Occurrence of Heavy Metal Residues in Fish and Fishery Products Exported from India

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Several species of fish and shellfish from marine and freshwater sources are exported to foreign countries. These products are to be monitored for the toxic heavy metal residues such as mercury, cadmium and lead. Some species like cephalopods have a tendency to concentrate these metal residues, particularly cadmium, in their tissues. Heavy metal residues in samples of fish and fishery products processed for export from India were monitored for one year. Out of sixty different samples, only five specimens showed high values of Pb (>3 ppm). All other specimen showed lead content much below the tolerance limit. The values for cadmium was in the range 0 – 4.39 ppm. Out of 60 samples, only in one sample Cd was above the tolerance limit of 3 ppm. The levels of mercury in all the samples were either nil or much below the tolerance limit of 0.5 ppm. Heavy metals in the edible parts of the fish samples were in the safe permissible levels for human consumption.

Key words : Heavy metal residue, seafood safety, tolerance limit

Fish are a major part of the human diet and it is, therefore, not surprising that numerous studies have been carried out on the presence of metal residues in different species of edible fish (Kucuksezgin *et al.*, 2001). Fish are widely used to evaluate the health of aquatic systems, and physiological changes in fishes serve as biomarkers of environmental pollution (Winger *et al.*, 1990; Barak and Mason, 1990; Evans *et al.*, 1993). The importance of biomonitoring of heavy metals have already been reported by many authors (Goldberg, 1980; Phillips and Rainbow, 1993).

Heavy metals like copper, zinc and iron are essential for fish metabolism while some others such as mercury, cadmium and lead have no known role in biological systems. For the normal metabolism of fish, the essential metals must be taken up from water, food or sediment. However, along with essential metals, non-essential ones are also taken up by fish and accumulated in their body organs

(Ba'lint *et al.*, 1997). The distribution of some heavy metals in samples of fish and fishery product, derived from seafood factories in southern India was studied, during 2003-04.

Materials and Methods

The method recommended by the AOAC (1980) was followed for digestion of samples with slight modification for microwave digestion. Tissues of fish or shrimp were cut into smaller sizes, the moisture in the samples removed using Whatman No.1 filter paper, homogenized completely, and kept in an oven at 90°C. After the tissues reached constant weights in the oven, the sample was weighed and transferred into digestion flasks. Perchloric acid (4 ml) and nitric acid 9 ml (Merck) were added and kept in microwave digestion chamber. The digests were diluted with double distilled de-ionized Milli-Q water appropriately in the range of standards that were prepared from stock standard solution of the metals (Merck).

Metal concentrations were measured using a Varian Spectra AA220 flame atomic absorption spectrophotometer with background correction. The metal concentration in the sample was presented as mg metal/kg wet weight. A blank was run for each digestion procedure to correct the measurements. For sets of every ten samples, a procedure blank and spike sample, involving all reagents, were run to check for interference and cross contamination. Varian Spectra AA 220 with VGA 77 vapour generation accessory with lamp current of 4.0 mA and background correction off is used for analysis of Hg. Mercury ions in solution can be reduced by $SnCl_2$ or $NaBH_4$ (25% $SnCl_2$ in 20% v/v HCl Merck grade) to metallic mercury which is swept out of the solution by an inert gas (together with hydrogen liberated by acid hydrolysis of $NaBH_4$) to a long-path quartz absorption cell for AAS measurement (Welz, 1985). The maximum absorbance was obtained by adjusting the cathode lamps at specific slit width and wavelengths.

Results and Discussion

The mean concentration of lead, cadmium, mercury, copper, and zinc in different samples have values lower than reported elsewhere, especially for cadmium, lead and mercury. The heavy metals showed differential bioaccumulation in fish organs. Among the analyzed metals (cadmium, lead, mercury, copper, and zinc), lead and cadmium were found in fish at mean concentrations above the permissible limits proposed by FAO in some samples. The study has shown that there was considerable variation in the concentration of heavy metals from one sample to the other.

Table 1. *Heavy metal concentrations (in ppm) in specimens collected from seafood industries of Southern India*

Fish	Period	Tissue	Pb	Cd	Hg	Cu	Zn
Cuttlefish	Jun - Jul	Muscle	0.02 - 1.0	0.008 - 0.80	0.03 - 0.05	0 - 0.163	Nil
Squid	Jun - Jul	Muscle	0.04 - 1.2	0.06 - 1.62	0.01 - 0.04	Nil	Nil
Octopus	Jun - Jul	Tentacle	0 - 0.12	0 - 0.008	0 - 0.03	Nil	0.065
Shrimp	Jun - Jul	Muscle	0.01 - 0.6	0.02 - 0.24	0.01 - 0.03	Nil	Nil
Octopus	Aug - Sep	Muscle	0.229 - 10.81*	0.08 - 0.17	0.003 - 0.021	Nil	Nil
Cuttlefish	Aug - Sep	Muscle	0.566 - 0.78	0.07 - 0.19	Nil	0.01	Nil
Squid	Aug - Sep	Tentacle	0.13 - 30.76*	0.13 - 0.53	0.019 - 0.04	Nil	Nil
Shrimp	Aug - Sep	Muscle	0.39 - 11.01*	0.03 - 0.08	0.003 - 0.048	Nil	Nil
Octopus	Oct - Nov	Muscle	Nil	0 - 1.148	Nil	Nil	Nil
Cuttlefish	Oct - Nov	Muscle	0 - 13.12*	0 - 0.02	Nil	Nil	Nil
Squid	Oct - Nov	Muscle	Nil	0 - 0.122	Nil	Nil	Nil
Shrimp	Oct - Nov	Muscle	0 - 0.98	0 - 0.122	Nil	0.012	Nil
Octopus	Dec - Jan	Muscle	Nil	Nil	Nil	Nil	Nil
Cuttlefish	Dec - Jan	Muscle	Nil	0 - 0.026	Nil	Nil	Nil
Squid	Dec - Jan	Muscle	Nil	0 - 0.122	Nil	Nil	Nil
Shrimp	Dec - Jan	Muscle	0 - 0.98	0 - 0.122	Nil	0.013 - 1.00	Nil
Cut crab	Feb - Jun	Muscle	0.093	Nil	Nil	Nil	Nil
Cuttlefish	Feb - Jun	Muscle	0.56 - 0.86	0 - 4.39*	Nil	0.04	Nil
Shrimp	Feb - Jun	Muscle	0 - 3.76*	0.58	Nil	Nil	Nil

*Above the tolerance limit.

Out of 60 commercial samples, five specimens showed very high values of Pb above 3 ppm (range: 10.81 – 30.76 ppm). Some cephalopod samples had lead and cadmium in higher levels of 25.75 ppm and 4.40 ppm, respectively, which exceeded the tolerance limits for lead (1.5 ppm) and cadmium (3 ppm). All other specimens showed lead content much below the tolerance limit (0-1 ppm). The values for cadmium was in the range 0 – 4.39 ppm. Out of 60 samples, only in one sample Cd was above the tolerance limit of 3 ppm (Table 1).

Organisms retain both metals, Cu and Zn, through specific binding proteins known as metallothioneins in their liver (Allen-Gil and Martynov, 1995). Metallothioneins play an important role in metal homeostasis and in protection against heavy-metal toxicity (Olsson *et al.*, 1989). Metallothioneins for lead binding has been discovered in kidney, liver, and brain (Beck, 1992). The low concentrations of Cu and Zn in the muscles of the examined fish species may reflect the low levels of these metal binding proteins in the muscle.

The levels of mercury in all the commercial samples are either nil or much below the tolerance limit of 0.5 ppm. On the basis of the recommended daily dietary allowances (RDA) for safe consumption of fish muscle, the allowed intake is regulated at ppm levels (NRC, 1980). Based on the results, it could be concluded that the examined fish were not associated with enhanced metal contamination in their muscle and were within safe limits for human consumption.

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