International Journal of Fisheries and Aquatic Studies 2015; 2(4): 204-207

ISSN: 2347-5129
IJFAS 2015; 2(4): 204-207

www.fisheriesjournal.com
Received: 09-01-2015
Accepted: 20-02-2015

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Accumulations of Zn, Ni, B, Al and Co in *Megalaspis cordyla* from fish marketed by Karachi Fish Harbor of Pakistan

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Abstract
Zn, Ni, B, Al and Co concentrations were determined in muscle tissues of *Megalaspis cordyla* from fish marketed by Karachi Fish Harbor of Pakistan during January 2007- December 2007. The mean (±SE) of Zn, Ni, B, Al and Co levels in fish muscle tissues were 3±0.25, 0.25±0.035, 0.24±0.038, 0.29±0.026 and 0.24±0.027 mg/kg dry wt., respectively. It was concluded that the level of heavy metals in muscles of the fish species were within acceptable limits by international standards.

Keywords: Heavy metals, *Megalaspis cordyla*, Karachi Fish Harbor, Pakistan.

1. Introduction
Municipal and industrial discharges, urban storm-water runoff and agricultural drainage can result in heavy metals transported into marine coastal areas. The heavy metal contamination in coastal areas is a significant problem, since heavy metals constitute some of the most hazardous substances that can accumulate in aquatic organisms and cause both ecological damage and risk to human health. Karachi is the most important fish harbour in Pakistan coast. However very important industrial zones and marine transport facilities are located along Karachi coast. Industrial activities have led to heavy metal contamination in the marine coast. It is well known that heavy metals are persistent and non-biodegradable pollutants and to conduce toxic effects in fish via food chains by this way posing potential health risk to human fish consumers.

At low levels, some heavy metals such as copper, cobalt, zinc, iron and manganese are essential for enzymatic activity and many biological processes. Other metals, such as cadmium, mercury, and lead have no known essential role in living organisms, and are toxic at even low concentrations. The essential metals also become toxic at high concentrations [1].

Fish are used as marine environmental bio-indicator species to monitor heavy metals pollution. In this study, the torpedo scad *M. cordyla* in the Karachi coastal waters were chosen based on their economic value. The torpedo scad *M. cordyla* is a pelagic fish and feed mainly on fishes and is used as bio-indicator species in different marine waters [2, 3, 4, 5]. The concentrations of Zn, Ni, B, Al and Co were analyzed on the eatable portions of fishes. Zn is an essential element for the aquatic organisms and human beings. Ni is also considered as an essential trace element at very low levels. The main sources of Zn pollution in the environment are zinc fertilizers, sewage sludge and mining. Ni is used as an alloy in the steel industry, electroplating, Ni/Cd batteries, arc-welding, rods, pigments for paints and ceramics, surgical and dental prosthesis, glass containers, computer components and catalysts [6]. Al has no known biological role and its classification into toxic metals is controversial. Co may cause damage to the liver, kidney, circulatory and nerve tissues due to long-term exposure. Although it is well known that fish muscle is not target tissue in accumulating heavy metals, the present study is concerned in heavy metal concentrations in the fish muscles because they are the most consumed portion by the people.

2. Material and Methods
During the January 2007- December 2007, a total of 30 *Megalaspis cordyla* were taken from fish marketed by Karachi Fish Harbor of Pakistan in order to determine the concentrations of Zn, Ni, B, Al and Co and find out whether torpedo scad can serve as a bio-indicator in the marine

ecosystem. Fishes used in the study were first measured the total length and body weight. The muscle tissues of the fish were prepared for analysis according to the method described by [7]. Five grams of muscle tissues were weighted and homogenized. Homogenized fish samples were put into the 50 ml flasks and dried at 105 °C for 24 hours. The flasks taken from drying oven were reweighted out and after the dried weights of samples were obtained, put in test tube separately and 10 ml HNO_3 is included in each 1 g dried weight. Then covered with watch-glass and left overnight. When the fish tissue was dissolved completely, the sample was placed on a hot plate and gradually heated to 105-110 °C until the vapor and the acid fluid inside the flask turned clear. Then the watch-glasses were removed and the samples heated again at 105-110 °C to evaporate the excess acid. The samples were cooled at room temperature and then the 1 ml HNO_3 was used to wash and completed with 25 ml distilled water. Then they were filtered via Whatman filter paper with 45 micron bore diameter. Finally, the digests were quantified into the volumetric flasks with labels and protected at +4 ºC and thus made prepared for analysis [8, 9]. All chemicals used for heavy metal determination were of Analytical Grade (Merck, Germany) and all solutions were prepared using deionized water. Standards of particular elements were prepared from 1000 mg/L stock solutions. The levels of heavy metals were determined by Atomic Absorption Spectrometry (AAS). The solutions were analyzed by using the instrument Analyst 700 and were prepared programme win lab 32 software for heavy metals within the study. The heavy metal analyses in the fish samples were recorded as means ± standard error (SE) of triplicate measurements. The values of heavy metals are expressed as mg/kg dry wt. of the sample. Statistical analysis (ANOVA) was performed to test the differences between seasons and Tukey test was used to determine the differences [10].

3. Results and Discussion

The mean lengths (cm) and weights (g) with standard deviations and ranges of *M. cordyla* from Karachi Harbor are summarized in Table 1. The number of fish samples in each season was 10.

The concentrations of heavy metals found in the torpedo scad muscle tissues are given in Figure 1. The ranges of Zn, Ni, B, Al and Co levels in fish muscle tissues were 1.06-6.63, 0.01-0.78, 0.03-0.88, 0.11-0.74 and 0.02-0.56 mg/kg dry wt., respectively. The statistical results presented in Table 2 indicate that Zn concentrations were considerably higher in the muscle tissues of *M. cordyla* than other metals ($P<0.05$) and that there was a statistically significant difference between the concentrations of the metals among seasons. The Zn concentrations in fish tissues were 11 to 13 times higher than those of other heavy metals. From the data presented in Figure 1, it is observed that, during post-monsoon Zn, Al and Co were higher levels than those in pre-monsoon and monsoon, whereas maximum Ni and B levels were found in monsoon. Similarly Ahmed *et al*. [5] (2014) showed that Fe, Mn, Cd, Pb and Cr concentrations in *M. cordyla* varied significantly with seasons. The differences of metal levels in *M. cordyla* at different seasons most probably depend on the condition of the fish in its habitat. *M. cordyla* showed positive allometric growth in post-monsoon indicating the fish feeds more in that time [11].

The data presented on the heavy metal contamination of marine organisms were different depending on pollution sources, metals and species. Table 3 gives the results of the selected heavy metals (Zn, Ni, B, Al and Co) in fish species collected from the Karachi coasts of Pakistan. The Karachi coasts of Pakistan itself has already been the victim of unmanaged fisheries, of unrestricted intense shipping activities and of the dumping of toxic wastes [12, 13]. Consequently, persistent substances are concentrated in fish and man may be exposed to an accumulated hazard. When the metal concentrations were compared among the Pakistan coasts (Table 3), Zn concentrations were found to be highest in *Trichiurus lepturus* of Karachi coasts [14] and it was followed by *Acanthopagrus berda* of Baluchistan coasts [15] and *Thunnus tonggol* of Karachi coasts [16]. Ni concentrations were found to be highest in *Tenualosa ilisha* and it was followed by *Kowala coval* and *Platycephalus indicus* of Keti Bunder [17]. Co was highest in *Protonibea diacanthus* and followed by *Pampus chinensis* of Karachi coasts [15]. In terms of metal pollutants load from Pakistan coast many researches (Table 3) concluded that heavy metal pollution in living organisms of the marine environment has attracted considerable research attention since last 12 years. Since *M. cordyla* is commercial importance [11] and local people consume them as a fresh food [18] it is very important to assess the risk of consumption. According to the Food and Agriculture Organization, the average quantity of fish consumed per a person (assuming a 70-kg person) per a day in Pakistan is 5 g, which is equivalent to 35 g for a week [19]. Multiplying this value by the average concentration of each metal (Zn, Ni, B, Al and Co) in *M. cordyla*, the average weekly intake of the metals from fish can be estimated. The daily consumption of Zn, Ni, B, Al and Co in the torpedo scad of the present study was ranged from 0.04 to 0.23, 0.0004 to 0.03, 0.001 to 0.03, 0.004 to 0.03 and 0.0007 to 0.02, respectively. Results indicated that the concentrations were below the limits for fish proposed by FAO/WHO and safe within the limits for human consumption in the edible parts of fish species in that region.

It can be concluded that the mean levels of heavy metals in muscle tissue of the torpedo scad taken from the Karachi Harbor of Pakistan were very low and the current limit for residues, which is valid in the international standards, was not exceeded in any case. It may be said that Pakistan is developed country where industrial and urban development's mostly occur in coastal areas through increased input of wastes impose a further stress on the Karachi coasts of Pakistan. Thus it is better to continue the searches on the heavy metal pollution effects on fish comparatively before reaching any exact conclusion.

Table 1: Mean± SD, minimum and maximum of length (cm) and weight (g) of *Megalaspis cordyla* during different seasons of January 2007 and December 2007.

Seasons	N	Length (cm) mean ±SD (min-max)	Weight (g) mean ±SD (min-max)
Pre-monsoon	10	24±4 (19-32)	140±25 (112-186)
Monsoon	10	29±4 (22-36)	175±25 (118-216)
Post-monsoon	10	30±4 (24-38)	178±25 (144-228)
Total	30	28±5 (19-38)	164±30 (112-228)

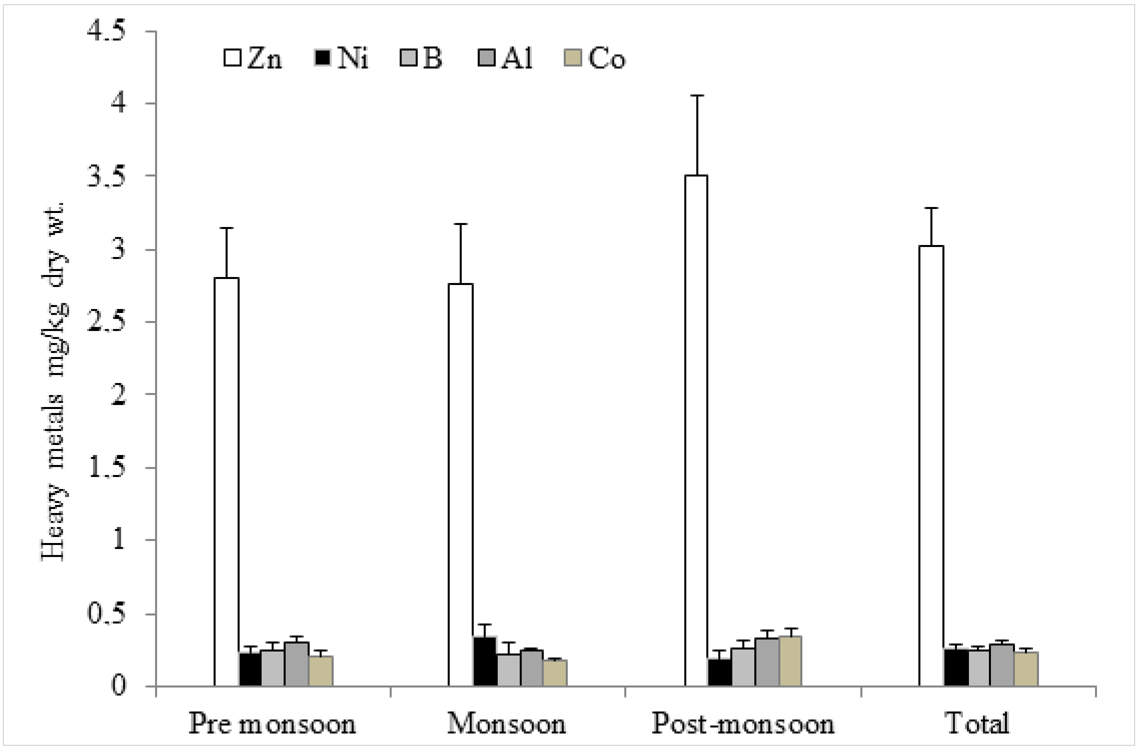

Fig 1: Heavy metal levels (mg/kg dry wt.) in muscle tissues of *Megalaspis cordyla* during January-2007-December-2007.

Table 2: Analysis of variance (ANOVA) in *Megalaspis cordyla* from the Karachi Fish Harbour during different seasons of January 2007 and December 2007.

Metals		Sum of Squares	df	Mean Square	F	Sig.
Zn	Between Groups	3.5	2	1.77	0.91	0.42
	Within Groups	53	27	1.95		
	Total	56	29			
Ni	Between Groups	0.11	2	0.06	1.59	0.22
	Within Groups	0.97	27	0.04		
	Total	1.1	29			
B	Between Groups	0.004	2	0.002	0.05	0.95
	Within Groups	1.23	27	0.05		
	Total	1.24	29			
Al	Between Groups	0.04	2	0.02	0.89	0.42
	Within Groups	0.55	27	0.02		
	Total	0.59	29			
Co	Between Groups	0.15	2	0.08	4.39	0.02
	Within Groups	0.48	27	0.02		
	Total	0.63	29			

Table 3: Heavy metal concentrations in muscle tissues of fish from the Pakistan coasts (expressed in µg metal g^{-1} wet wt., * =dry wt.)

Fish species	Area	Heavy Metals					References
		Zn	Ni	B	Al	Co	
Pampus argenteus	Karachi	--	--	--	--	0.248± 0.02	[20]
Pampus chinensis	Karachi	--	--	--	--	0.350± 0.02	[20]
Parastromateus niger	Karachi	--	--	--	--	0.159± 0.02	[20]
Protonibea diacanthus	Karachi	--	--	--	--	0.490± 0.02	[20]
Otolithes ruber	Karachi	--	--	--	--	0.137± 0.01	[20]
*Acanthopagurus berda**	Baluchistan	3.65-4.32	--	--	--	--	[15]
Pampus argenteus	Keti Bunder	1.425± 0.186	0.180± 0.11	--	--	--	[17]
Tenualosa ilisha	Keti Bunder	0.460± 0.100	1.420± 0.152	--	--	--	[17]
Sardinella sindensis	Keti Bunder	1.215± 0.136	0.244± 0.003	--	--	--	[17]
Labeo rohita	Keti Bunder	1.490± 0.109	0.149± 0.002	--	--	--	[17]
Platycephalus indicus	Keti Bunder	1.029± 0.060	0.266± 0.003	--	--	--	[17]
Kowala coval	Keti Bunder	1.184± 0.070	0.286± 0.003	--	--	--	[17]
*Trichiurus lepturus**	Karachi	9.86±0.49	--	--	--	--	[14]
*Thunnus tonggol**	Karachi	1.93-3.89	0.18-0.35	--	--	--	[16]
Megalaspis cordyla	Karachi	3±0.25	0.25±0.035	0.24±0.038	0.29±0.026	0.24±0.027	This study

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