# Heavy Metals Contamination in Fish and Shrimp from Coastal Regions of Karachi, Pakistan

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**Abstract.** In the present study, the heavy metals (Pb, Cu, Cd, Fe, Zn) concentration was determined by using atomic absorption spectrophotometer (AAS) in 5 species of fish and 3 species of shrimp commonly taken by locals at the coastal regions of Karachi, Pakistan Concentrations of Cd and Pb studied in tissues of Mushka (*Otolithes ruber*, 0.120 and 1.018 μg/g wet weight) and *Palaemon longirostris* shrimp (2.457 and 0.480 μg/g wet weight) were found near to safe level for human consumption. Mullet, Tarli, Surmai, Dohtar fishes and Blacktiger shrimp were found contaminated by Cd and Pb but still within the limits fit for and human consumption. The distribution of trace metals detected in all fish and shrimp species followed the order of Zn >Pb> Fe>Cu> Cd and Cd> Fe > Zn> Cu>Pb, respectively. Metal concentration exhibited significant species variation and followed the order in fishes as *Otolithes ruber> Liza vaigiensis>Sardinella albella >Scomberomorus guttatus>Pomadasys olivaecum* and in shrimp as *Palaemon longirostris>Penaeus monodon>Penaeus penicillatu*.

Keywords: heavy metals, fish, shrimp, tissues, Karachi coast

## Introduction

Heavy metals discharged into the marine environment can damage both marine species diversity and ecosystem due to their toxicity (Turkmen et al., 2009). Heavy metals including essential and non-essential elements have particular significance in ecotoxicology because they are highly persistent and have toxic potential for living organisms (Storelli et al., 2005). These toxic effects of metals and organic contaminants have been well studied at numerous locations throughout Pakistan (Tariq et al., 2007). Fish are often at the top of the aquatic food chain and may contain large amount of some metals from the water (Mansour and Sidky, 2002), making it necessary to determine the levels of certain heavy metals in the fish species and shrimp that are consumed by coastal villagers in order to minimize their health risk. It has been reported that the presence of metals particularly lead (Pb) in certain foods enhances toxicological effect frequencies in man (Levy et al., 1985). For example, cadmium (Cd), lead (Pb) and mercury (Hg) producing injury to kidneys leading to features of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension,

tumors and hepatic dysfunction (Varsha *et al.*, 2010). The limits of metal contaminants particularly in fish and shrimp have led to health concerns for high-risk populations, such as pregnant women and children (EPA, 1989).

International level of Cd, Zn, and Cu are given as 3, 50 and 20  $\mu$ g/g wet wt, respectively by US FDA (1993a) and 1.5, 60 , 200 and 3 in marine biota muscle (ppm dry weight) for Cd, Cu, Zn, and Pb (US FDA, 2003).The maximum level of Cd in fish meat and Crusactean 0.05-1.00(mg/kg wet weight) and maximum levels of lead in fish has been changed to 0.30 mg/kg fresh weight by the EU (2006).

Generally residents of our coastal areas are very poor and do not have a good sense of food security therefore, it is the duty of the concerned authorities to focus on this aspect and ensure that food security objectives are incorporated into national poverty reduction strategies. This would have impact at the national, sub-national, household and individual levels with particular emphasis on reducing hunger and extreme poverty (FAO, 1983).

The present study was undertaken to determine the concentration of heavy metals (Pb, Cu, Zn, Fe, Cd) in

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commonly eaten food of fish and shrimp species of coastal regions of Karachi, Pakistan.

## **Materials and Methods**

**Sampling.** All samples of fishes and shrimps were collected from January to December 2011 at a frequency of twice per week.

The most eaten fish were identified as *P. olivaecum* (Dhotar), *S. albella* (Tarli), *L. vaigiensis* (Mullet), *O. ruber* (Mushka), *S. guttatus* (Surmai) and three species of shrimp *P. pencillatus*, *P. monodon* and *P. longirostris*. Five specimen of each species were collected. The samples were dried in filter paper, packed in pre cleaned polyethylene bags and stored below -20 °C prior to further analysis (Yilmaz *et al.*, 2007).

Samples were collected from kitchens of village houses, so all fishes were already washed in their kitchens and in Laboratory these were again washed with de-ionized water before sub sampling.

**Sample preparation.** The homogenized fish tissues (edible part) and shrimps sample (2 g each) were digested in concentrated HNO<sub>3</sub> (65%) and HCl (35%) of analytical grade (Merck, Darmstadt, Germany) (Zachariadis *et al.*, 1995). The samples were placed on a hot block for digestion at 70 °C for 1 h: before they were fully digested at high temperature (140 °C) for at least 3h.

The digested samples were then diluted to 50 mL with de-ionized water and filtered through Whatman No. 42 filter paper.

Standard solution of Cd, Pb, Cu, Fe and Zn were prepared from stock solution (1000  $\mu g/mL$ ) Fluka Kamica (Switzerland) of corresponding metal ions. Standard reference material (SRM) was purchased from National Institute of Standards and Technology (NIST), working solution of Cd, Pb, Cu, Fe and Zn were prepared from standard solution (1000  $\mu g/mL$ , Merck). Immediately before use blanks were also prepared in the same manner as that of the samples.

**Instrumentation.** Hitachi Z-5000 Graphite and Flame Atomic Absorption Spectrophotometer with Zeeman background was used for the determination of Cd and Pb, while essential Fe, Cu and Zn were analysed by the flame atomic absorption spectrophotometer (FAAS).

**Statistical analysis.** Statistical analysis was done using Tukey's mean comparison test. All calculations were

carried out by using Excel for Windows on the basis of linear equations (Table 2).

Quality control. The standard addition approach was adopted in order to avoid matrix interferences (Beavington *et al.*, 2004) and appropriate dilutions were made prior to the analysis. The known amount of standards (0.2, 0.4, 0.8 mg/L) was spiked using replicate 6 samples of each, and applied both digestion methods. For quality control, standard solutions of Cd, Pb, Zn, Cu, Fe, were analyzed in every 5 samples to check for the recoveries (Yap *et al.*, 2004).

Mean values of triplicate sample were subjected to calculation and correlation matrices were produced to examine the inter-relationships between the investigated metal concentrations of the fish samples.

#### **Results and Discussion**

The metal concentration (µg/g) of Cd, Pb, Zn, Cu and Fe is presented in Table 1 for 5 fish and 3 shrimp species. Relative concentration of metals detected in 5 fish species and 3 shrimp species have shown a relationship between metals and among species variation in case of shrimp as well as fish (Fig. 1-2). Results show that concentration of Cd varied from 0.017 up to the maximum 0.120 with a mean value 1.25 µg/g (Table 1) which is higher than 0.32-0.66  $\mu/g$  found in Saudian tuna (Voegborlo et al., 1999) and 0.35 µg/g in fish from Arabian sea (Tariq et al., 1993). This is due to recent increase in metal pollution in Arabian sea from where these fish were caught and may be due to interspecies differences (uptake, deposition or excretion). Similarly, the level of Pb ranged from 0.122 to 1.018 with a mean of 0.63 µg/g which is also higher than average permissible values however Zn, Cu and Fe were found within the permissible limits (EC, 2005). Metal contents along with relevant statistical data means with standard deviation are given in Table 2. The coefficient of variation were collectively calculated for fish and shrimp samples and only two elements were strongly correlated. The significant correlation coefficient (r <1.00) was found between Pb, Cu and Cd.

Good recoveries (%) 97, 96, 98, 99 and 101 for Cd, Pb, Fe, Zn and Cu, respectively of spiked sample demonstrates the accuracy of the method used. Detection limits were calculated as for  $0.001 \mu g/g$ , Cd  $0.003 \mu g/g$  for Pb and  $0.005 \mu g/g$  for Fe (Table 2).

The metal content in all three species were found lower than detected in other countries, as in Bangladesh the 48 Syed Sanower Ali *et al.* 

level of Pb and Cd was 0.8-1.3 and 0.2-0.4 in *P. monodon* (Fig. 1-2) (Hossain and Khan, 2001).

In case of shrimp, all metals' concentrations were found in lower range as compared to selected fish species (Table 1). Level of contamination of any metal in marine fauna depends upon accumulation of that metal. The level of Cu in the liver was found to be higher than the muscle (Papagiannis *et al.*, 2004). The maximum concentration of Pb and Cd was 0.489 and 2.457 μg/g, respectively in *P. longirostris* which is lower than observed in the same species of India that is 62.5 for Pb (Mitra *et al.*, 2000) and 2.50 for Cd in *P. monodon* (Mitra *et al.*, 2012). Metals accumulate differentially in fish organs and cause serious health hazards to

humans. For this reason, the problem of fish and other aquatic contamination by toxic metals has received much attention (Mansour and Sidky, 2002).

The results of the analysis indicate that concentration of the Cd varied from 0.02 to 0.12 with a mean of 0.0-08  $\mu$ g/g in 5 species of fish and in shrimp ranged from a mean of 0.21-0.25. The concentration of Cd in all samples of fish and shrimp analysed were below the permissible limit of 0.05 mg/kg limit of Cd set by European Union (EU, 2001) and also lower than 3.70 ( $\mu$ g/g wet wt.) recommended limit by United States Food and Drug Administration (USFDA, 1993b).

The mean concentration of lead was found to be 0.12-1.012  $\mu$ g/g and shrimp samples were much below the

**Table 1.** Toxic and essential element contents in fish and shrimp species from coastal regions of Karachi

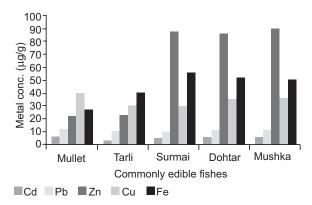
Fish and shrimp	Common	Cd	Pb	Zn	Cu	Fe	
species	names	(μg/g wet weight)					
Fish species							
Liza vaigiensis	Mullet	0.121-0.233	0.095-0.270	1.012-1.185	0.490-0.635	0.014-1.102	
	$0.030\pm0.05$	$0.160\pm0.07$	$0.007 \pm 0.04$	$0.160\pm0.07$	$0.180\pm0.07$		
Sardinella albella	Tarli	0.022-0.235	0.090-0.335	0.026-1.635	0.502-0.585	1.010-1.635	
	$0.040\pm0.22$	$0.157 \pm 0.07$	$1.530\pm0.07$	$0.007\pm0.04$	$0.125\pm0.050$		
Scomberomorus guttatu.	s Surmai	0.027-0.031	0.097-0.321	0.026-0.031	0.057-0.491	0.613-1.321	
	$0.026\pm0.01$	$0.122 \pm 0.03$	$1.026 \pm 0.01$	$0.006 \pm 0.05$	$0.140\pm0.039$		
Pomadasys olivaecum	Dohtar	0.02-0.250	nd*	1.01-0.050	0.055-0.680	1.015-1.421	
	$0.017 \pm 0.06$		$1.018\pm0.08$	$0.008\pm0.07$	$0.131\pm0.048$		
Otolithes ruber	Mushka	0.036-0.343	1.02-0.450	0.045-0.076	0.054-0.665	0.692-1.141	
	$0.120\pm0.03$	$1.018\pm0.07$	$0.008 \pm 0.07$	$0.050\pm0.01$	$0.158\pm0.07$		
Shrimp species							
Penaeus penicillatus	Jaira or	0.205	0.395	0.931	0.515	1.024	
•	redtail prawn	(0.126-0.204)	(0.216-0.384)	(0.560-1.302)	(0.316-0.764)	(0.659-1.389)	
Penaeus monodon	Blacktiger	0.215	0.415	0.915	0.415	1.011	
	shrimp	(0.124-0.254)	(0.416-0.494)	(0.516-1.264)	(0.416-0.564)	(0.547-1.089)	
Palaemon longirostris	Roshma prawn	2.457	0.489	0.895	0.546	0.956	
	(English)	(2.192-2.322)	(0.454-0.519)	(0.496-1.364)	(0.485-0.606)	(0.659-1.389)	

nd = not detected

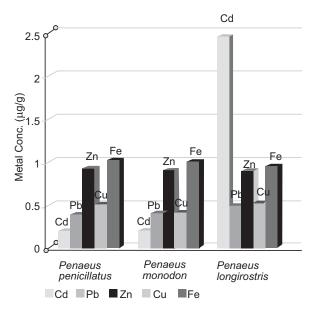
**Table 2**. Metal contents along with relevant statistical parameters in fish and shrimp samples

Metals	Detection limit (μg/g)	Range	X	±SD	CV%	*Permissible limits (µg/g wet wt.)
Cd	0.001	0.017- 2.457	1.25	1.24	25.8	0.05
Pb	0.003	0.122- 1.018	0.63	0.63	41.3	0.20
Zn	0.005	0.008- 1.530	0.77	0.76	39.8	120.0
Cu	0.003	0.006- 0.546	0.28	0.28	24.8	30
Fe	0.005	0.956 -1.024	1.47	1.44	41.3	125.0

<sup>\* =</sup> Maximum acceptable levels of heavy metals in fish muscles (EC, 2005)



**Fig. 1.** Relative concentration of metals detected in fish meat as part of meal.



**Fig. 2.** Leave of toxic metals in shrimp species.

permissible limit. For Cu ( $\mu$ g/g) Canadian Food Standard (2011) is 100, acceptable Hungarian standard 60, the range of international standard is 10-100. Turkish range of international standard is 10-100, limit 20 (Papagiannis *et al.*, 2004), USEPA (2000) limit 120, and toxic limit for fish by FAO (1983) is 30 mg/kg. Cu concentration in all fish and shrimp samples analyzed was below the corresponding authorized limits.

The potential hazards of metals transferred to humans are probably dependent on the amount of fish/shrimp consumed by an individual. Average intake of fish in Pakistan is plus 2 kg per capita per annum according to National Policy and Strategy for Fisheries and Aquaculture Development in Pakistan (NPSFAD, 2007). The estimates of JECFA (2003) recommended provisional tolerable total weekly intake (PTWI) for

Pb as 1.5 mg/week and JECFA (2000) regarding provisional daily intake (PTDI) for Pb as 25  $\mu$ g/kg which is equivalent to 0.21 mg/day. The dietary intake of fish and prawn estimated from the present study is well below these dietary intakes and the tested fish and prawn samples therefore do not represent any known health risk to local population. If the consumer take the prawn or fish for 7 consecutive days, then he will consume 1.20  $\mu$ g Cd (1.20×7 days) from fish or 1.50  $\mu$ g Cd (0.147×7 days) from prawn than expected Cd intake is lower than the recommended limit for provisional tolerable weekly intake of Cd (6.70-8.30  $\mu$ g/adult) recommended by JECFA (2003) which is 490  $\mu$ g.

A linear regression correlation test was performed to investigate the metal to metal correlation studies. Correlations between metal concentrations in fish are presented in Table 3. A positive correlation exists between Cu & Zn, Fe & Cu, Pb & Zn, Pb & Cu, Pb & Fe, Cd & Zn and Cd & Cu with corresponding 'r' values of 0.137, 0.275, 0.051, 0.192, 0.521 and 0.011, respectively. A negative correlation exists between Fe & Zn, Cd & Fe and Cd & Pb with corresponding 'r' values of -0.445, -0.547 and -0.265, respectively. The significant correlation was found positively between Cd & Zn and negatively between Cd & Fe only (P-value < 0.05) (Table 3).

Levels of heavy metals (copper, cadmium, lead, iron and zinc) in tissues of *P. penicillatus* were found to be below the acceptable limits of heavy metal pollution in fish and shell fish (FAO/WHO, 1984). Mean levels of lead (Pb), and cadmium (Cd) were observed to be higher than the world standard but not significantly higher. The joint Food and Agricultural Organization/World Health Expert Committee on food additives has suggested a provisional tolerable intake of 400-500 µg Cd/week for man and allowed Pb intake of 3 mg/week. This shows that the levels of lead and cadmium in the fishing areas of Karachi

**Table 3.** Pearson correlation coefficient among the metals content found in fishery samples

Elements	Zn	Cu	Fe	Pb	Cd
Zn	1.000	-	-	-	-
Cu	0.137	1.000	-	-	-
Fe	-0.445	0.275	1.000	-	-
Pb	0.051	0.192	0.231	1.000	-
Cd	0.521	0.011	-0.547	-0.265	1.000

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Location	Species	Zn	Cu	Pb	Cd	Fe	References
Karachi coast	Penaeus monodon	0.516-	0.416-	0.416-	0.124-	0.547-	Present study-
		1.264	0.564	0.494	0.254	1.089	2011-12
Gulf of Fonseca	Penaeus monodon	19-30	2.1-	0.035-	0.002+0.03	-	Carbonell and
			6.9	0.5			Zona, 1994
Bangladesh	Penaeus monodon	24.2-	12.2-	0.8-	0.2-0.4	-	Hossain and
		35.7	21.3	1.3			Khan, 2001
Indian Sundarbans	Penaeus monodon	16-80	10-60	5.50-10	BDL-2.50	-	Mitra at al., 2012
Winam Gulf,	Oreochromis niloticus,	28.9-	2.13-	0.47-	0.17-0.40	31.4-	Ongeri et al., 2012
Lake Victoria	Lates niloticus and	409.3	8.74	2.53		208.1	
	Rastrineobola argentea						

**Table 4.** Metals concentration found in fish and shell fish of other countries

coast are still tolerable and comparable with finding from other countries (Table 4).

Levels of various metals in fishery may vary due to a variety of factors. The results of present study indicate that, metal contaminated fish is consumed as food and neadst proper planning to control/check the supply of contaminants free fish. Maximum effort should be done to control marine pollution. Fish harbour hygiene condition and regular inspection of supply should be carried out. It must be implicated to have daily testing of fishery before they are supplied to the consumers. The concentrations of cadmium and lead previously reported were 0.006-0.088 and 0.016-0.049 µg/g are similar to our results.

The specificity of concentrations of heavy metals irrespective of the locality of fish capture and the route of uptake of the metals has been reported by Eneji (2010). Varied level of contamination in the fish species is a reflection of different thresholds of metals which are a function of homeostasis. Species difference in heavy metals bioaccumulation could be linked to difference in feeding habits and behaviour of the species (Altindag and Yigit, 2005). It has been reported that fish species can accumulate heavy metals above the abiotic environment to incur bioaccumu-lation (Olaifa *et al.*, 2004) and it is directly related to marine pollution status of the specific region, type of fishery and specific time period of breeding season.

Maximum mean Pb and Cd concentrations in *Penaeus* shrimp species in Trinidad are  $22.84\text{-}26.78~\mu\text{g/g}$  wet wt. which are below the maximum admissible limits of human consumption according to international and local standards thus safe for consumption although coastline

of Gulf of Paris is considered to be highly polluted due to industrialized area of the region (Dhoray and Teelucksingh, 2007). In the present study, the maximum mean concentration was found as 2.457 and 0.489  $\mu g/g$  which is also below the maximum residual limits of Pb and Cd.

## **Conclusion**

The present study clearly indicates low accumulation of heavy metals in the edible fishery of Karachi coast. Most of the metal concentrations (except Pb) in the fish and shrimp samples analyzed were well within the permitted limits set by various authorities and therefore, does not poses any health risk. However, regular monitoring on heavy metals accumulation in fish and shrimp tissues by local agencies should be emphasized.

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