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Assessment of Heavy Metal Residues in Fish as a Biomarker of Pollution in Suez Province

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ABSTRACT

Fish and their products are significant sources of protein, minerals and omega-3 polyunsaturated fatty acids. However, small amounts of heavy metals in fish tissues can counteract the positive effects of their omega-3 fatty acids, causing considerable damage to organisms. The present study was carried out to assess the pollution caused by the presence of heavy metals (lead and manganese) detected in the Suez province. This purpose was achieved by monitoring their concentrations in surface water at different sites (Attaka Harbor, Oyon Mousa and Kornish) as well as in fish (*Siganus rivulatus and Pomadasys stridens*). In addition, the relationship between the level of the recorded heavy metals in water and its corresponding residual concentrations in fish tissues was investigated. Tissue samples (liver, gills and musculature) of Sigan, *Siganus rivulatus* (n=96) and Shokhrom, *Pomadasys stridens* (n= 48) were collected from different regions (Attaka harbor, Oyon Mousa, kornish region and local markets) during the four seasons of the year. Results revealed that the periodic difference of lead concentration, based on the obtained data of water samples, showed decreasing levels in the following sequence: spring> winter> autumn> summer, while the concentrations of manganese showed the following results: summer> winter> autumn> spring. Levels of lead in musculature of both *Siganus rivulatus and Pomadasys stridens* exceeded the permissible limits proposed by FAO/WHO. Nevertheless, manganese recorded concentrations were within the limits proposed by FAO/WHO for food standards of fish. Heavy metals concentrations were markedly higher in fish tissues compared to water. Liver and gill tissues showed metal concentrations higher than other tissues. In conclusion, these findings indicate that fish can be used as a biomarker for heavy metal pollution in aquatic ecosystems.

INTRODUCTION

The consumption of fish and fish products is beneficial for human health, protecting human body from diseases **(Cahu *et al*., 2004)**. Fish are important source of protein, minerals and omega-3 polyunsaturated fatty acids **(Guérin *et al*., 2011)**.

Nonetheless, the presence of heavy metals pollutants in fish tissues can counteract the positive effects of their omega-3 fatty acids and can cause considerable damage to organisms even if found in small amounts **(Domingo *et al*., 2007)**. Suez is a coastal city where people basically depend in their diet on fish as a main source of animal protein; most are caught from the Gulf of Suez. In Suez water area, high metal load is detected in water due to the combined effects of wastes discharge, maritime activities, shipping processes, industrial activities and fishing ports **(Abouhend & El-Moselhy, 2015; El-Metwally *et al*., 2019)**. The toxicity of heavy metals is attributed to their tendency to bind with SH-group containing enzymes and protein, preventing their metabolic functions **(Rahman *et al*., 2012)**. The assessment of heavy metals' pollution in the aquatic environment is determined by measuring their concentrations in water and living organisms. Biological monitoring of heavy metals' accumulation in the different organs or body compartments is a representative measure of exposure **(Serafim & Bebianno, 2001; Mustafa & Guluzar, 2003)**. Therefore, this study aimed to address the concentrations of lead (Pb) and manganese (Mn) in fish (sigan and shokhrom) musculature, liver and gills as well as in the surface water of different regions along the Suez Gulf during the four seasons of the year.

MATERIALS AND METHODS

Study area

This study was conducted to assess the levels of lead and manganese in surface water samples and their residual bioaccumulation in fish liver, gills and musculature at four different locations in Red Sea, Suez Province in Egypt during the four seasons (winter, spring, summer and autumn). The three locations of water samples included Kournish (located in the western part of Suez near the southern entrance of the Suez Canal); Oyon Mousa and Attaka harbor (located on the southwestern shore of the Suez Bay). Fish samples (liver, gills and musculature) were collected from Kournish, Oyon Mousa, Attaka harbor and local markets as showed in Fig. (1).

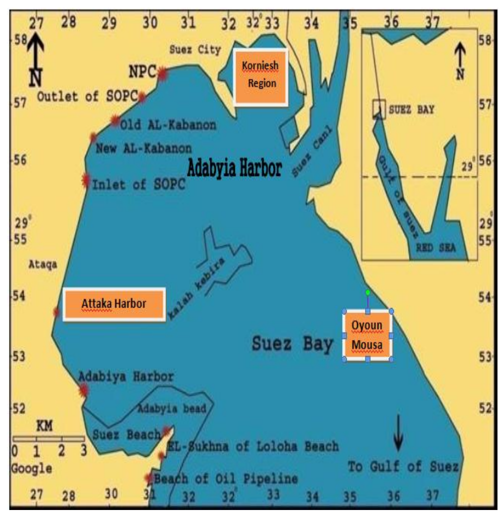

Fig.1. Map of study area showing sampling localities along the Suez Gulf, Egypt

Sampling

Water samples

A total amount of 60 water samples were collected. Fifteen samples for each season (summer, autumn, winter and spring), and five samples were taken from each area (Oyon Mousa, Kournish and Attaka). The technique of water sampling was conducted according to recommendations of the American Public Health Association **(APHA, 1985)**.

Fish samples

A total of 144 fish samples were collected. Ninety six samples of *S.rivulatus* (14-18 cm length and 110 ± 0.50 g weight) were collected from the above mentioned localities along Gulf of the Suez in the Suez Province, Egypt. Six fish were obtained from each district during each season (summer, autumn, winter and spring). Forty eight fish samples of *P.stridens* (12-16 cm length and 90±0.50g weight) were collected from the same four different localities. Six fish samples were obtained from each district during only two seasons (winter and autumn). At laboratory, liver, gills and musculature were collected from each fish, washed with de-ionized water, identified and kept frozen at -20ºC till measurement of heavy metal residues.

Metal analysis

Digested water and fish tissue samples were analyzed for their heavy metals' contents using **UNICAM 969** Atomic Absorption Spectrophotometer.

Statistical Analysis

Data of the present study were analyzed using ANOVA procedures according to **Snedecor and Cochran (1989)**, followed by Duncan's Multiple Range test **(Duncan, 1955)**. Statistical analyses were conducted by SPSS for windows SPSS version 25. Results are considered significant at probability level of $P \leq 0.05$.

RESULTS

This study showed the relationship between the level of the investigated heavy metals in water and its corresponding residual concentrations in fish tissues.

1. Water samples

1.1. Lead concentration in water samples

The obtained results showed that water samples from the examined ecosystem (Suez Bay) had different concentrations with respect to both Pb and Mn. Lead levels ranged from 0.049 – 0.061 mg/l, which was within the permissible limit guideline values for water quality of **WHO (2004)**, recording 0.05 mg/l except at Attaka Harbor, where concentrations exceeded the permissible limits. According to the Egyptian Organization for Standardization and Quality Control (EOS), lead levels in the three locations were significantly higher than the permissible limits **(EOS, 2005**) for Pb (0.01 mg/l) as shown in Figs. (2, 3).

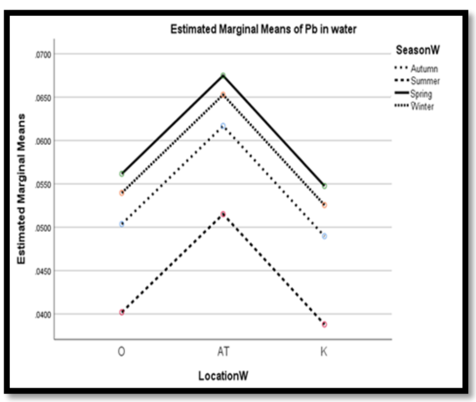

Fig. 2. Different mean concentrations of Pb in water of three different localities of Suez Bay

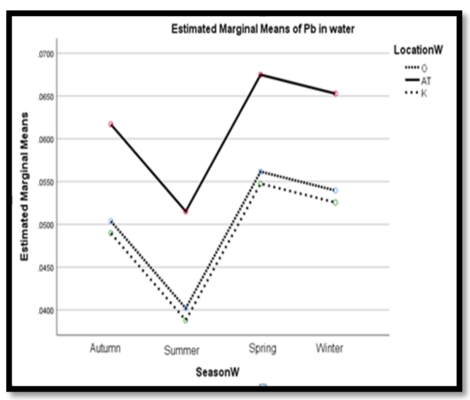

Fig. 3. Different mean concentrations of Pb in water of Suez Bay in four different seasons

1.2. Manganese concentration in water samples

Regarding the recorded manganese levels in surface water of the investigated localities, it ranged from 0.132 to 0.162 mg/l, which was within the permissible limits for water quality **(WHO, 1989)** for Mn (0.4 mg/l) as shown in Figs. (4, 5).

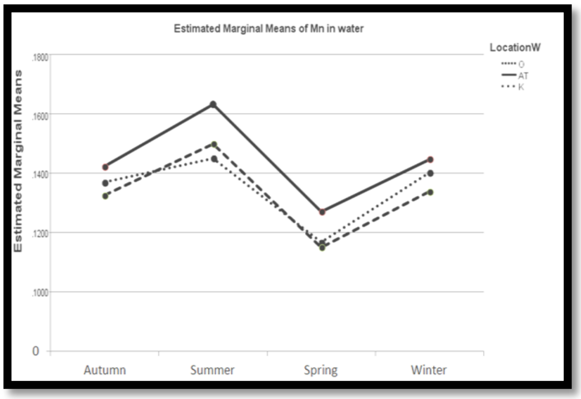

Fig. 4. Different mean concentrations of Mn in water of Suez Bay in four different seasons

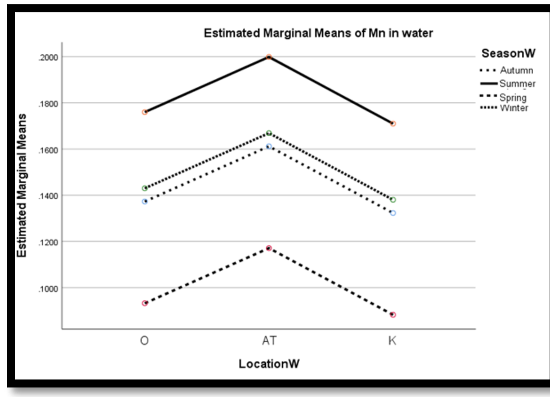

Fig. 5. Different mean concentrations of Mn in water of three different localities of Suez Bay

2. Fish samples

2.1. Lead concentration in *S.rivulatus* fish

For the mean concentrations of Pb in *S.rivulatus*, significant higher levels were recorded in liver (3.833±0.356 mg/kg), followed by gills (2.260±0.235 mg/kg) then musculature (1.054±0.106 mg/kg) compared to the permissible limits of WHO and EOS. The highest levels determined in *S.rivulatus* fish tissue was in spring and autumn, followed by summer and winter. The highest concentrations were recorded in samples collected from Attaka harbor, followed by those of Oyon Mousa then of the Kournish region; whereas, the lowest levels were recorded in samples collected from local markets. The values of Pb in edible parts were more than the permissible limits (0.5 ppm according to **WHO (2000**) and (0.1 ppm according to **EOS (2005**). Thus, a hazard has been detected with respect to pollution with lead (Table 1 & Figs. 6, 7, 8, 9).

Table 1. Means and standard errors for Pb concentrations by mg/Kg in different organs (musculature, liver and gills) of *S.rivulatus* fish at different locations

Location	Organs (Mean ± S.E. of Pb (mg/Kg))			Mean ± S.E. of Pb (mg/Kg) for each location
	musculature	Liver	Gills	
AT	2.170^{cd}±0.220	5.631^{ab}±0.540	4.582^{b}±0.436	4.128^{a}±0.295
S	0.330^{e}±0.056	0.405^{e}±0.076	0.256^{e}±0.063	0.329^{d}±0.038
O	0.620^{e}±0.051	6.439^{a}±0.523	2.035^{cd}±0.150	3.032^{b}±0.345
K	1.098d^{e}±0.214	2.426^{c}±0.653	2.000^{cd}±0.510	1.841^{c}±0.289
Mean ± S.E. of Pb (mg/Kg) for each organ	1.054^{c}±0.106	3.833^{a}±0.356	2.260^{b}±0.235	2.368±0.160

The means with different letters in the same row or column are significantly different at ($P \leq 0.05$).
O= Oyoun Mousa region, S= samples collected from markets AT= Attaka harbor and K= Kornish region.

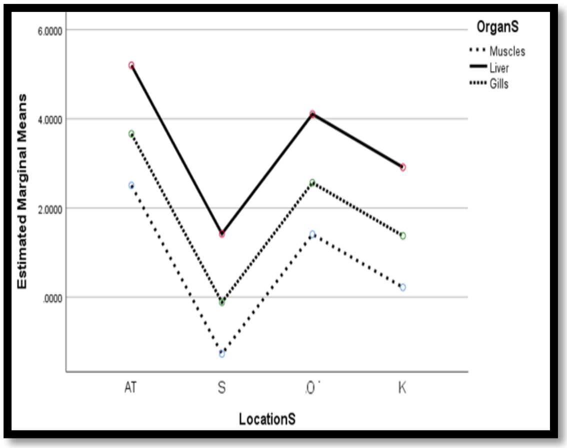

Fig. 6. A histogram showing different mean conc. of Pb in *S.rivulatus* fish tissues in winter

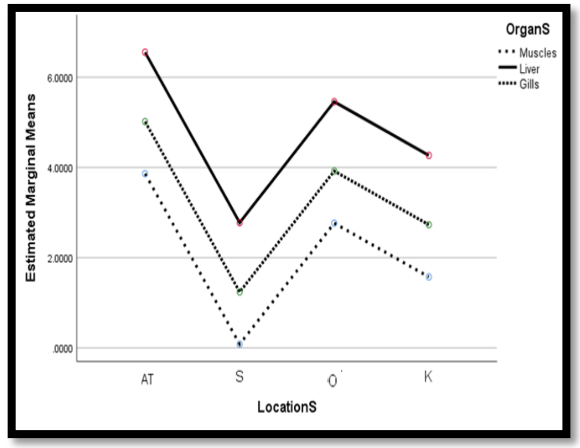

Fig. 7: A histogram showing different mean conc. of Pb in *S.rivulatus* fish tissues in spring

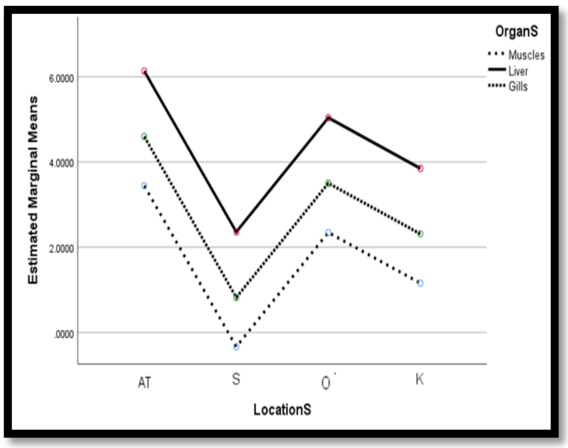

Fig. 8: A histogram showing different mean conc. of Pb in *S.rivulatus* fish tissues in summer

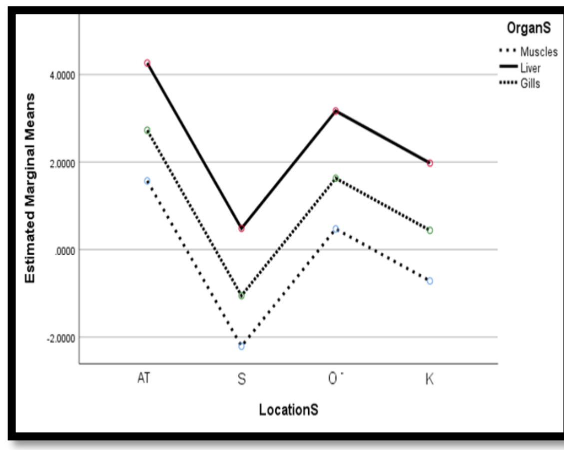

Fig. 9: A histogram showing different mean conc. of Pb in *S.rivulatus* fish tissues in autumn

2.2. Lead concentration in *P.stridens* fish

Concerning the mean concentrations of Pb in *P.stridens* fish, significant higher levels were recorded in liver (2.020±0.072 mg/kg), followed by gills (1.717±0.040 mg/kg) then musculature (1.460±0.052 mg/kg). The highest concentrations found in *P.stridens* fish tissue was in autumn followed by winter. The highest levels were recorded in samples collected from Attaka harbor. The values of Pb in edible parts were more than the permissible limits (0.5 ppm according to **WHO (2000)** and (0.1 ppm according to **EOS (2005**). Hence, a hazard was determined due to pollution with lead (Table 2 & Figs. 10, 11**)**.

Table 2. Means and standard errors for Pb concentration by (mg/Kg) in different organs (musculature, liver and gills) of *P.stridens* fish at four different locations (O, S, AT and K)

Location	Organs (Mean ± S.E. of Pb (mg/Kg))			Mean ± S.E. of Pb (mg/Kg) for each location / all tissue
	musculature	Liver	Gills	
O	**1.298^{d}±0.086**	**1.869^{b}±0.158**	**1.630^{bc}±0.103**	**1.599^{b}±0.078**
S	**1.473cd±0.115**	**1.804bc±0.070**	**1.714bc±0.076**	**1.663b±0.055**
AT	**1.595^{bcd}±0.100**	**2.623^{a}±0.093**	**1.821^{b}±0.063**	**2.013^{a}±0.089**
K	**1.474^{cd}±0.108**	**1.782^{bc}±0.077**	**1.701^{bc}±0.069**	**1.652^{b}±0.053**
Mean ± S.E. of Pb (mg/Kg) for each organ / all location	**1.460^{c}±0.052**	**2.020^{a}±0.072**	**1.717^{b}±0.040**	

The means with different letters in the same row or column are significantly different at ($P \le 0.05$).
O= Oyon Mousa region, S= samples collected from markets AT= Attaka harbor and K= Kornish region.

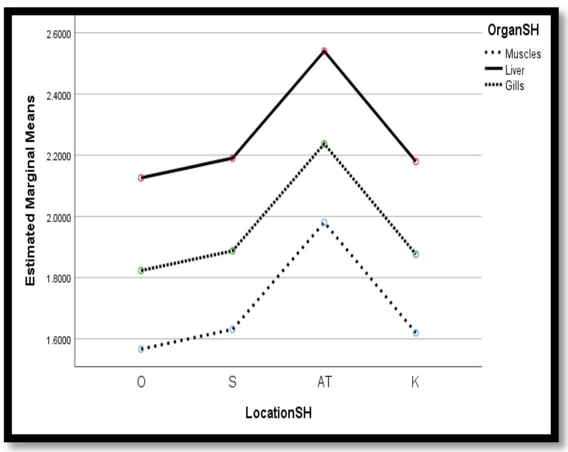

Fig. 10. A histogram showing different mean conc. of Pb in *P.stridens* fish tissues in winter

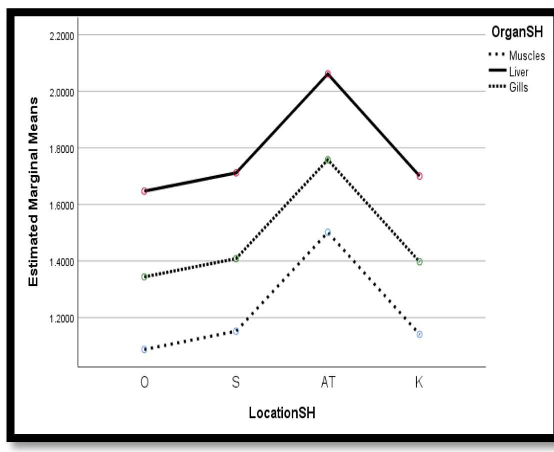

Fig. 11. A histogram showing different mean conc. of Pb in *P.stridens* fish tissues in winter

2.3. Manganese concentration in *S. rivulatus* fish

The mean concentrations of manganese in *S.rivulatus* fish recorded significant high levels in gills (1.759±0.126 mg/kg), followed by liver (1.130±0.148 mg/kg) then musculature (0.532±0.049 mg/kg). The highest values found in *S.rivulatus* fish tissue was detected in summer, followed by spring and autumn, while the lowest values were found in winter. The highest concentrations were recorded in the samples collected from Attaka harbor, followed by those gathered from Oyon Mousa then the Kournish region. The lowest values were registered in the samples collected from local markets. The values of manganese in edible parts of fish were within the permissible limits (1 ppm according to **WHO (1989)**. Consequently, no hazards were defined from manganese (Table 3 & Figs. 12 -15).

Table 3. Means and standard errors for Mn concentrations (mg/Kg) in different organs (musculature, liver and gills) of *S.rivulatus* fish at different locations (AT, S, O and K) in all seasons

Location	Organs (Mean ± S.E. of Mn (mg/Kg))			Mean ± S.E. of Mn (mg/Kg) for each location/ all tissues
	musculature	Liver	Gills	
AT	$0.874^{def}\pm0.149$	$2.386^{ab}\pm0.460$	$1.946^{bc}\pm0.312$	$1.735^{a}\pm0.204$
S	$0.271^{fg}\pm0.047$	$0.187^{g}\pm0.037$	$0.822^{defg}\pm0.093$	$0.432^{c}\pm0.050$
O	$0.293^{fg}\pm0.026$	$0.745^{efg}\pm0.055$	$2.827^{a}\pm0.237$	$1.288^{b}\pm0.154$
K	$0.680^{efg}\pm0.058$	$1.163^{de}\pm0.167$	$1.441^{cd}\pm0.074$	$1.095^{b}\pm0.073$
Mean ± S.E. of Mn (mg/Kg) for each organ/ all locations	$0.532^{c}\pm0.049$	$1.130^{b}\pm0.148$	$1.759^{a}\pm0.126$	

The means with different letters in the same row or column are significantly different at ($P \leq 0.05$).
O= Oyon Mousa region, S= samples collected from markets AT= Attaka harbor and K= Kornish region.

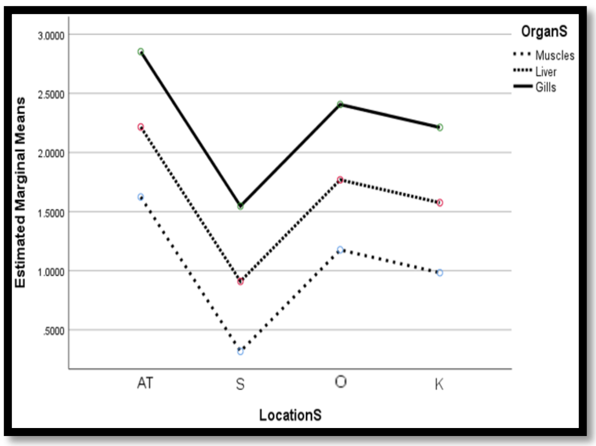

Fig. 12. A histogram showing different mean concentrations of Mn in winter in *S.rivulatus*

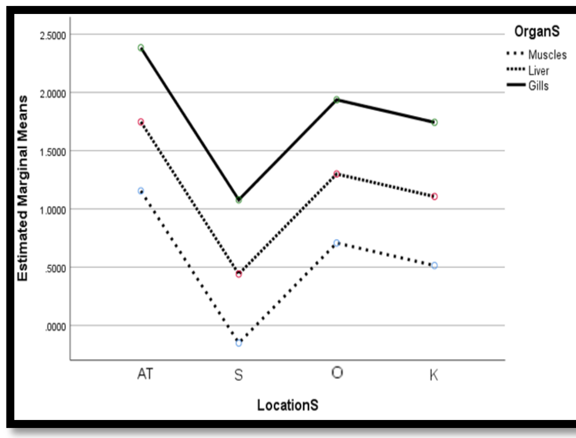

Fig. 13. A histogram showing the different mean concentrations of Mn in spring in *S.rivulatus*

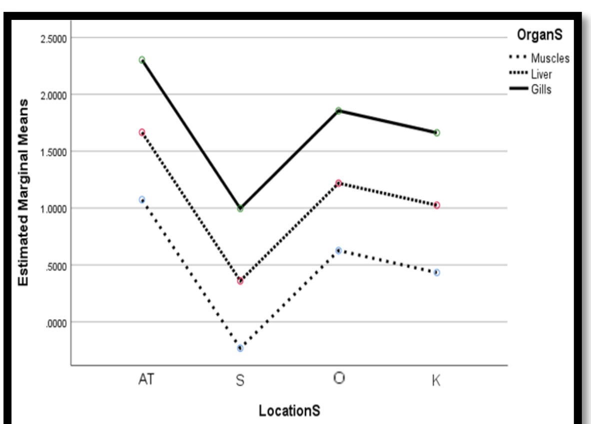

Fig. 14. Histogram showing different mean concentration of Mn in summer season *S.rivulatus* fish

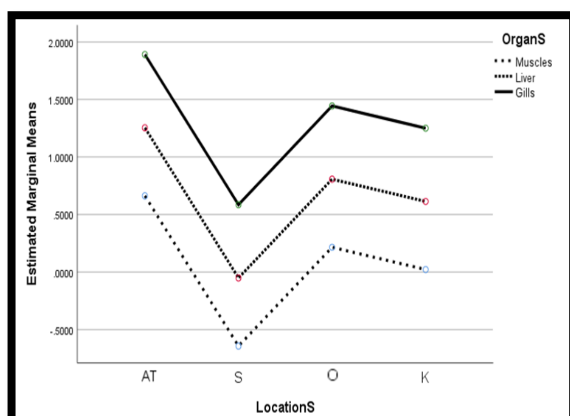

Fig. 15. Histogram showing different mean concentration of Mn in autumn season in *S.rivulatus* fish

2.4. Manganese concentration in *P.stridens* fish

Concerning the mean concentrations of manganese in *P.stridens* fish, non-significant higher levels were detected in liver (0.357±0.046 mg/kg), followed by gills (0.273±0.006 mg/kg) then musculature (0.199±0.015 mg/kg) compared with the permissible limits of **WHO (1989)**. The highest values found in *P.stridens* fish tissues were in autumn followed by winter. No significant variations were found among the values of Mn concentrations in *P.stridens* collected from the four locations (Attaka harbor, Oyon Mousa, Kournish region and local markets (Table 4 & Figs. 16, 17).

Table 4. Means (±) standard errors for Mn concentration by mg/kg in different organs (musculature, liver and gills) of *P.stridens* fish at the four different locations (O, S, AT and K) in all seasons

Location	Organs (Mean ± S.E. of Mn (mg/kg))			Mean ± S.E. of Mn (mg/kg) for each location / all tissues
	musculature	Liver	Gills	
O	0.164^{c}±0.012	0.488^{a}±0.183	0.300^{bc}±0.016	0.318^{a}±0.064
S	0.254b^{c}±0.052	0.284^{bc}±0.012	0.270^{bc}±0.008	0.269^{a}±0.017
AT	0.190b^{c}±0.010	0.375ab±0.013	0.280^{bc}±0.008	0.282^{a}±0.014
K	0.188^{c}±0.018	0.280^{bc}±0.010	0.240^{bc}±0.009	0.236^{a}±0.010
Mean ± S.E. of Pb (mg/L) for each organ/ all locations	0.199^{b}±0.015	0.357^{a}±0.046	0.273^{b}±0.006	

The means with different letters in the same row or column are significantly different at (P ≤ 0.05).
O= Oyon Mousa region, S= samples collected from markets AT= Attaka harbor and K= Kornish region.

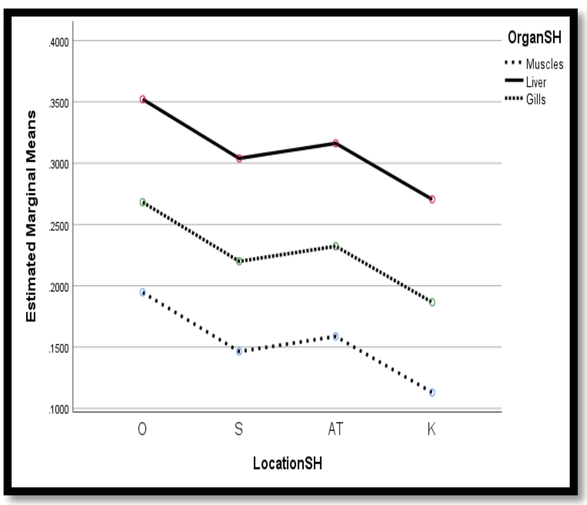

Fig. 16. Histogram showing the different mean conc. of Mn in winter in *P.stridens* fish

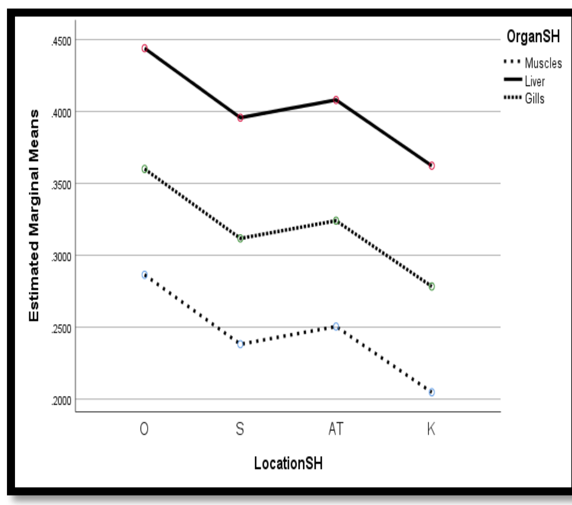

Fig. 17. Histogram showing the different mean conc. of Mn in autumn in *P.stridens* fish

DISCUSSION

The current results agree with those of **El-Metwally *et al*. (2019** who mentioned that, sea water at the Suez has significantly higher concentrations of Pb compared to the other sites along the Red Sea. That may be related to the anthropogenic activities at Suez. Our results revealed also that Attaka Harbor showed the highest concentrations of Pb compared to the other localities. This finding may be due to the nature of the Suez gulf environment that receives a variety of stresses as a result of human activities, including mixed sources of industrial pollution as wastewater discharges from oil refineries **(Mansour & Abd El Razik, 2005; Mehanna & Abd El-Azim, 2018**). This result coincides with that of **El-Shenawy and Farag (2009)** who attributed the high concentrations of heavy metals in the Suez gulf to the different anthropogenic activities such as recreational resorts, urban agglomeration, marine shipping, fishing ports and some sewage discharges. When comparing the recorded levels of manganese in the three investigated localities of Suez bay, the highest mean concentrations of Mn were detected in Attaka harbor (0.161±0.036 mg/l) that may be linked to human activities **(El-Metwally *et al.*, 2019**). High averages of leachable Mn indicates the effect of the anthropogenic inputs within these basins (boats mooring and repairing, corrosion of constructions and pipes) as well as the reducing conditions inside these basins due to the high percentages of fine sediments and organic matter **(Elgendy *et al*., 2018)**. The distribution patterns of heavy metals in water with regard to hot seasons (spring and summer) is a result of releasing heavy metals from sediments to the overlying water under the effect of high temperature, winds and fermentation process resulted from the decomposition of organic matter. This data could explain the higher levels of Pb and Mn in spring and summer, respectively **(El-Serafy *et al.*, 2003; Elewa *et al*., 2007; El-Damhogy *et al*., 2019)**. The relative increase in Pb during spring may be attributed to phytoplankton blooming during this season **(El-Moselhy, 1993)**. In the present study, the mean concentrations of Pb and Mn in the livers and gills of *Siganus rivulatus* and *Pomadasys stridens* fish were markedly higher than those present in the edible parts of the fish. Moreover, the mean concentrations of heavy metals found in the Suez bay water were lower than those obtained from different parts of the fish. These results concur with those of **Saad *et al.* (1981)** and **Mohammad and Gad (2008)**. The potential of high accumulation of the liver is a result of the activity of metallothionein, metal binding proteins, which plays an important role in metal regulation and detoxification of nonessential metals **(Roesijadi, 1992)**. It is well known that musculature is not an active site for metal biotransformation and accumulation. Nevertheless, in polluted aquatic habitats, the concentration of metals in fish musculature may exceed the permissible limits for human consumption and imply severe health threats **(Elnabris *et al*., 2013)**. Gills are important site of direct metal uptake from water, high metals concentrations in gills can point out the water as main source of contamination as reported in the study of **Gogus and Smith (2010)**. Toxic metals, such as lead and cadmium have higher values in herbivorous fish (*Siganus* *rivulatus*) compared to carnivorous fish **(***Pomadasys stridens***) (Tayel & Shriadah, 1996; Omayma *et al*., 2015**). The result matches with that of **El-Moselhy *et al*. (2014**) who postulated that, the highest concentrations of Mn in fish collected from Suez bay were in gills compared to liver and fish musculature, which recorded the lowest concentrations of Mn. Fish samples either S.*rivulatus* or *P.stridens* collected from local market (that mainly collected from deep water in the Red Sea rather than the other three locations in the current study) showed the lowest concentrations of heavy metals. These results were in line with the previous studies that reported high metal levels in fish collected from the seawater of Suez Bay, compared to those from the Red Sea proper which is mainly due to the industrial and anthropogenic input of metals from the Suez city and the maritime activities through the Suez canal **(El-Moselhy, 1993; Hamed & Emara, 2006; El-Moselhy *et al*., 2014)**. The metal levels recorded in the present study are generally lower or within the ranges of those found in the fish of the Red Sea recorded in the studies of **Emara *et al*. (1993)**, **Ahmed *et al.* (1996)**, **Ali *et al*. (2011)** and **ElMoselhy *et al*. (2014)**.

CONCLUSION

Lead and manganese concentrations in fish liver, gills and musculature were significantly higher than those in water, indicating their bioaccumulation in these tissues. For lead, liver was the primary site of its accumulation, followed by gills then musculature in both *Siganus rivulatus* and *Pomadasys stridens*. With respect to manganese, the accumulation in *S.rivulatus* fish was ranked as follows: gills (as primary site of manganese accumulation), followed by liver and musculature; while, in *P.stridens* fish, it was similar to that of lead. The recorded manganese concentrations in fish musculature were within the permissible limits for human consumption, except for lead concentrations that exceeded the permissible limits causing hazards to human.

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