

Heavy Metals (Cu, Fe, Mn, Zn) Content in *Thunnus tonggol* (Family-Scombridae) from Karachi Coast

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Abstract: Determination of metal levels in 40 fishes were collected from Karachi fish harbour during the period from Sep 2008 to Aug 2009. Heavy metal (Cu, Zn, Mn, and Fe) concentrations were measured in the liver and muscles of fish (*Thunnus tonggol*) by atomic absorption spectrophotometry by the dry ashing method.

The liver of *thunnus toggol* shows higher concentration of metals in all seasons of the year. Highest concentration of Cu (245.86 ug/g) were recorded in liver in the autumn season. Maximum concentration of Zn (27.42 ug/g) were recorded in liver in summer season. However in all season concentration of Fe, Zn, Cu, and Mn in liver were higher than muscles. Metal accumulated very rapidly in the fish liver but slowly in the fish flesh. No significant correlation between metal levels in muscles and liver and length and weight of fish. The decreasing order of concentration of metals in liver was Cu > Mn > Fe > Zn and in muscles Cu > Zn > Mn > Fe.

Key Words: Trace Metal, *Thunnus tonggol*, Karachi coast, liver and muscles.

INTRODUCTION

Heavy metals from geological and anthropogenic sources are increasingly being released into natural waters [1]. Contamination of aquatic ecosystems with heavy metals has seriously increased worldwide attention, and a lot of studies have been published on the heavy metals in the aquatic environment [2, 3]. The coastal region along the Karachi coast is exposed to pollution through domestic and industrial effluents, shipping and fishing traffic, and associated pollutants from agricultural run-off from various point and non point sources [4, 5]. Industrial wastes and mining can create a potential source of heavy metal pollution in the aquatic environment [6, 7]. Fish are the top of the aquatic food chain and may concentrate large amounts of some metals from water [8].

Under certain environmental conditions, heavy metals might accumulate up to toxic concentrations and cause ecological damage [9]. Thus, heavy metals, acquired through the food chain as a result of pollution, are potential chemical hazards, threatening consumers. Diet is the main route of exposure to heavy metals in the case of population not exposed to them. Fish are often at the top of the Aquatic food chain and may concentrate large amounts of some metals from the water. Accumulation patterns of contaminants in fish depend both on uptake and elimination rates [10]. Muscles (flesh) is a fish tissue commonly chosen for assay because this part of fish commonly used in human food. However, liver is an important organ for trace metal storage and decontamination in fish where the synthesis of

metallohionein induced by trace metals takes place [11]. Heavy metals are considered the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms, such as fish [12].

Increased metal concentrations in liver may represent storage of sequestered products in this organ. Liver, on the other hand is now widely recognized as an indicator for pollution monitoring [13].

The objective of this study to determine the concentration of heavy metals (Cu, Zn, Fe, Mn) in the fish parts liver and muscles collected from the coast of Karachi by the atomic absorption spectrometry after the Dry ashing technique.

MATERIALS AND METHODS

Fish Sampling

Total ten fishes were collected in each season (summer, autumn, winter and spring) from the fish harbour of Karachi during September 2008- August 2009.

Sample Preservation

The collected samples were quickly washed with distilled water and taken length (cm) and weight (g) of each fish. Identified the fish species and then stored at -20 °C prior to analysis.

Sample Preparation

Dissect and remove entire liver and dorsal muscles of each fish and weighted samples. Samples were ground and calcinated at 600 °C in furnace for three (hrs) to dry ash,

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weighted dry ash and then ash were dissolved with 10 ml HCl (con) and then filtered brought to a final volume with distilled water [14].

Metal Analysis

Take 1 ml of prepared sample and dilute it in 25 ml of distilled water. Start the equipment atomic absorption spectrophotometer (AAAnalyst 700) and prepare programme on win lab 32 soft ware. Prepare three standards from 1000 ppm stock solution to 2 ppm, 4 ppm, and 6 ppm. Calibrate the equipment with the above mentioned standards. Aspirate the sample one by one to detect the required metals. All metal values were given in ug/g.

RESULTS

Table 1 shows mean length and weight of fish (*Thunnus tonggol*). Maximum length (29.94 ± 6.82) was measured in summer season and minimum (24.77 ± 2.67) was in winter. Highest weight (230.66 ± 135.46) was in spring season and lowest weight (119.77 ± 14.74) was in autumn season. These Tables (2, 3, 4, 5) shows concentration level of metals in fish tissues (liver and muscles) in all seasons of the year (Sep 2008-Aug 2009). The highest concentration of Fe (26.38 ug/g) was detected in liver in the season of summer (Table 2). Where as highest concentration of Cu (245.86 ug/g) was obtained in liver in the autumn season (Table 3). The highest concentration of Mn (239.12 ug/g) were recorded in liver in autumn season (Table 4). Fe was low in muscles in all seasons of year as compare to liver (Table 2). The lowest

Table 1. Mean, Length and Weight of *Thunnus tonggol*

Fish	Season	No. of Fish	Weight (g)	Length (cm)
<i>Thunnus tonggol</i>	Autumn	10	3650 ± 214.99	68.6 ± 0.309
	Winter	10	3800 ± 398.46	69.1 ± 0.686
	Spring	10	3750 ± 456.55	68.6 ± 0.8342
	Summer	10	4150 ± 217.050	69.8 ± 0.222

Table 2. Mean Concentration of Fe (ug/g) in Liver and Muscles of *Thunnus tonggol* in Different Seasons

Fish	Tissue	Seasons			
		Autumn	Winter	Spring	Summer
<i>Thunnus tonggol</i>	Muscles	1.81 ± 0.712	0.98 ± 0.49	1.65 ± 1.35	1.75 ± 0.76
	Liver	20.20 ± 17.19	8.39 ± 7.79	2.30 ± 2.47	26.38 ± 16.33

Table 3. Mean Concentration of Cu (ug/g) in Liver and Muscles of *Thunnus tonggol* in Different Seasons

Fish	Tissue	Seasons			
		Autumn	Winter	Spring	Summer
<i>Thunnus tonggol</i>	Muscles	9.88 ± 7.06	9.04 ± 4.82	8.27 ± 5.79	10.29 ± 3.33
	Liver	245.86 ± 79.17	0.64 ± 0.62	29.87 ± 14.62	2.06 ± 1.58

Table 4. Mean Concentration of Mn (ug/g) in Liver and Muscles of *Thunnus tonggol* in Different Seasons

Fish	Tissue	Seasons			
		Autumn	Winter	Spring	Summer
<i>Thunnus tonggol</i>	Muscles	0.05 ± 0.02	12.57 ± 7.86	2.8 ± 1.37	3.76 ± 1.83
	Liver	239.12 ± 115.07	110.41 ± 37.16	26.23 ± 8.45	1.82 ± 1.17

Table 5. Mean Concentration of Zn (ug/g) in Liver and Muscles of *Thunnus tonggol* in Different Seasons

Fish	Tissue	Seasons			
		Autumn	Winter	Spring	Summer
<i>Thunnus tonggol</i>	Muscles	1.06±0.64	0.43±0.28	0.79±0.35	17.47±7.56
	Liver	11.54±7.67	4.89±4.52	3.01±2.57	27.42±17.23

Table 6. Analysis of Variance (ANOVA) of Different Parameters Fish *Thunnus tonggol*

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Length						
No.of Sample	9	1793.95	1793.95	199.33	34.71***	0.000
Parts of tissue	1	0.00	0.00	0.00	0.00	1.000
Seasons	3	461.22	461.22	153.74	26.77***	0.000
Error	66	379.03	379.03	5.74		
Total	79	2634.20				
Weight						
No.of Sample	9	446554	446554	49617	9.84***	0.000
Parts of tissue	1	0	0	0	0.00	1.000
Seasons	3	265724	265724	88575	17.57***	0.000
Error 66	332730	332730	5041			
Total	79	1045008				
Fe						
No.of Sample	9	391.8	391.8	43.5	0.41	0.928
Parts of tissue	1	3336.8	3336.8	3336.8	31.12***	0.000
Seasons	3	1825.2	1825.2	608.4	5.67**	0.002
Error	66	7076.8	7076.8	107.2		
Total	79	12630.7				
Cu						
No.of Sample	9	66915	66915	7435	0.97	0.476
Parts of tissue	1	7191	7191	7191	0.93	0.337
Seasons	3	22541	22541	7514	0.98	0.409
Error	66	507703	507703	7692		
Total	79	604350				
Mn						
No.of Sample	9	121171	121171	13463	1.60	0.132
Parts of tissue	1	27393	27393	27393	3.26*	0.075
Seasons	3	38035	38035	12678	1.51	0.220
Error	66	554072	554072	8395		
Total	79	740671				
Zn						
No.of Sample	9	496.5	496.5	55.2	0.55	0.836
Parts of tissue	1	1668.3	1668.3	1668.3	16.49***	0.000
Seasons	3	3163.4	3163.4	1054.5	10.42***	0.000
Error	66	6675.7	6675.7	101.1		
Total	79	12003.9				

* = significant at P < 0.05
 ** = significant at P < 0.01
 *** = significant at P < 0.001

concentration of Fe (0.98 ug/g) was recorded in winter season. The maximum levels of Cu concentration in all season of the year in muscles and Cu (10.29 ug/g) was recorded in summer (Table 3). Highest Mn concentration (12.57 ug/g) as corded in muscles in the season of winter, Mn concentration also low in muscles then liver (Table 4). Result of the present study showed that metal accumulation in liver was high especially Cu, Mn, in liver were high in autumn and winter season and low in summer season (Table 3,4). The levels of Fe, and Zn in liver were low in the spring season, and highest in summer season (Table 2 and 5). The completely randomized design with nested treatments analysis of variance (ANOVA) model were used to test the significant differences of heavy metals in fish (*Thunnus tonggol*) between number of samples (10), parts of tissue (2) and seasons (4) (Table 6). The results show that there were high significant variations found between number of samples and seasons for length (F= 34.71 and F=26.77 respectively) and weight (F= 9.84 and F= 17.57 respectively). Significant variations were also found in between parts of tissue and seasons for Fe (F=31.12 and F= 5.67 respectively) and Zn (F= 16.49 and F= 10.42 respectively). The Table 6 showed that significant difference were not found in between number of samples, parts of tissue and seasons for Cu and Mn.

DISCUSSION

Our result shows that generally metal accumulation in *thunnus tonggol* were highest in

Liver and low in muscles. In present study the Cu concentrations was high in liver then muscles in all seasons of the year especially in autumn season. The highest concentration of Cu (245.86 ug/g) was examined in liver in autumn season and lowest concentration of Cu observed (0.62 ug/g) in winter. Liver accumulate high concentration of metals then fish muscles (flesh). Highest concentration of Mn (239.12 ug/g) was observed in autumn in liver where as lowest concentration of Mn (0.05 ug/g) was examined in fish (flesh) of *thunnus tonggol* in same season (autumn). Highest Zn concentration (27.42 ug/g) was observed in summer in the liver of the fish and like high concentration of Zn (7.56 ug/g) was examined in summer in muscles of the *thunnus tonggol*. Feeding habits and life style of species are strongly related to accumulation levels. Bioaccumulation is species dependent and therefore feeding habits and life style can be strongly related to the sediments exposure [15]. The present study found the liver to have accumulated metals higher than other tissue i.e., [16].

The general accumulation pattern of Cd, Cu and Mn (liver > kidney > muscle) was confirmed previously by most authors [17-22]. A number of studies described that various factors such as season [23] length and weight, physical and chemical status of water [24] can play a role in the tissue accumulation of metals. The results show that there were high significant variations found between number of samples, parts of tissue and seasons for length, weight and heavy metals (Fe and Zn). However, it is concluded that, the

metals accumulated easily in liver as compared to muscles, due to it is more delicate part of a body then muscles.

REFERENCES

- [1] Eisler, 1988 Eisler, R. (1988). Zink Hazards to fish, Wildlife and Invertebrates: a synoptic review. US Fish Wildlife Serv. *Biology of Reproduction*, vol.85.
- [2] Karadede and Unlu, 2000 H. Karadede and E. Unlu, Concentrations of some heavy metals in water, sediment and fish species from the Ataturk Dam Lake (Euphrates), Turkey, *Chemosphere* 41 (2000), pp. 1371-1376.
- [3] Wagner And Boman, 2003 A. Wagner And J. Boman, Biomonitoring of trace elements in muscle and liver tissue of freshwater fish, *Spectrochimica Acta Part B* 58 (2003), pp. 2215-2226.
- [4] Saleem and Kazi, G.H., 1998. Concentration and distribution of heavy metals (lead, cadmium, chromium, copper, nickel, zinc) in Karachi shore and offshore sediments. *Pakistan J. mars sci.*, 7, (1998) 71-79.
- [5] Saifullah *et al.*, 2002 S.M. Saifullah, S.H. Khan and S. Ismail, Distribution of nickel in pollut mangrove habitat of the Indus Delta, *Marine Pollution Bulletin* 44 (2002), pp. 551-576.
- [6] Gungum *et al.*, 1994 B. Gungum, E. Unlu, Z. Tez and Z. Gulsun, Heavy metal pollution in water, sediment and fish from the Tigris River in Turkey, *Chemosphere* 290 (1994) (1), pp. 111-116.
- [7] Lee and Stuebing, 1990 Y.H. Lee and R.B. Stuebing, Heavy metal contamination in the River Toad, *Bufo juxtasper* (Inger), near a copper mine in East Malaysia, *Bulletin Environmental. Contamination and Toxicology* 45 (1990), pp. 272-279.
- [8] Mansour, S. A., and Sidky, M. M. 2002. Ecotoxicological studies 3. Heavy metals contaminating water and fish from Fayoum, Governorate, Egypt. *Food chemistry* 78:15-22.
- [9] Guven *et al.*, 1999 K. Guven, C. Ozbay, E. Unlu and A. Satar, Acute Lethal Toxicity and Accumulation of Copper in *Gammarus pulex* (L.) (Amphipoda), *Turkish Journal of Biology* 23 (1999), pp. 513-521.
- [10] L. Hakanson, Metals in fish and sediment from the River Kolbacksan water system, Sweden. *Arch. Hydrobiol.* 101 (1984), pp. 373-400.
- [11] Boudou, A., and Ribeyre, F. 1989. Fish as "biological model" for experimental studies in ecotoxicology. In *Aquatic ecotoxicology: Fundamental concepts and methodologies*, eds. (1989).
- [12] Emami Khansari *et al.*, Emami Khansari, M. Ghazi-Khansari and M. Abdollahi, Heavy metals content of canned tuna fish, *Food Chemistry* 93 (2005), pp. 293-296.
- [13] Badsha Ks & Goldspink CR. 1988. Heavy metal levels in three species of fish in Tjeukemeer, a Dutch polder lake. *Chemosph*, 17: 459-462. Barak Na & Mason CF. 1990b. Mercury, cadmium and lead in eels and roach: The effect of size, season and locality on metal concentrations in flesh and liver. *Sci Total Env*, 92 (1988) 249-259
- [14] Gutierrez, M., R. E stablier and A.M Arias. 1978. Acumulacion y efectos histpatologicos del Cd y el Hg en el pez sapo (*Halobatrachus didactylus*). *Investigaciones pesqueras* 42 (1978) 141-154.
- [15] Chen, M. H., and Chen, C.Y. 1999. Bioaccumulation of sediments bound heavy metal in grey mullet, *liza marcollepis*. *Marine pollution Bulletin* 39 (1999) 238-243.
- [16a] Yousafzai, A.M. and Shkoori, A.R., 2006. Bioaccumulation of chromium, nickel, lead, copper and zinc in the skin of *Tor putitora* as an indicator of the presence of the heavy metal load in River Kabul, Pakistan. *Pakistan J. Zoo.*, 38 (2006) 341-347.
- [16b] Yousafzai, A.M. And Shkoori, A.R., 2007. Chromium, nickel, lead, copper and zinc bioaccumulation in the muscles of Mahaseer, *Tor putitora* as an evidence of the presence of heavy metal pollution in River Kabul, Pakistan *J. Zool.*, 38 (2007) 1-8.

- [17] Mackay *et al.*, 1975 N.J. Mackay, M.N. Kazacos, R.J. Williams and M.I. Leedow, Selenium and heavy metals in Black Marlin, *Mar. Pollut. Bull.* 6 (4) (1975), pp. 57–61.
- [18] Jaffar and Ashraf, 1988 M. Jaffar and M. Ashraf, Selected trace metal concentrations in different tissues of fish from coastal waters of Pakistan (Arabian Sea), *Indian J. Mar. Sci.* 17 (1988), pp. 231–234
- [19] Canli and Atli, 2003 M. Canli and G. Atli, The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species, *Environ. Pollut.* 121 (1) (2003), pp. 129–136
- [20] Bustamante *et al.*, 1998 P. Bustamante, F. Caurant, S.W. Fowler and P. Miramand, Cephalopods as a vector of the transfer of cadmium to top marine predators in the North-East Atlantic Ocean, *Sci. Total Environ.* 220 (1998), pp. 71–80
- [21] Storelli *et al.*, 2005a M.M. Storelli, R. Giacomini, A. Storelli and G.O. Marcotrigiano, Accumulation of mercury, cadmium, lead and arsenic in Swordfish and Bluefin tuna from the Mediterranean Sea: a comparative study, *Mar. Pollut. Bull.* 44 (2005), pp. 281–288.
- [22] Licata *et al.*, 2005 P. Licata, D. Trombetta, M. Cristani, C. Naccari, D. Martino, M. Caló and F. Naccari, Heavy metals in liver and muscle of Bluefin Tuna (*Thunnus thynnus*) caught in the straits of Messina (Sicily, Italy), *Environ. Monit. Assess.* 107 (1–3) (2005), pp. 239–248
- [23] Kargin, 1996 F. Kargin, seasonal changes in levels of heavy metals in tissues of *Mullus barbatus* and *Sparus aurata* collected from Iskenderun Gulf (Turkey), *water, Air and soil pollution* 90 (1996), pp.557-562.
- [24] Jezierska And Witeska, 2001 Jezierska, B., AND Witeska, M. (2001). Metal toxicity to fish. University of podlasie. Monografie No. 42.