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Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards

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Abstract

Heavy metals are an important group of chemical contaminants and food is the major vehicle for entry into the system. Fish constitute a major source of heavy metals in food. Concentration of heavy metals in commercially important species of fish, shellfish and fish products from fish markets in and around the Cochin area was evaluated using an atomic absorption spectrometer. The concentration ranges of Cd, Pb, Hg, Cr, As, Zn, Cu, Co, Mn, Ni, and Se in the samples were <0.07–1, <0.07–1.32, <0.05–2.31, <0.05 to 3.65, <0.1–4.14, 0.6 to 165, 0.15 to 24, <0.02 to 0.85, <0.08 to 9.2, <0.032–1.38 and; <0.03–1.35 mg/kg, respectively. The present study showed that different metals were present in the samples at different levels but within the maximum residual levels prescribed by the EU and USFDA and the fish and shellfish from these areas, in general, are safe for human consumption.

Keywords: Heavy Metals; Mollusks; Cephalopods; Crustaceans; Fish; Fish products; Cochin; Kerala; EU; USFDA; FAO

1. Introduction

Marine organisms, in general, accumulate contaminants from the environment and therefore have been extensively used in marine pollution monitoring programmes (UNEP, 1993; Uthe et al., 1991). In many countries, significant alterations in industrial development lead to an increased discharge of chemical effluents into the ecosystem, leading to damage of marine habitats. Heavy metal discharged into the marine environment can damage both marine species diversity and ecosystems, due to their toxicity and accumulative behaviour (Matta, Milad, Manger, & Tosteson, 1999). As the spawning and nursery grounds of many marine species, including the commercially valuable shrimps and fish, are located in estuarine and coastal areas, they are directly affected by such influx of chemical contaminants into the marine ecosystem (Gibson, 1994).

The accumulation patterns of contaminants in fish and other aquatic organisms depend both on their uptake and elimination rates (Guven, Ozbay, Unlu, & Satar, 1999). Heavy metals are taken up through different organs of the fish and many are concentrated at different levels in different organs of the body (Bervoets, Blust, & Verheyen, 2001; Rao & Padmaja, 2000; Scharenberg, Gramann, & Pfeiffer, 1994). Fish form an important part of human food and it is therefore not surprising that numerous studies have been carried out on metal pollution in different species of edible fish (Kucuksezgin, Altay, Uluturhan, & Kontas, 2001; Kureishi, Sujatha, & Analia, 1981; Lakshman & Nambisan, 1983; Lewis et al., 2002; Prudente, Kim, Tanabe, & Tatsukawa, 1997; Radhakrishnan, 1994; Ramamurthy, 1979; Sankaranarayanan, Purushan, & Rao, 1978; Senthilnathan & Balasubramanian, 1998; Sultana & Rao, 1998).

Industrial wastes and mining can create a potential source of heavy metal pollution in the aquatic environment (Gumgum, Unlu, Tez, & Gulsun, 1994; Lee & Stuebing, 1990). Under certain environmental conditions, heavy metals might accumulate up to toxic concentrations and cause ecological damage (Guven et al., 1999). Thus, heavy metals, acquired through the food chain as a result of

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pollution, are potential chemical hazards, threatening consumers.

Metals, such as iron, copper, zinc and manganese, are essential metals since they play important roles in biological systems, whereas mercury, lead and cadmium are toxic, even in trace amounts. The essential metals can also produce toxic effects at high concentrations. Only a few metals with proven hazardous nature are to be completely excluded in food for human consumption. Thus, only three metals, lead, cadmium and mercury, have been included in the regulations of the European Union for hazardous metals (EC, 2001), while the USFDA has included a further three metals chromium, arsenic and nickel in the list (USFDA, 1993).

The consequence of heavy metal pollution can be hazardous to man and it often becomes mandatory to check chemical contaminants in foods from the aquatic environment to understand their hazard levels. Therefore, this study aims to take stock of heavy metal concentrations (zinc, copper, cadmium, lead, cobalt, nickel, manganese, chromium, arsenic, selenium and mercury) in the edible portion of mollusks, crustaceans, fish and fish products collected from fish markets in Cochin, Kerala, India, during the period from July 2003 to Jan 2005, in order to evaluate their hazard level in relation to the maximum residual limit for human consumption.

2. Material and methods

2.1. Sample collection

Fresh samples, numbering 67, comprising mollusks, crustaceans, fish and fish products, were collected from fish markets in and around Cochin, India. The samples were placed in ice, brought to the laboratory, washed, separated by species and then stored frozen at −23 °C prior to analysis.

2.2. Reagents

All reagents used were of analytical grade. Working standards of zinc, copper, cadmium, lead, cobalt, nickel, manganese, chromium, arsenic, selenium and mercury were prepared by diluting concentrated stock solutions (Merck, Germany) of 1000 mg/l in ultra-pure water (MilliQ, Millipore-USA).

2.3. Sample preparation

The edible portions of the meat from the samples were removed, homogenized and about 2.5 ± 0.5 g was taken for analysis. Ten milliliters of nitric acid–perchloric acid (10:4) mixture were added to the sample, covered and left overnight at room temperature. Then the samples were digested, using a microwave digester (Milestone ETHOS PLUS, Italy). The completely digested samples were allowed to cool to room temperature, filtered (glass wool), and made up to 50 ml.

Table 1
Working conditions for the analysis of trace elements by atomic absorption spectrophotometer

Metals	Wavelength (nm)	Silt width (nm)	Lamp current (mA)	Gas	Support
Zn	213.9	1.0	5	Acetylene	Air
Cu	324.8	0.5	4	Acetylene	Air
Pb	217.0	1.0	10	Acetylene	Air
Cd	228.8	0.5	5	Acetylene	Air
Ni	232.0	0.2	4	Acetylene	Air
Mn	279.5	0.2	5	Acetylene	Air
Cr	357.9	0.2	7	Acetylene	Air
Co	240.7	0.2	7	Acetylene	Air
As	193.7	0.5	10	Acetylene	Air
Se	196.0	1	10	Acetylene	Air
Hg	253.7	0.5	4	Nitrogen	–

Table 2
Recovery (%) of heavy metals from mollusks, cephalopods, crustaceans, fish and fish products

S. No	Heavy metals	Sample wt (g)	Spiked concentration (mg/kg)	Recovery concentration (mg/kg)	Percentage of recovery (%)
1	Zn	2.5 ± 0.5	0.250	0.240	96
		2.5 ± 0.4	0.500	0.480	96
		2.5 ± 0.5	1.00	1.01	101
2	Cu	2.5 ± 0.3	0.300	0.310	103
		2.5 ± 0.5	0.600	0.589	98
		2.5 ± 0.2	1.20	1.220	101
3	Pb	2.5 ± 0.1	0.025	0.026	104
		2.5 ± 0.4	0.050	0.0485	103
		2.5 ± 0.6	0.100	0.0925	92
4	Cd	2.5 ± 0.6	0.030	0.0280	93
		2.5 ± 0.3	0.060	0.0601	100
		2.5 ± 0.2	0.120	0.119	99
5	Cr	2.5 ± 0.1	0.200	0.199	99
		2.5 ± 0.6	0.400	0.400	99
		2.5 ± 0.2	0.800	0.801	100
6	Ni	2.5 ± 0.3	0.060	0.0601	100
		2.5 ± 0.5	0.120	0.112	99
		2.5 ± 0.2	0.240	0.220	91
7	Co	2.5 ± 0.5	0.250	0.250	99
		2.5 ± 0.4	0.500	0.489	97
		2.5 ± 0.6	0.100	0.999	99
8	Mn	2.5 ± 03	0.050	0.0485	97
		2.5 ± 0.3	0.100	0.0975	97
		2.5 ± 0.4	0.200	0.999	93
9	As	2.5 ± 0.2	0.025	0.0230	92
		2.5 ± 0.5	0.050	0.0488	97
		2.5 ± 0.2	0.100	0.0987	98
10	Hg	2.5 ± 0.6	0.050	0.0489	97
		2.5 ± 0.4	0.100	0.979	97
		2.5 ± 0.3	0.200	0.198	99
11	Se	2.5 ± 0.3	0.050	0.0485	97
		2.5 ± 0.2	0.100	0.0976	97
		2.5 ± 0.7	0.200	0.197	98

2.4. Chemical analysis

All digested samples were analyzed, in triplicate, using an atomic absorption spectrophotometer (Varian 220, USA) as per standard conditions (Table 1). Zinc, copper, cadmium, lead, cobalt, nickel, manganese and chromium were estimated using an air–acetylene flame. Hydride generation and cold vapour techniques (VGA 77) were used for analysis of arsenic, selenium and mercury. The blanks and calibration standard solution were also analyzed in the same way as for the samples.

2.5. Determination of recovery

Homogenized samples (2.5 ± 0.5 g) were spiked with three different concentrations (Table 2) of heavy metals for determination recovery, each run in triplicate and blanks were carried through the whole procedure described above.

3. Results and discussion

The results of analysis showed good recovery when spiked with standards. On average, above 97% recovery was obtained for all the metals studied (Table 2). The concentrations of different metals detected in the edible portion of the mollusks, crustaceans, fish and fish products are given in Tables 3–6, respectively. The mollusk samples analyzed included mussels and clams. Sixteen percent of the samples did not contain cadmium and, in the remaining, the cadmium content was much below the legal limit of 1 mg/kg meat (EC, 2001). Among crustaceans, cadmium was not detected in about 90% of the samples while, in the others, very low concentrations (up to 0.47 mg/kg) were detected. Cephalopods (50% of the samples) and fish (53% of the samples) contained cadmium (0.02–1.32 mg/kg) and only one of the six samples of the brackish water fish *E. suratensis* was found to contain Cd above the EC limit of 0.1 mg/kg but none above the FAO limit (FAO, 1983). Humans are exposed to cadmium through food and the average daily intake for adults has been estimated to be approximately 50 mg (Calabrese, Canada, & Sacco, 1985). The threshold for acute cadmium toxicity would appear to be a total ingestion of 3–15 mg. Severe toxic symptoms are reported to occur with ingestions of 10–326 mg. Fatal ingestions of cadmium, producing shock and acute renal failure, occur from ingestions exceeding 350 mg (NAS-NRC, 1982).

Lead was present in about 66% of the total samples, which included 15% of mollusks (0.07–0.98 mg/kg), 9% of cephalopods (0.07–0.76 mg/kg), 15% of the crustaceans (0.11–75 mg/kg) and 25% of the fish (01–1.32 mg/kg) in their edible portion. The highest concentration was detected in one of the six samples of *Scomberomorus guttatus* (1.32 mg/kg). However, about 70% of the samples contained lead below 0.4 mg/kg (EC, 2001) and 82% below 0.5 mg/kg (FAO, 1983). Lead causes renal failure and liver damage in humans (Emmerson, 1973; Luckey & Venugopal, 1977).

Mercury was not detected in 88% of the total samples and only 3% of the total samples contained mercury above the permitted limit of 1.0 mg/kg (EC, 2001) in the edible portion. Two fish samples, namely *E. affinis* (2.31 mg/kg) and *E. suratensis* (1.76 mg/kg) had the highest concentrations of mercury. For humans, the most significant source of mercury in the diet is fish. In Minamata Bay, Japan, an area heavily polluted with mercury, fish were found to contain from 1 to 20 mg/kg of the edible flesh (NAS-NRC, 1977).

Chromium, arsenic and nickel are group of hazardous metals notified by the USFDA (1993a), even though not covered by EC regulations for fish and other aquatic products. Chromium was detected in almost all the samples and the highest concentration (3.7 mg/kg) was detected in *V. cyprinoides* but the values were within the limits of 12–13 mg/kg (USFDA, 1993a). Chromium is an essential trace element (Mertz, 1969) and the biologically usable form of chromium plays an essential role in glucose metabolism. It has been estimated that the average human requires nearly 1 μg/day. Deficiency of chromium results in impaired growth and disturbances in glucose, lipid, and protein metabolism (Calabrese et al., 1985). Water contributes a major share of chromium in humans (Underwood, 1977).

The arsenic content in the samples varied widely among the different samples; 8, 22, 33 and 80%, respectively, of mollusks, fish, crustaceans and fish products analyzed contained arsenic. Fish and crustaceans contained arsenic above 1 mg/kg with the highest concentration (4.14 mg/kg) in the fresh water fish, *Oreochromis mossambica*, but this is well below the accepted limit of 76 mg/kg (USFDA, 1993 b). The estimated US daily intake of arsenic is approximately 70 μg (USEPA, 1985). Arsenic concentrations as high as 170 mg/kg have been reported in crustaceans and other shellfish (Calabrese et al., 1985). Chronic arsenic poisoning symptoms include pigmented skin lesions, gangrene of the lower extremities (blackfoot disease), along with neuritis and paralysis, anemia and disturbances of the liver and circulatory system (Tseng, 1977; Tseng et al., 1968).

The MRL for nickel is 70–80 mg/kg (USFDA, 1993c), and the samples analyzed showed concentrations only up to 1.38 mg/kg meat. The major source of nickel for humans is food and uptake from natural sources, as well as food processing (NAS-NRC, 1975). The normal range of oral intake of nickel for humans is 300–600 μg/day. An increased incidence of cancer of the lung and nasal cavity has been reported in workers in nickel smelters (NAS-NRC, 1975).

The other metals screened in the samples include zinc, copper, cobalt, manganese and selenium. The zinc content in the samples ranged from 0.6 to 164 mg/kg meat, with a high level in fish (0.66–39.15 mg/kg) and mollusk (3.8–164 mg/kg) samples. The highest concentration was

Table 3
Concentration (mg/kg) of heavy metals in mollusks and cephalopods

		Month of sample collection	Zn	Cu	Cd	Pb	Cr	Ni	Co	Mn	As	Hg	Se
Mollusks													
1	*Perna viridis*	2003 July	37.7 ± 0.14	11.7 ± 0.28	nd	0.37 ± 0.01	0.36 ± 0.04	0.89 ± 0.02	0.17 ± 0.02	0.43 ± 0.02	nd	nd	0.66 ± 0.02
2	*Villorita cyprinoides*	2003 Oct	18.5 ± 0.07	3.9 ± 0.07	0.05 ± 0.28	0.32 ± 0.02	1.36 ± 0.06	nd	0.06 ± 0.03	0.46 ± 0.14	nd	nd	nd
3	*Villorita cyprinoides*	2003 Nov	25.1 ± 0.01	4.69 ± 0.08	0.03 ± 0.21	0.65 ± 0.04	1.66 ± 0.04	nd	nd	0.83 ± 0.4	nd	nd	0.46 ± 0.14
4	*Villorita cyprinoides* (Bo)	2003 Dec	44.0 ± 0.07	7.34 ± 0.05	0.03 ± 0.07	0.39 ± 0.02	1.28 ± 0.04	0.76 ± 0.06	0.4 ± 0.28	1.45 ± 0.07	nd	nd	0.13 ± 0.01
5	*Villorita cyprinoides* (Bo)	2004 Jan	20.5 ± 0.21	5.25 ± 0.07	0.14 ± 0.01	0.57 ± 0.04	1.56 ± 0.03	0.05 ± 0.03	0.05 ± 0.02	2.83 ± 0.07	nd	0.33 ± 0.04	0.18 ± 0.04
6	*Perna viridis* (Bo)	2004 Feb	3.8 ± 0.03	1.17 ± 0.09	0.03 ± 0.02	0.98 ± 0.03	0.18 ± 0.02	0.05 ± 0.06	nd	3.75 ± 0.05	0.69 ± 0.22	0.06 ± 0.02	0.09 ± 0.02
7	*Villorita cyprinoides*	2004 mar	12.7 ± 0.21	4.55 ± 0.07	0.15 ± 0.07	0.07 ± 0.29	3.65 ± 0.36	nd	0.5 ± 0.14	2.5 ± 0.14	nd	nd	0.89 ± 0.02
8	*Villorita cyprinoides*	2004 may	165 ± 0.64	24.1 ± 0.07	0.64 ± 0.01	0.09 ± 0.02	2.24 ± 0.08	0.08 ± 0.02	0.76 ± 0.01	0.08 ± 0.02	nd	nd	0.51 ± 0.13
9	*Villorita cyprinoides*	2004 july	33.5 ± 0.45	5.68 ± 0.141	0.18 ± 0.02	0.18 ± 0.04	2.38 ± 0.04	0.07 ± 0.01	0.85 ± 0.04	3.1 ± 0.02	nd	nd	0.25 ± 0.05
10	*Villorita cyprinoides*	2004 Sep	114 ± 0.71	16.0 ± 0.07	0.35 ± 0.02	0.46 ± 0.08	2.20 ± 0.01	0.37 ± 0.03	0.76 ± 0.02	3.7 ± 0.14	nd	nd	0.13 ± 0.03
11	*Perna viridis* (fz)	2004 oct	8.46 ± 0.43	1.44 ± 0.014	nd	nd	2.25 ± 0.04	nd	nd	2.7 ± 0.03	nd	nd	1.16 ± 0.06
12	*Villorita cyprinoides*	2004 Dec	19.9 ± 0.22	5.44 ± 0.028	0.98 ± 0.03	nd	1.28 ± 0.04	0.09 ± 0.02	0.19 ± 0.02	1.07 ± 0.07	nd	nd	0.91 ± 0.01
Cephalopods													
1	*Loligo* sp. whole	2003 Nov	14.4 ± 0.57	10.7 ± 0.14	0.03 ± 0.01	0.55 ± 0.01	0.62 ± 0.14	0.08 ± 0.01	0.04 ± 0.01	nd	nd	nd	nd
2	*Sepia* sp. cleaned	2003 Dec	16.3 ± 0.45	2.5 ± 0.56	0.03 ± 0.01	0.35 ± 0.01	0.52 ± 0.01	0.94 ± 0.03	0.36 ± 0.21	nd	nd	nd	1.35 ± 0.04
3	*Loligo* sp.	2004 Feb	12.3 ± 0.08	9.51 ± 0.08	nd	0.35 ± 0.09	0.64 ± 0.02	0.06 ± 0.02	0.10 ± 0.01	nd	nd	nd	0.44 ± 0.02
4	*Loligo* sp. whole	2004 Oct	7.62 ± 0.08	2.07 ± 0.65	nd	0.76 ± 0.02	1.33 ± 0.07	0.22 ± 0.01	nd	nd	nd	nd	0.15 ± 0.02
5	*Loligo* sp.	2004 Dec	3.99 ± 0.01	0.65 ± 0.071	0.47 ± 0.01	0.76 ± 0.02	nd	0.62 ± 0.02	0.07 ± 0.01	0.43 ± 0.02	nd	nd	nd
6	*Loligo* sp.	2005 Jan	8.13 ± 0.07	2.64 ± 0.07	nd	0.07 ± 0.04	0.53 ± 0.04	nd	0.43 ± 0.02	0.46 ± 0.14	nd	0.60 ± 0.02	nd

Data as mean ± SD in wet weight; sp-species; fz-frozen; Bo-Boiled; nd- not detected.

Table 4
Concentration (mg/kg) of heavy metals in crustaceans

		Month of sample collection	Zn	Cu	Cd	Pb	Cr	Ni	Co	Mn	As	Hg	Se
1	*Penaeus indicus*	2003 Mar	27.4 ± 0.14	18.9 ±0.58	nd	0.41 ± 0.01	0.89 ± 0.06	0.06 ± 0.02	0.05 ± 0.01	0.08 ± 0.02	nd	0.28 ± 0.04	0.19 ± 0.04
2	*Penaeus monodon*	2003 Oct	18.9 ± 0.07	14.0 ± 0.06	nd	0.3 ± 0.03	0.25 ± 0.04	0.71 ± 0.02	0.07 ± 0.02	3.1 ± 0.02	nd	nd	0.21 ± 0.01
3	*Penaeus indicus*	2003 Oct	15.6 ± 0.07	12.5 ± 0.07	nd	0.61 ± 0.01	0.34 ± 0.03	0.41 ± 0.02	0.04 ± 0.01	3.7 ± 0.14	nd	nd	0.58 ± 0.04
4	*Penaeus monodon*	2003 Nov	16.5 ± 0.07	13.8 ± 0.07	nd	0.45 ± 0.01	0.76 ± 0.05	nd	nd	2.7 ± 0.03	nd	0.11 ± 0.14	nd
5	*Scylla serrata*	2003 Nov	43.5 ± 0.28	3.94 ± 0.03	nd	nd	0.1 ± 0.01	0.03 ± 0.02	0.05 ± 0.01	1.07 ± 0.07	nd	0.05 ± 0.03	0.35 ± 0.04
6	*Penaeus monodon*	2003 Dec	14.5 ± 0.36	5.74 ± 0.07	nd	0.6 ± 0.01	1.06 ± 0.08	nd	nd	2.87 ± 0.7	nd	nd	0.76 ± 0.05
7	*Penaeus indicus*	2003 Dec	15.8 ± 0.16	11.9 ± 0.05	nd	0.42 ± 0.03	0.33 ± 0.05	nd	nd	2.8 ± 0.14	nd	nd	0.44 ± 0.03
8	*Penaeus monodon*	2004 Jan	15.0 ± 0.15	6.51 ± 0.02	nd	nd	0.31 ± 0.01	0.51 ± 0.02	0.12 ± 0.05	9.2 ± 0.14	nd	nd	0.33 ± 0.4
9	IFDP shrimp	2004 Feb	10.9 ± 0.04	3.48 ± 0.04	nd	nd	0.46 ± 0.02	0.13 ± 0.02	nd	2.45 ± 0.35	2.98 ± 0.03	0.42 ± 0.02	0.11 ± 0.02
10	Block PUD shrimp frozen	2004 Feb	15.8 ± 0.08	4.61 ± 0.04	nd	nd	0.54 ± 0.03	0.12 ± 02	nd	2.77 ± 0.07	1.37 ± 0.42	nd	0.13 ± 0.03
11	Shrimp (fz)	2004 Feb	30.5 ± 0.36	8.63 ± 0.07	nd	nd	0.51 ± 0.01	0.18 ± 0.02	nd	1.32 ± 0.01	1.64 ± 0.03	nd	0.53 ± 0.04
12	PUD shrimp (fz)	2004 Mar	17.6 ± 0.57	4.21 ± 0.02	nd	nd	0.44 ± 0.21	0.2 ± 0.2	0.09 ± 0.01	3.20 ± 0.14	1.25 ± 0.02	0.47 ± 0.02	0.76 ± 0.07
13	BlockPUD (fz)	2004 Mar	5.14 ± 0.71	1.88 ± 0.07	nd	0.11 ± 0.03	0.39 ± 0.02	0.12 ± 0.02	nd	0.52 ± 0.04	0.31 ± 0.14	0.41 ± 0.01	0.16 ± 0.04
14	Block PUD (fz)	2004 Mar	15.4 ± 0.21	4.51 ± 0.08	nd	0.75 ± 0.04	0.22 ± 0.03	0.23 ± 0.03	nd	0.54 ± .02	0.10 ± 0.01	nd	0.16 ± 0.05
15	Shrimp whole Choodan	2004 Apr	16.2 ± 0.21	10.1 ± 0.01	nd	nd	0.42 ± 0.03	0.22 ± 0.04	nd	1.43 ± 0.03	1.53 ± 0.08	nd	nd
16	Shrimp (fz)	2004 Apr	8.17 ± 0.08	2.31 ± 0.04	nd	nd	0.15 ± 0.04	nd	nd	0.81 ± 0.02	nd	nd	nd
17	*Parapenaeopsis stlifera*	2004 July	49.6 ± 0.71	6.91 ± 0.07	nd	0.94 ± 0.06	1.65 ± 0.06	nd	nd	4.75 ± 0.14	nd	nd	0.54 ± 0.32
18	PUD shrimp (fz)	2004 Oct	10.3 ± 0.71	9.41 ± 0.07	0.12 ± 0.01		1.87 ± 0.01	0.28 ± 0.01	0.16 ± 0.03	0.80 ± 0.07	nd	nd	0.19 ± 0.14
19	PUD shrimp (fz)	2004 Nov	12.9 ± 0.07	10.4 ± 0.07	0.07 ± 0.02	0.43 ± 0.04	1.11 ± 0.03	0.09 ± 0.01	0.03 ± 0.04	0.38 ± 0.02	nd	nd	0.22 ± 0.02
20	*Penaeus indicus*	2004 Dec	8.38 ± 0.14	6.22 ± 0.07	nd	nd	0.54 ± 0.02	0.37 ± 0.08	0.1 ± 0.02	1.69 ± 0.07	nd	nd	nd
21	*Penaeus monodon*	2005 Jan	4.91 ± 0.07	12.1 ± 0.07	nd	nd	0.64 ± 0.01	1.38 ± 0.01	nd	1.42 ± 0.07	nd	nd	nd

Data as mean ± SD in wet weight; PUD – peeled undeveined shrimp; IFDP – individually frozen deveined prawn; Fz – frozen; nd – not detected.

Table 5
Concentration (mg/kg) of heavy metals in fish

		Month of sample collection	Zn	Cu	Cd	Pb	Cr	Ni	Co	Mn	As	Hg	Se
1	*Etroplus suratensis*	2003 Dec	12.3 ± 0.14	2.19 ± 0.07	1.32 ± 0.02	0.23 ± 0.01	0.3 ± 0.28	nd	nd	1.01 ± 0.02	nd	nd	0.46 ± 0.22
2	*Labeo rohita*	2003 Dec	12.3 ± 0.04	14.7 ± 0.08	0.02 ± 0.01	0.32 ± 0.01	0.33 ± 0.07	nd	0.02 ± 0.01	1.17 ± 0.02	nd	nd	0.35 ± 0.1
3	*Chanos chanos*	2003 Dec	9.25 ± 0.01	12.5 ± 0.05	0.02 ± 0.01	0.32 ± 0.01	0.2 ± 0.01	nd	0.02 ± 0.02	3.36 ± 0.07	nd	nd	0.03 ± 0.01
4	*Etroplus suratensis*	2004 Jan	11.7 ± 0.14	6.25 ± 0.03	0.03 ± 0.01	0.25 ± 0.02	0.47 ± 0.02	0.15 ± 0.07	0.06 ± 0.01	1.71 ± 0.04	1.515 ± 0.03	nd	0.27 ± 0.1
5	*Scomberomorus guttatus*	2004 Feb	14.5 ± 0.14	3.03 ± 0.04	0.03 ± 0.01	nd	0.34 ± 0.02	0.59 ± 0.02	0.03 ± 0.06	0.59 ± 0.02	1.66 ± 0.03	nd	0.12 ± 0.14
6	*Etroplus suratensis*	2004 Feb	11.5 ± 0.36	5.33 ± 0.02	0.06 ± 0.02	0.76 ± 0.03	0.53 ± 0.02	0.53 ± 0.07	0.06 ± 0.01	1.94 ± 0.03	2.53 ± 0.01	nd	0.53 ± 0.06
7	*Scomberomorus guttatus* (fz)	2004 Mar	39.2 ± 0.08	3.16 ± 0.06	0.04 ± .01	0.24 ± 0.28	0.24 ± 0.05	0.07 ± 0.02	0.02 ± 0.02	0.72 ± 0.02	0.16 ± 0.02	0.28 ± 0.21	0.76 ± 0.04
8	*Catla catla* (fz)	2004 Apr	0.66 ± 0.03	0.13 ± 0.03	nd	nd	0.24 ± 0.06	0.07 ± 0.04	nd	0.85 ± 0.04	nd	nd	nd
9	*Saurida* sp.	2004 July	5.82 ± 0.03	2.27 ± 0.07	0.11 ± 0.02	nd	0.9 ± 0.07	0.03 ± 0.02	0.03 ± 0.01	0.23 ± 0.03	nd	nd	0.95 ± 0.07
10	*Otolithus* sp.	2004 July	12.3 ± 0.43	9.42 ± 0.07	0.11 ± 0.03	0.48 ± 0.01	0.95 ± 0.04	0.09 ± 0.03	0.05 ± 0.07	0.36 ± 0.05	nd	nd	0.04 ± 0.03
11	*Euthynnus affinis* (fz)	2004 Oct	8.61 ± 0.03	0.69 ± 0.02	0.13 ± 0.04	nd	1.3 ± 0.14	0.2 ± 0.14	0.2 ± 0.02	0.43 ± 0.01	nd	nd	0.68 ± 0.01
12	*Scomberomorus guttatus* (fz)	2004 Oct	6.44 ± 0.05	0.83 ± 0.03	0.08 ± 0.01	nd	1.87 ± 0.01	0.4 ± 0.07	0.08 ± 0.03	0.6 ± 0.14	nd	nd	0.26 ± 0.06
13	*Pompus argenteus* (fz)	2004 Oct	6.46 ± 0.05	2.21 ± 0.01	0.09 ± 0.01	0.19 ± 0.01	1.47 ± 0.01	nd	0.05 ± 0.04	0.51 ± 0.01	nd	nd	nd
14	*Scomberomorus guttatus* (fz)	2004 Oct	6.92 ± 0.02	1.19 ± 0.07	nd	nd	1.46 ± 0.07	0.06 ± 0.04	nd	0.14 ± 0.11	nd	nd	0.19 ± 0.02
15	*Scomberomorus guttatus* (fz)	2004 Nov	7.54 ± 0.05	2.00 ± .01	nd	0.10 ± 0.01	1.37 ± 0.01	0.22 ± 0.01	nd	0.28 ± 0.01	nd	nd	0.15 ± 0.02
16	*Etroplus suratensis*	2004 Dec	7.11 ± 0.02	2.32 ± 0.02	nd	0.6 ± 0.14	0.46 ± 0.03	0.42 ± 0.01	0.67 ± 0.02	0.73 ± 0.03	nd	nd	nd
17	*Etroplus suratensis*	2005 Jan	6.33 ± 0.03	1.62 ± 0.03	nd	0.27 ± 0.05	0.31 ± 0.02	0.69 ± 0.02	0.3 ± 0.01	0.58 ± 0.01	nd	nd	nd
18	*Oreochromis mossambicus*	2005 Jan	4.56 ± 0.02	1.12 ± 0.04	nd	0.2 ± 0.01	nd	0.62 ± 0.02	0.12 ± 0.01	nd	4.14 ± 0.01	nd	nd
19	*Etroplus suratensis*	2005 Jan	6.06 ± 0.06	1.92 ± 0.02	nd	0.52 ± 0.02	0.32 ± 0.02	nd	0.57 ± 0.02	0.57 ± 0.01	nd	1.76 ± 0.12	nd
20	Euthynnus affinis	2005 Jan	4.52 ± 0.08	1.64 ± 0.04	nd	0.35 ± 0.04	0.51 ± 0.05	nd	0.43 ± 0.03	0.19 ± 0.4	nd	2.31 ± 0.12	nd
21	*Catla catla*	2005 Jan	1.47 ± 0.07	0.14 ± .02	nd	0.13 ± 0.04	0.52 ± 0.01	nd	0.03 ± 0.05	0.17 ± 0.01	nd	nd	nd
22	*Labeo rohita*	2005 Jan	3.54 ± 0.07	0.17 ± 0.01	nd	0.1 ± 0.01	0.51 ± 0.07	nd	0.17 ± 0.01	1.02 ± 0.02	nd	nd	nd
23	*Scomberomorus guttatus*	2005 Jan	2.08 ± 0.05	0.48 ± 0.04	nd	1.32 ± 0.01	0.52 ± 0.01	nd	0.27 ± 0.01	0.32 ± 0.02	nd	nd	nd

Data as mean ± SD in wet weight; fz: frozen; sp: species; nd: not detected.

Table 6
Concentration (mg/kg) of heavy metals in fish product

		Month of sample collection	Zn	Cu	Cd	Pb	Cr	Ni	Co	Mn	As	Hg	Se
1	Fish kheema	2004 Mar	4.31 ± 0.08	0.66 ± 0.014	0.04 ± 0.03	nd	nd	nd	nd	0.83 ± 0.4	0.30 ± 0.01	0.30 ± 0.01	nd
2	Fish finger	2004 Mar	5.33 ± 0.07	0.85 ± 0.42	nd	nd	0.05 ± 0.01	nd	nd	1.45 ± 0.07	1.52 ± 0.03	0.03 ± 0.01	nd
3	Fish steaks	2004 Mar	6.5 ± 0.14	0.85 ± 0.07	nd	nd	0.24 ± 0.02	0.11 ± 0.02	nd	2.83 ± 0.07	0.15 ± 0.03	0.11 ± 0.01	nd
4	Fish cutlet	2004 Nov	7.9 ± 0.15	14.6 ± 0.14	nd	0.22 ± 0.14	1.81 ± 0.03	0.62 ± 0.02	0.12 ± 0.14	3.75 ± 0.05	nd	nd	nd
5	Fish kheema (fz)	2004 Nov	6.55 ± 0.36	1.1 ± 0.14	nd	nd	0.95 ± 0.14	nd	0.66 ± 0.02	2.5 ± 0.14	0.85 ± .01	nd	nd

Data as mean ± SD in wet weight; fz: frozen; nd: not detected.

detected in black clam *(V. cyprinoides)*. The zinc concentration in the samples compares well with the earlier report in grey mullet from the Tigris river (Unlu, Akba, Sevim, & Gumgum, 1996). Zinc is an essential trace element for both animals and humans. The recommended daily allowance is 10 mg/day in growing children and 15 mg/day for adults (NAS-NRC, 1974). A deficiency of zinc is marked by retarded growth, loss of taste and hypogonadism, leading to decreased fertility. Zinc toxicity is rare but, at concentrations in water up to 40 mg/kg, may induce toxicity, characterized by symptoms of irritability, muscular stiffness and pain, loss of appetite, and nausea (NAS-NRC, 1974). Zinc appears to have a protective effect against the toxicities of both cadmium (Calabrese et al., 1985) and lead (Sanstead, 1976).

The concentrations of copper in the samples analyzed ranged from 0.13 to 24.1 mg/kg meat, with the highest concentrations in *V. cyprinoides* (24.1 mg/kg) and *Penaeus indicus* (18.9 mg/kg). But the concentrations in the samples were much below the toxic limit of 30 mg/kg (FAO, 1983). Copper is an essential part of several enzymes and it is necessary for the synthesis of hemoglobin. The richest sources of copper are shellfish, especially oysters and crustaceans (Underwood, 1977). No deficiencies of copper in adults have been reported but, in infants, anemia and hypoproteinemia are reported (Underwood, 1977).

Cobalt was detected in 83% of fish, 43% of crustaceans, 83% cephalopods and 75% of mollusks analysed in a range of 0.02–0.85 mg/kg meat. The highest concentration (>0.7 mg/kg) was detected in *V. cyprinoides*. Cobalt is an essential nutrient for man, and is an integral part of vitamin B_{12}. The average daily intake of cobalt, in all forms, ranges from 0.30 to 1.77 mg/day (Underwood, 1977). Cobalt has also been implicated in blood pressure regulation (Perry, Schroeder, Goldstein, & Menhard, 1954), and has been found to be necessary for proper thyroid function (Blakhima, 1970). Excessive ingestion of cobalt is reported to cause congestive heart failure and polycythemia and anemia (Alexander, 1972).

Manganese was detected in almost all the samples and the concentration ranged from 0.08 to 9.2 mg/kg, with the highest concentration bring detected in *V. cyprinoides* and *P. monodon*. Manganese is an essential element for both animals and plants and deficiencies result in severe skeletal and reproductive abnormalities in mammals. It is widely distributed throughout the body with little variation and does not accumulate with age. Total daily intake varies from 2.5 to 7 mg (NAS-NRC, 1977).

Selenium was present in trace levels in almost all the samples. Selenium was detected in 92% of the mollusks, 50% of the cephalopods, 81% of crustaceans and 43% of fish and the concentration ranged from 0.03 to 1.35-mg/kg meat. High levels of selenium were reported in cereal products, meat and seafood (Morris & Levander, 1970). Selenium is an essential element in some oxidation–reduction processes and is a component of glutathione peroxidase, the cellular enzyme responsible for converting hydrogen peroxide to water and CO_2. However, excessive ingestion or inhalation of selenium can be toxic to man and animals and the symptoms include depression, nervousness, and dermatitis, garlic odour of the breath, gastrointestinal disturbances, and excessive tooth decay (Calabrese et al., 1985). Selenium appears to be protective against a variety of toxic agents, including methyl mercury (Ganther et al., 1972) and cadmium (Mason & Young, 1967).

4. Conclusion

The marginally higher concentrations of Cd, Pb and Hg in fish in the markets samples could be related to industrialization and related activities in these areas. The results of this study supply valuable information about metal contents in fish and shellfish from internal markets around Cochin and indirectly indicate the environmental contamination along the Cochin coastal area. Moreover, these results can also be used to understand the chemical quality of fish and to evaluate the possible risk associated with their consumption. The heavy metal concentrations in the majority of the samples analyzed were well within the prescribed limits set by various authorities, except in a few cases. Therefore, the fish and shellfish from this region, in general, are safe for human consumption.

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