon for this study is presented in table 22 and 23 respectively. In wet season, the mean value of GST in *S. melanotheron* ranged from 19.83±2.09µmol/mg to 20.18±1.99µmol/mg and that *T. guinensis* ranged from 21.45.±3.24µmol/mg to 23.69±2.21µmol/mg. In dry season the mean value of GST in *S. melanotheron* ranged from 20.40±2.04µmol/mg to 22.08±1.98µmol/mg and that of *T. guinensis ranged* from 22.14±2.44 µmol/mg to 23.78±2.64µmol/mg. Analysis of variance (ANOVA) showed that there was no significant difference (p>0.05) in GST activities in the livers of *S. melanotheron and T. guinensis* between stations and seasons in Mahin lagoon.

Table 2: Seasonal variation in Biochemical Parameters of *S. melanotheron* from Mahin lagoon

Parameter	Stations	Dry	Wet	T stat	T crit	P
	Mahin 1	20.57±2.34[a]	20.00±2.51[a]	-0.70	2.03	0.49
	Mahin 2	21.08±1.98 [a]	20.18±1.99 [a]	-1.36	2.03	0.18
GST	Mahin 3	20.40±2.04 [a]	19.83±2.09 [a]	-0.83	2.03	0.41
	Mahin 4	20.58±2.09 [a]	20.01±2.14 [a]	-0.81	2.03	0.43
	Mean	**20.66±2.09 [a]**	**20.00±2.15 [a]**	**-1.85**	**1.98**	**0.07**
	Mahin 1	3.81±1.98 [a]	3.29±2.07 [a]	-0.76	2.03	0.45
	Mahin 2	3.03±2.10 [a]	2.60±1.92 [a]	-0.64	2.03	0.53
CAT	Mahin 3	3.20±2.01 [a]	2.34±1.79 [a]	-1.36	2.03	0.18
	Mahin 4	3.85±1.97 [a]	3.34±1.93 [a]	-0.80	2.03	0.43
	Mean	**3.47±2.01 [a]**	**2.89±1.94 [a]**	**-1.90**	**1.98**	**0.06**
	Mahin 1	202.23±14.39 [a]	201.66±14.41 [a]	-0.12	2.03	0.91
	Mahin 2	225.38±8.36 [a]	224.81±8.38 [a]	-0.20	2.03	0.84
SOD	Mahin 3	188.23±48.40 [a]	187.66±46.40 [a]	-0.04	2.03	0.97
	Mahin 4	180.83±38.79 [a]	179.93±38.45 [a]	-0.07	2.03	0.94
	Mean	**199.17±35.13 [a]**	**198.52±35.09 [a]**	**-0.11**	**1.98**	**0.91**
	Mahin 1	2.84±1.80 [a]	2.33±1.65 [a]	-0.90	2.03	0.38
	Mahin 2	2.90±1.86 [a]	2.41±1.79 [a]	-0.80	2.03	0.43
GSH	Mahin 3	2.98±1.84 [a]	2.54±1.73 [a]	-0.74	2.03	0.46
	Mahin 4	2.58±1.75 [a]	2.09±1.69 [a]	-0.85	2.03	0.40
	Mean	**2.82±1.78 [a]**	**2.34±1.69 [a]**	**-1.67**	**1.98**	**0.10**

Mean value with same superscripts along the rows were not significantly different (p>0.05).

Table 3: Seasonal variation in Biochemical Parameters of *T. guinensis* from Mahin lagoon

Parameter	Stations	Dry	Wet	T stat	T crit	P
	Mahin 1	23.78±2.64[a]	22.83±2.83[a]	-1.04	2.03	0.31
	Mahin 2	22.14±2.44 [a]	21.52±2.48[a]	-0.76	2.03	0.45
GST	Mahin 3	23.72±1.96 [a]	23.69±2.21[a]	-0.04	2.03	0.97
	Mahin 4	22.46±2.78 [a]	21.45±3.24 [a]	-1.01	2.03	0.32
	Mean	**23.02±2.53 [a]**	**22.37±2.82 [a]**	**-1.47**	**1.98**	**0.15**
	Mahin 1	3.51±1.88 [a]	2.91±1.84 [a]	-0.97	2.03	0.34
	Mahin 2	3.84±2.18 [a]	2.93±2.23 [a]	-1.25	2.03	0.22
CAT	Mahin 3	3.75±2.01 [a]	2.77±2.00 [a]	-1.46	2.03	0.15
	Mahin 4	3.78±1.87 [a]	3.21±1.90 [a]	-0.90	2.03	0.37
	Mean	**3.72±1.95 [a]**	**2.95±1.96 [a]**	**-2.35**	**1.98**	**0.02**
	Mahin 1	183.37±21.39 [a]	189.05±16.68 [a]	0.89	2.03	0.38
	Mahin 2	226.20±61.50 [a]	238.99±53.02 [a]	0.67	2.03	0.51
SOD	Mahin 3	169.86±29.01 [a]	158.14±25.57 [a]	-1.29	2.03	0.21
	Mahin 4	201.94±42.44 [a]	218.30±49.94 [a]	1.06	2.03	0.30
	Mean	**195.34±45.84 [a]**	**201.12±49.37 [a]**	**0.73**	**1.98**	**0.47**
	Mahin 1	3.05±1.84 [a]	2.54±1.77 [a]	-0.85	2.03	0.40
	Mahin 2	3.82±2.21 [a]	2.87±2.15 [a]	-1.31	2.03	0.20
GSH	Mahin 3	3.68±2.35 [a]	2.49±2.25 [a]	-1.56	2.03	0.13
	Mahin 4	3.54±2.12 [a]	2.55±1.77 [a]	-1.52	2.03	0.14
	Mean	**3.52±2.12 [b]**	**2.61±1.96 [a]**	**-2.68**	**1.98**	**0.01**

Mean value with same superscripts along the rows were not significantly different (p>0.05).

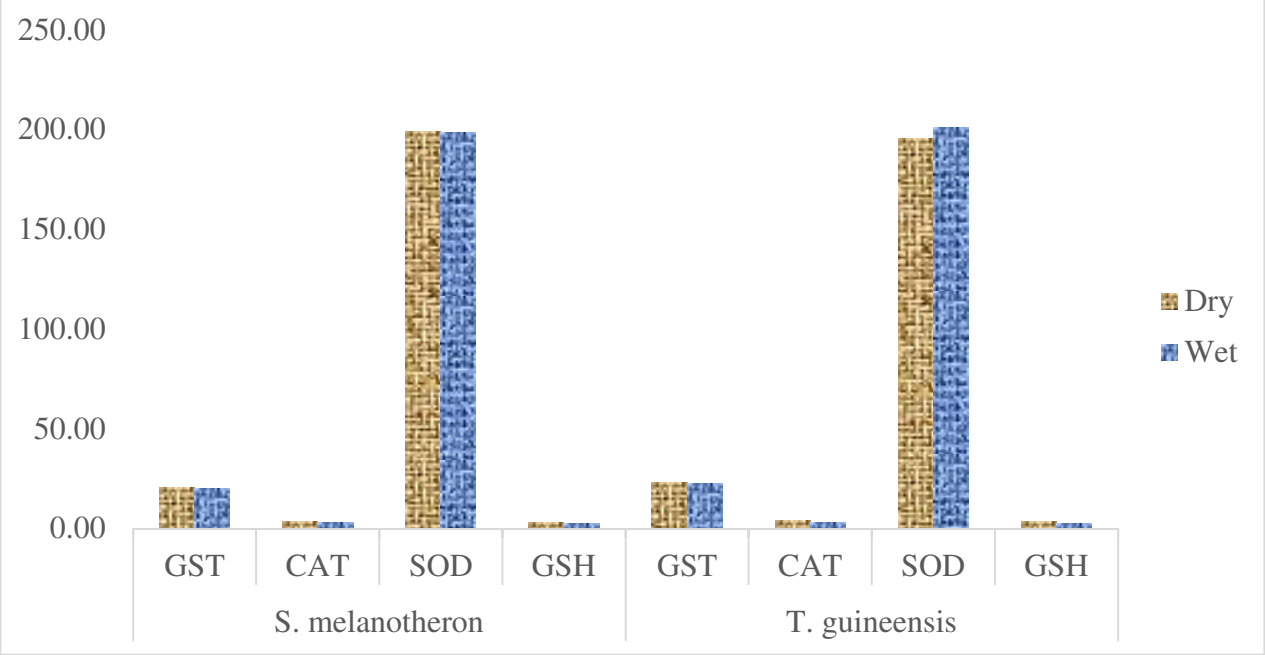

Fig. 2: Mean variation in enzymatic activities in *S. melanotheron* and *T. guineensis* from Mahin lagoon

Discussion

The study revealed that all the metals analysed were observed to concentrate significantly in the tissues of both fish species. Among the metals analyzed, Zn and Fe were observed to have the highest concentrations in all fishes. Moreover some metals were observed to have mean values higher than the WHO/FEPA recommended limit. The level of heavy metals recorded in this study were generally high when compared to WHO (2003) and FEPA (2007) recommendations. This was similar to the repot of Abulude *et al*. (2006) from different market in Southwest, Nigeria and Jimoh *et al*. (2011) from Epe lagoon.

The observed high concentrations of Pb, Cu, Cr, Cd, Ni and Co during this study are consistent with the findings of Obire *et al*. (2003) in Elechi creek in Port Harcourt. These high concentrations may be due to high agro-chemical usage and industrial activities around the study areas, which are the major sources of heavy metal concentrations in aquatic environment (Banjo *et al*., 2010; Olawusi-Peters, 2014). Trace metals such as Zn Cu and Fe play a biochemical role in the life processes of all aquatic plants and animals, therefore, they are essential in the aquatic environment in trace amount. The results of many field studies of metal accumulations in fish living in polluted waters show that considerable amounts of various metals may be deposited in fish tissues without causing mortality. This support the arguments that various metals are accumulated in fish body in different amount. Thus, the concentration of Zn in the sampled fishes were within the FAO (2007) guideline of 30mg/kg.

In this study, the observed mean values of Fe in fish were within the WHO/FEPA recommendation limit 0.5 -50mg/kg in fish foods. Even though Fe becomes

poisonous when it exceed this limit, it is an essential micronutrient which comprises nearly 300 enzymes in marine organisms and is responsible for certain biological functions that require relatively higher Fe (Asaolu and Olaofe, 2004). Iron is a mineral essential for life. It is present in every living cell and is necessary for the production of hemoglobin, myoglobin, and certain enzymes. Fe deficiency can cause weakness, inability to concentrate and susceptibility to infection.

Cu is an essential part of several enzymes and it is necessary for the synthesis of haemoglobin but can cause harm at high concentrations (McCluggage, 1991; Sivaperrumal *et al*., 2007). According to Cogun and Kargin (2004), accumulation of Cu by aquatic organisms is higher at lower pH. The profile of Cu in this study revealed that the concentrations of Cu in the fish species were lower, below the FAO (1983, 2007) guidelines of 3mg/kg and FEPA (2003) permissible limit of 1.00mh/l respectively.

The mean concentrations of lead (Pb) in the two study species exhibited no significant difference ($p>0.05$) across stations and seasons. Also the concentrations of Pb observed in some fish species were high, but still fell within the permissible limit of 0.01mg/l of FEPA (2003) and 2mg/kg of FAO (1983, 2007) respectively. Pb is classified as one of the most toxic heavy metals. The biological effects of sublethal concentration of Pb include delayed embryonic development, suppressed reproduction and inhalation of growth, increased mucous formation, neurological problems, enzyme inhalation and kiney dysfunction (Akan *et. al*., 2012). Cr is an essential trace element in humans and some animals but in excess, it could have undesirable lethal effect on fish and wildlife (Akan *et al.,* 2009). Concentrations of Cr in the fish muscles from Mahin lagoon were high, thou below the maximum guideline, 12–13 mg/kg, stipulated by the United States Food and Drug Administration (USFDA, 1993).

Aquatic environment is a sink for many environmental contaminants which can be absorbed by aquatic organisms which may eventually disturb the antioxidant/pro-oxidant balance in fish (Hegazi *et al.*, 2010). The disturbance in antioxidant/ pro-oxidant balance in fish may cause oxidative stress which has been described as a state when antioxidant defenses are overcome by pro-oxidant forces (Hegazi *et al.*, 2010).

In the present study, activates of antioxidant enzymes (SOD, CAT, and GST) and in liver of *S. melanotheron* and *T. guineensis* collected from Mahin lagoon, were varied significantly ($P \leq 0.05$) across stations and seasons. There was observed increase in antioxidant enzymes activities indicates adaptive responses of fish to counteract the oxidative effect of generated ROS or due to resist the water pollutants toxicity against the damage caused by excessive amount of oxygen free radicals and oxidative stress (Gad, 2009 and Carvalho *et al.*, 2012).

Reduced glutathione (GSH) is responsible for protection against reactive oxygen and nitrogen species and detoxification of endogenous and exogenous toxins of electrophilic nature. Reduced glutathione was depleted in the liver of *S. melanotheron and T. guinensis* from Mahin lagoon. The reduction may be as a result of the overwhelming toxic effect of the heavy metals present in the environment. However, it has been reported that severe oxidative stress may

suppress GSH levels due to the impairment of adaptive mechanisms (Zhang *et al*., 2004).

Antioxidant enzymes such as Superoxide dismutase (SOD), Catalase and Glutathione S-transferase (GST) help to neutralize toxic effects of ROS on fish, just like in mammals. Superoxide dismutase is one of the key enzymes that provide the first line of defence against pro-oxidants and catalyses the transformation of superoxide radicals to H_2O_2 and O_2 (Lauterburg *et al*., 1983). Glutathione-S-transferase (GST) in conjugation with reduced glutathione (GSH) act as defence against reactive oxygen species (ROS) and protect cells against oxidative injuries. The activity of SOD, Catalase and GST increased in the liver of both *S. melanotheron and T. guineensis* from Mahin lagoon. This was in agreement with the findings of Farombi *et al*. (2007) who reported elevation in the activities of the antioxidant enzymes in *Clarias gariepinus* from Ogun River, Nigeria. Which was also corroborated by the findings of Khali *et al*. (2017). However the report disagreed with the findings of Arojoye and Adeosun (2016), who reported decreased activities of SOD, GST and CAT in *C. gariepinus* from Asejire River, which was also corroborated by the findings of Awoyemi *et al*. (2014), who also reported decreased activities of antioxidant enzymes in *C. gariepinus* and *Oreochromis niloticus* exposed to heavy metals. Also increase in GST activity is known to be attributed to high production of superoxide anion radical (Alves *et al*., 2002), this might also explain the observed increase in catalase activity. Similar to this findings, Ganesan *et al.* (2011) also reported significant increase in the activity of catalase and SOD in fish from a polluted lake in India, and Awoyemi *et al.* (2014) also observed significant increase in the activity of catalase and SOD in *C. gariepinus* exposed to lead. Also the increase in GST activity observed in the tissue of the fish corroborates the findings of Wilhelm Filho *et al.* (2001) who also reported an increase in GST activity in the liver of *Geophagus brasiliensis* from a polluted River (Benedito River) in Southern brazil and Farombi et al. (2007), who observed an increase in GST activity in the gill of *C. gariepinus* from Ogun River in Nigeria. Dilek *et al*. (2014) also observed an increase in GST activity in *O. niloticus* exposed to cadmium and copper.

Conclusion

This study revealed that high concentration of heavy metals Zn, Pb, Fe, Cu, Cr, Cd, Ni and Co accumulated in the tissues of fishes from Mahin lagoon, presumably due to the high level of anthropogenic activities near the lagoon. This could be related to the alterations in antioxidant enzyme activities as biomarkers of oxidative stress in both *S. melanotheron and T. guineensis* which may cause biochemical dysfunction in this specie. This study also showed that enzymatic responses of both *S. melanotheron and T. guineensis* to heavy metal exposures lead to a significant increase in activity of antioxidant defense system enzymes superoxide dismutase (SOD) and glutathione-S-transferase (GST), in white muscles of both fish species from polluted Mahin lagoon. In addition, the results provide evidence that enzymic biomarkers of oxidative stress can be sensitive indicators of aquatic pollution.

References

Abdus-Salam, N., Adekola, F.A. and Apata, A.O. (2010). A Physicochemical Assessment of Water Quality of Oil Producing Areas of Ilaje, Nigeria. *Advances in Natural and Applied Sciences,* 4(3): 333-344.

Akinrinade, O.J., Adesina, A.B., Ogundare, M.O. and Ashiru O.R. (2016). Baseline physico-chemical and bathymetry assessment of Mahin Lake, Southwestern, Nigeria. *Journal of Oceanography and Marine Science*, 7(4): 33-41. DOI: 10.5897/JOMS2016.0133.

Ayoola, S.O., Idowu, A.A. Babalola, O.E. and Ademoye, M.K. (2014). Heavy Metals Accumulation and Enzymatic Biomarker in Commercially Important Fish Species (*Hemichromis fasciatus* and *Chrysichthys nigrodigitatus*) at the Landing Site, Bariga, Lagos Lagoon. *World Applied Sciences Journal*, 29(2): 298-306.

Chindah, A. C. (2004). Toxicity of Cypermethrin to *Tilapia guineensis* juveniles. *Journal of Agric. Biotech Env.* 2 (2):60 - 66.

Chindah, A. C. and Hart, A. I. (2000). Occurrence and distribution of epi fauna and in-fauna community in shallow mangrove wet land in the tropical West African Region. *Afri. J. Env. Stud*. 6(1&2): 76-83.

Farombi, E.O., Adelowo, O.A. and Ajimoko, Y.R. (2007). Biomarkers of Oxidative Stress and Heavy Metals Levels as Indicators of Environmental Pollution in Africa Cat Fish (*Clarias gariepinus*) From Nigeria Ogun River. *International Journal of Environmental Research and Public Health,* 4(2): 158-165.

Habig, W.H., Pabst, M.J. and Jacoby, W.B. (1974). Glutathione-S-transferases. The first enzymatic step in mercapturic acid formation. *J. Biol. Chem.,* 249: 7130-7139.

Hegazi, M.M., Attia, Z.I. and Ashour, O.A. (2010). Oxidative stress and antioxidant enzymes in liver and white muscle of Nile tilapia juveniles in chronic ammonia exposure. *Aquat. Toxicol*., 99(2): 118-125.

Jollow, D.J., Michell, J.R., Zampaglione, N. and Gillete, J.R. (1974). Bromobenzene induced liver Necrosis: Protective role of GSH and evidence for 3, 4 - Bromobenzene oxide as the Hepatotoxic metabolite. *Pharmacology,* 11: 151 - 169.

Kadar, E., Bettencourt, R., Costa, V., Santos, R. S., Lobo-Da-Cunha, A. and Dando, P. (2005). Experimentally induced endosymbiont loss and reacquirement in the hydrothermal vent bivalve *Bathymodiolus azoricus*. *J. Exp. Mar. Biol. Ecol*., 318: 99–110.

Kalay, M., Ay, P. and Canil, M. (1999). Heavy metal concentration in fish tissues from the northeast Mediterean sea. *Bull Environ. Contam. Toxicol.,* 6: 673-671.

Khali, M.T., Gad, N.S., Ahmed, N.A.M. and Moustafa, S.S. (2017). Antioxidant Defense System Alternations in Fish as a Bio-Indicator of Environmental Pollution. *Egyptian Journal of*

Aquatic Biology and Fisheries, 21(3): 11-28.

Kim, S.G., Park, D.K., Jang, S.W., Lee, J.S., Kim, S.S. and Chung, M.H. (2008). Effect of Dietary Benzo pyrene on Growth and Hematological Parameters in Juvenile Rockfish, *Sebastes schlegill* (Hilgendorf). *Bull. Environ. Contam. Toxico*l., 81: 470-474.

Magwere, T., Naik, Y. S. and Hasler, J. A. (1997). Effect of chloroquine treatment on antioxidant enzymes in rat liver and kidney. *Free Rad. Biol. Med.*, 22: 321-327

Olaosebikan, B.D. and Raji, A. (2013). Field guide to Nigerian Freshwater Fishes. Revised Edition. Federal College of Freshwater Fisheries Technology, New Bussa, Nigeria, 144pp.

Onyema, I.C., Otudeko, G.O. and Nwankwo, D.I. (2003). The distribution and composition of plankton around a sewage disposal site at Ido, Nigeria. *Journal of Scientific Research Development*, 7: 11- 26.

Velkova-Jordanoska L., Kostoski, G. and Jordanoska, B. (2008) Antioxidative enzymes in fish as biochemical indicators of aquatic pollution. *Bulg J Agric Sci*., 14: 235-237.

Xu, J., Yuan, X. and Lang, P. (1997). The determination of enzymic activity and its inhibition on catalase by ultraviolet spectrophotometry. *Environ Chem*. 16(1): 73-79.

Zhang, Z., He, L., Li, J. and Wu, Z. (2007). Analysis of Heavy Metals of Muscle and Intestine Tissue in Fish – in Banan Section of Chongqing from Three Gorges Reservoir, China. *Polish J. of Environ. Stud.* 16: 949-958.