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Analysis of heavy metals in marine fish from Mumbai Docks

Aditi Deshpande · Sandeep Bhendigeri · Tejas Shirsekar · Dhanashri Dhaware · R. N. Khandekar

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Abstract Seafood containing heavy metals as a result of environmental contamination causes toxicity in human beings. To evaluate such kind of contamination, our study targeted the analysis of metals such as lead, copper, cadmium, mercury, and arsenic in muscle tissue of the fish. The fish commonly consumed such as *Brama brama* (Pomfret), *Rachycentron canadus* (Surmai/King Fish), *Rastrelliger kanagurta* (Mackerel), *Eleutheronema tetradactylum* (Ravas/Indian salmon), and *Metapenaeus monoceros* (Brown Prawn) were collected from four different docks in the city. The heavy metals in tissue samples of fish were estimated using voltammeter and cold vapor atomic absorption spectrophotometer. Heavy metal concentration in the tissues varied significantly depending upon the locations from where the fish were collected. Although the concentration of arsenic, copper, cadmium, and lead were in normal range, the concentration of mercury was found to exceed the daily permissible levels (1 μg/g) as a food source for human consumption. We have analyzed heavy metals from different locations in Mumbai—Versova dock, Sassoon dock, Navi Mumbai dock, and Mazgaon dock.

A. Deshpande (✉) · S. Bhendigeri · T. Shirsekar · D. Dhaware · R. N. Khandekar
Indian Institute of Environmental Medicine, Mumbai, India
e-mail: iiem@bom8.vsnl.net.in

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Introduction

Heavy metals enter the aquatic environment naturally through weathering of the earths crust. In addition to geological weathering, human activities have also introduced large quantities of metals to local water bodies, thereby disturbing the natural balance in the ecosystem (Forstner and Wittmann 1983). Over the past several decades, increasing use of metals in industry has lead to serious environmental pollution through effluents and emanations (Goldberg et al. 1978; Phillips 1980; Sericano et al. 1995). Under certain environmental conditions, heavy metals may accumulate to a toxic concentration (Güven et al. 1999) and cause ecological damage (Harms 1975; Jefferies and Freestone 1984; Freedman 1989).

The last few decades were witness to several reports on the toxicity of heavy metals in human beings, due to the contamination in aquatic organisms. Predominantly, fish toxicological and environmental studies have prompted interest in the determination of toxic elements in seafood (Waqar 2006). Long-term intake of contaminated seafood could lead to toxicity of heavy metals in human beings. There are reports of high levels of heavy metals in seafoods, not only because many metals are natural components of foodstuffs but also because of environmental contamination and contamination during processing (Kalay et al. 1999).

Industrial effluents, agricultural runoffs, transport, burning of fossil fuels, animal and human excretions, and geologic weathering and domestic waste contribute to the heavy metals in the water bodies (Erdoğrul and Erbilir 2007). With the exception of occupational exposure, fish are acknowledged to be the single largest source of mercury and other heavy metals (cadmium, lead, and arsenic) affecting human beings. In some cases, fish catches were banned for human consumption because their total mercury content exceeded the maximum limits recommended by the Food and Agriculture Organization (FAO) and World Health Organization (WHO). Reports indicate that contamination of Arabian Sea due to the industrial activities has led to the death of many species. Among seafoods, fish are commonly consumed and, hence, are a connecting link for the transfer of toxic heavy metals in human beings (Waqar 2006).

Mumbai city, originally a cluster of seven tiny islands and now massively reclaimed to form a single landmass, has a coastline of 140 km along its western edge and creeks alongside. Hence, seafood is a staple among the locals. Being the commercial capital with the highest population and industries among other cities in India, the generation of waste water is enormous. This waste water after treatment is directly discharged through the outfalls in the sea. Similarly, many industries also discharge their effluents directly in the sea. This indirectly hampers the aquatic environment, and toxicity is transferred through the ecosystem—fish to human beings (NEERI and CMFRI 2005). Hence, our study targeted the seafood, mainly fish [four varieties—*Brama brama* (Pomfret), *Rachycentron canadus* (Surmai/King Fish), *Rastrelliger kanagurta* (Mackerel), *Eleutheronema tetradactylum* (Ravas/Indian salmon)] and prawns (*Metapenaeus monoceros*) procured from four docks in and around the island of Mumbai. Five metals—lead, copper, cadmium, arsenic, and mercury were analyzed from fish brought to the shore from high seas and coastal waters.

Materials and method

Reagents

The reagents used in the study were—nitric acid 69% (GR grade), hydrochloric acid 35% (GR grade), perchloric acid 70% (GR grade), stannous chloride ($SnCl_2$), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and double distilled water (Millipore).

Instrumentation–voltammeter and digital cold vapor mercury analyzer

Voltammeter from E.G. and G. Princeton Applied Research, Model 394 Analyser, Par x-y Recorder—model Re0074 and Static Mercury Drop Electrode assembly (PARC—303 A) was employed for analysis of the metals lead, copper, cadmium, and arsenic. For mercury estimation, the digital cold vapor atomic absorption method using a MA 5840 mercury analyzer from Electronic Corporation of India Limited, was performed.

Sampling

The fish samples were collected and analyzed during October 2007. Fish were collected from four docks in and around Mumbai city—Versova, Sassoon dock, Mazgaon dock, Navi Mumbai Dock. Samples selected for heavy metal analysis were Mackerel (*R. kanagurta*), Pomfret (*B. brama*), Indian Salmon also called as Rawas (*E. tetradactylum*), King fish also called as Surmai (*R. canadus*), and Brown prawns (*M. monoceros*; The Gazetteers Department—RATNAGIRI 2006). The samples were collected in sterile polythene bags and kept in the laboratory deep freezer (–20°C) to prevent deterioration till further analysis.

Sample pretreatment (wet ashing)

Fish samples were cleaned with sterile distilled water and then dissected. Two grams of muscle tissue near the gill area of the fish was removed and weighed for the analysis of each metal. For estimation of arsenic content 2 g of muscle tissue was taken in a 100-ml Borosil beaker. To this, 2 ml of HNO_3 and 1 ml of $HClO_4$ was added and kept for digestion on a hot plate at 100°C till complete digestion was achieved (Complete digestion involves removal of organic matter by reacting with acids.). It was ensured that the residue obtained after digestion was free from organic matter which acts as impurities in metal analysis (Khandekar et al. 1984; Raghunath et al. 1997). Residue was reconstituted using 1 M of 10 ml Hydrochloric acid (HCl) for further analysis on a voltammeter. Samples for estimation of lead, copper, and cadmium metals were also digested using the same protocol. For the analysis of mercury, 2 gm sample was placed into a 50-ml round bottom flask to which 2 ml nitric acid and 1 ml perchloric acid was added and then kept for digestion with the aid of condensation assembly for 2.5 h.

Sample analysis

Voltammetric analysis of the digested samples of lead, copper, and cadmium was carried out using differential pulse anodic stripping voltammetry. For the analysis of arsenic, square wave voltammetric technique was used (Khandekar et al. 1984; Raghunath et al. 1997).The instrumental parameters used for this analysis are shown in Table 1. Mercury was analyzed on cold vapor mercury analyzer (MA5840, Electronic Corporation of India Ltd.). Two milliliters stannous chloride and 8 ml 10% HNO_3 was added in impinger containing sample to liberate the atomic mercury from the sample with constant stirring. Depending on the absorption values, the mercury content of the samples was calculated as reported earlier (Nriagu 1996; Farkas et al. 2000).

Results and discussion

Heavy metals in fish and prawn samples were analyzed on a voltammeter (polarographic instrument) known for its sensitivity up to nanogram level (Khandekar et al. 1981). This method is an accepted and precise analytical routine method for such samples (Celik and Oehlenschläger 2004). The study was targeted at docks in and around the Island city of Mumbai at four different directions. Versova dock which is located at the northwest region of Mumbai faces the open Arabian Sea. Navi Mumbai dock is located at the northeast region of Mumbai, a part of the mainland and lies along the eastside of Thane creek, whereas Sassoon dock and Mazgaon dock are located at the southeast region of Mumbai island and toward the west side of the Thane creek. The significant differences in metal levels of seafood from these locations were visible in the results obtained.

Mercury

According to the results obtained, the mercury levels in the muscles of mackerel from Versova dock located on the western coast of Mumbai, (Table 2) were found to be 1.78 ppm, which was higher than the permissible level, i.e.,. 1 ppm

Table 1 Instrumental parameters employed for analysis of heavy metals

Metal	$E\ ^1/_2$ vs Ag/AgCl (V)	Scan rate (mV/s)	Pulse repetition time (s)	Modulation amplitude (mV)	Supporting electrolyte	Technique
Pb	−0.42	5	0.5 s	50	0.25% HNO_3	Differential pulse anodic stripping voltammetry (DPASV)
Cd	−0.6					
Cu	−0.02					
As	−0.5	2	0.5 s	50	0.1 M HCl	Square wave voltammetry
Hg	–	–	–	–	10% HNO_3, Stannous chloride	Cold vapor atomic absorption

Analysis of toxic trace elements in seafood samples by neutron activation

Table 2 Levels of heavy metals in seafood from Versova dock

Name of fish	Wt. of fish (g)	Levels of metals in sea food from Versova dock									
		Pb		Cu		Cd		As		Hg	
		μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish
Prawn	4.78	0.017	0.08	0.07	0.33	0.013	0.062	0.02	0.095	0.004	0.195
Mackerel	92.21	0.013	1.1	0.60	55.3	0.019	1.7	0.040	3.70	1.78	264.03
Pomfret	80.60	0.015	1.12	0.67	54	0.014	1.12	0.016	1.47	1.0	86.24
King fish	211.2	0.007	1.49	0.36	76.03	0.016	3.38	0.083	17.52	0.90	253.44
Indian Salmon	72.86	0.003	0.2	0.33	24.04	–	–	0.016	1.2	0.04	2.84

Table 3 Levels of heavy metals in seafood from Sassoon dock

Name of fish	Wt. of fish (g)	Levels of metals in sea food from Sassoon dock									
		Pb		Cu		Cd		As		Hg	
		μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish
Prawn	4	0.060	0.24	1.546	4.98	–	–	0.028	0.114	0.012	0.048
Mackerel	148.27	0.01	1.43	0.167	24.9	0.007	1.061	0.016	2.283	0.029	4.3
Pomfret	88.60	0.030	2.66	0.142	12.58	0.009	0.788	0.01	0.82	0.042	3.72
King fish	211.2	0.088	18.59	0.259	54.70	–	–	0.01	2.112	0.02	4.42
Indian Salmon	72.54	0.004	0.31	0.492	35.69	0.01	0.66	0.01	0.725	0.05	3.63

Table 4 Levels of heavy metals in seafood from Navi Mumbai dock

Name of fish	Wt. of fish (g)	Levels of metals in seafood from Navi Mumbai									
		Pb		Cu		Cd		As		Hg	
		μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish
Prawn	10	0.037	0.3	2.5	25.1	–	–	0.008	0.076	0.070	0.705
Mackerel	97	0.24	2.36	0.07	6.58	0.01	1.0	0.010	0.97	0.095	9.22
Pomfret	52.20	0.033	1.72	0.18	9.89	–	–	0.024	1.25	0.039	2.08
King fish	211.2	0.001	0.19	0.114	24.2	0.007	1.5	0.014	2.8	0.053	11.33
Indian Salmon	72.54	0.004	0.31	0.482	35.59	–	–	0.015	1.09	0.015	0.84

Table 5 Levels of heavy metals in seafood from Mazgaon dock

Name of fish	Wt. of fish (g)	Levels of metals in seafood from Mazgaon dock									
		Pb		Cu		Cd		As		Hg	
		μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish	μg/g	μg/fish
Prawn	10	0.094	0.94	4.57	45.7	0.199	1.99	0.20	2.07	0.12	1.22
Mackerel	96	0.026	2.58	0.21	20.26	–	–	0.11	10.65	0.11	10.59
Pomfret	64.20	0.049	3.145	0.24	15.92	–	–	0.007	0.47	0.085	5.513
King fish	212	0.019	4.17	0.22	48.52	–	–	0.63	135.41	0.070	14.95
Indian Salmon	72.2	0.014	1.01	0.48	35.30	0.009	0.66	0.26	19.27	0.090	6.5

(WHO, FDA Consumer, September 1994). The Food and Drug Administration (FDA) has set a maximum permissible level of one part of methyl mercury in a million parts of seafood (1 ppm). The higher level of mercury can be attributed to the sewage–sludge outfall present along this western coast. This sewage outfall consists of treated industrial effluents from chloralkali industries and other biochemical manufacturing units situated in that part of Mumbai. It is possible that though the sewage–sludge was treated, traces of heavy metals might have leached into the sea.

Fish analyzed from Sassoon dock showed normal levels which was in the range of 0.02 to 0.05 μg/g. In the case of Navi Mumbai region, mercury levels range from 0.03 to 0.095 μg/g, and also in Mazgaon dock, the mercury levels were found to be in the range of 0.07 to 0.1 μg/g which suggest that the fish brought to locations such as Sassoon dock, Navi Mumbai, and Mazgaon dock might be free from Mercury contamination as shown in Tables 2, 3, 4, and 5 and Fig. 1. The PTWI (permissible tolerable weekly intake) of mercury has been set at 5 μg/kg body weight (FAO-WHO 1972), equaling 300 μg mercury/week for a 60-kg person.

Mercury is known to be a latent neurotoxin compared to other metals like lead, cadmium, copper, arsenic. A high dietary intake of mercury (organic) from consumption of fish has been hypothesized to increase the risk of coronary heart disease (Salonen et al. 1995). In a recent case-control study, the joint association of mercury levels in toenail clippings and docosahexaenoic acid levels in adipose tissue with the risk of a first myocardial infarction in men was evaluated (Gullar 2002).When deposited in biota, mercury undergoes biotransformation, in which inorganic mercury may convert to organic mercury (methyl mercury). Microbes subsequently concentrate mercury through the food chain in the tissue of fish and marine animals (Altindag and Yigit 2005).

Arsenic

According to the observations (Tables 2–5 and Fig. 2), Arsenic content of fish from Versova, Sassoon dock, Navi Mumbai, and Mazgaon dock is within the range 0.01–0.63 μg/g which is below permissible level, i.e., 1 μg/g (Sarmani et al. 1993).

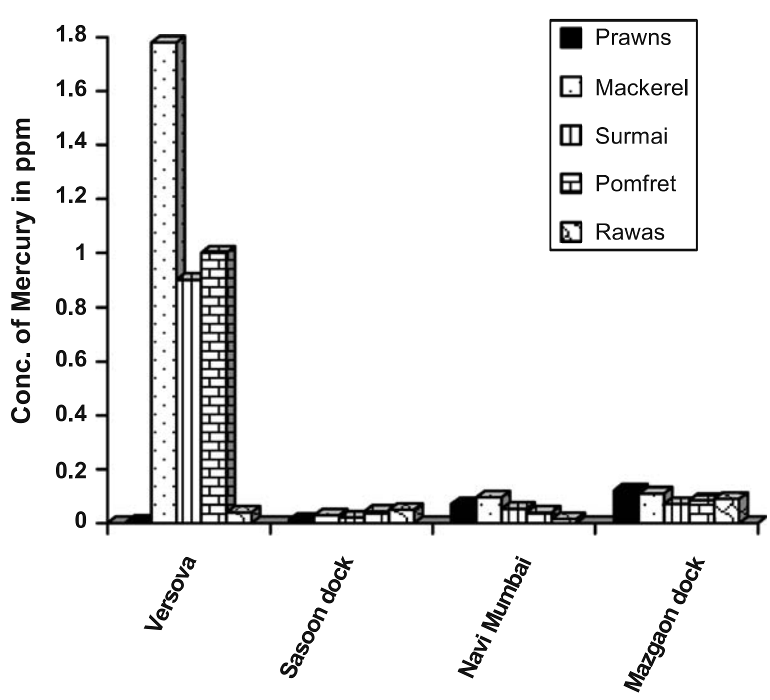
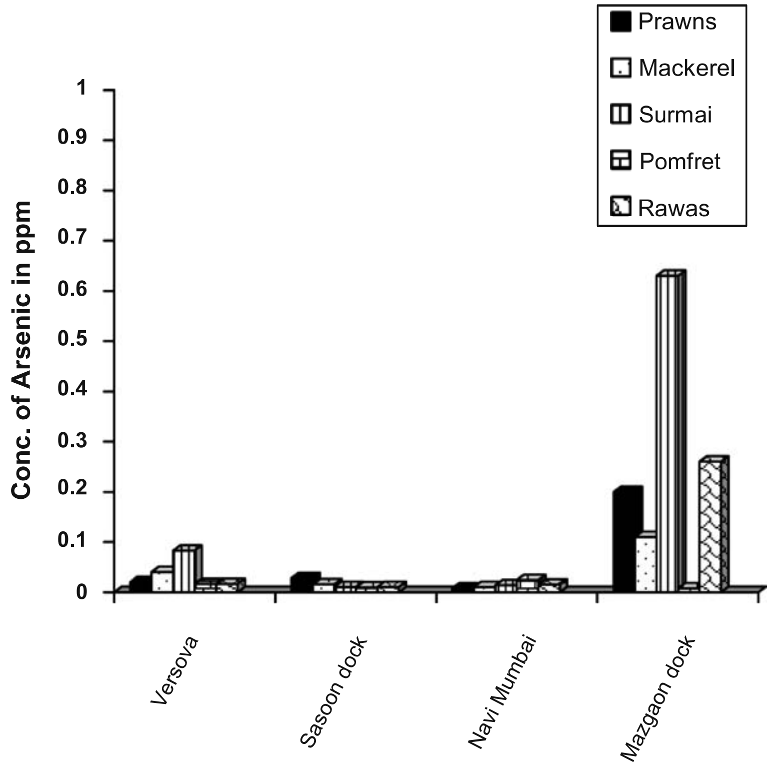


Fig. 1 Levels of mercury (Hg) from different locations in Mumbai

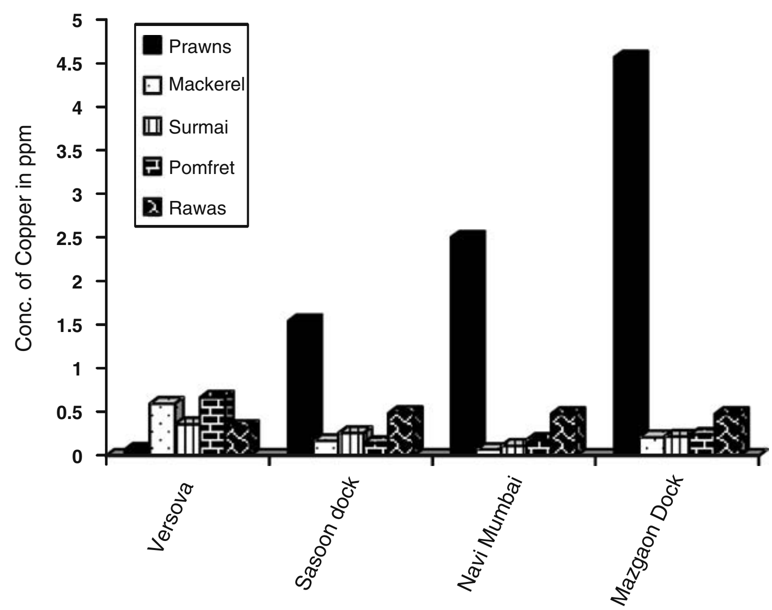
Fig. 2 Levels of Arsenic (As) from different locations in Mumbai



Copper

Levels of Copper in fish from Versova, Sassoon dock, Navi Mumbai, and Mazgaon dock were ranging from 0.2 to 2.5 μg/g, far below the normal permissible range, i.e., 10 μg/g. (Tables 2–5 and Fig. 3).

Fig. 3 Levels of Copper (Cu) from different locations in Mumbai



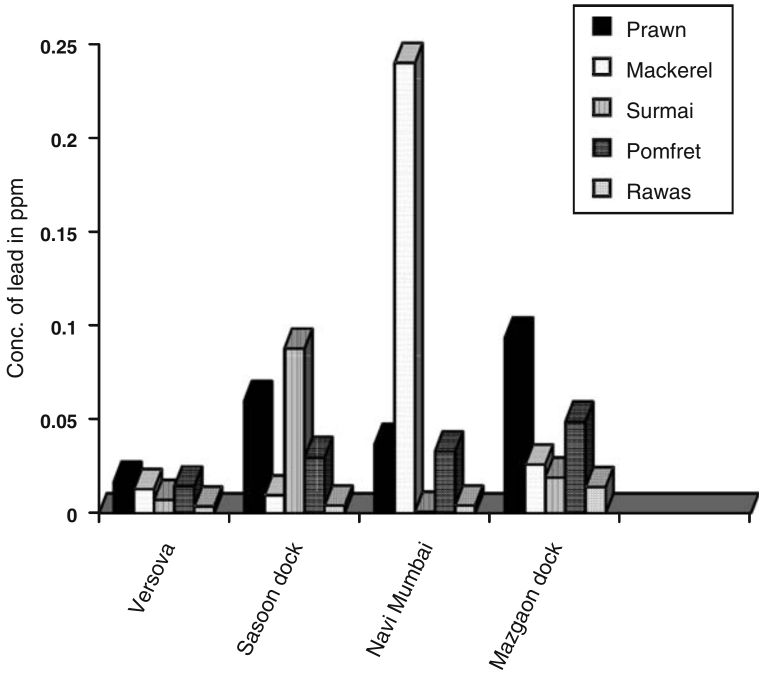


Fig. 4 Levels of Lead (Pb) from different locations in Mumbai

Cadmium

Cadmium levels in fish from the four locations were well below the normal range (0.02 μg/g) The PTWI of cadmium has been set at 7 μg/kg body weight (FAO-WHO 1989), equaling to 420 μg cadmium/week for a 60-kg person. In our observation, the metal cadmium was also below the normal estimated values as shown in Tables 2–5.

Lead

Similarly, levels of lead in fish from four locations were also below the permissible level which is 1.5 μg/g. FAO of the United Nations and WHO (1990) has established a provisional tolerable weekly intake (PTWI) of lead as 25 μg/kg body weight for humans, equaling 1,500 μg/g lead/week for a 60-kg person. It was observed that the intake of lead through fish from the locations such as Versova, Sassoon dock, Navi Mumbai, and Mazgaon dock was well below this limit as shown in Tables 2–5, Fig. 4.

Conclusions

From the results, it can be concluded that the metal contamination in fish brought to shore from the four selected locations was within the permissible level. Only in the case of mercury was it found to be high in Versova dock samples. It can be assumed that the sea around that part might be receiving outfalls from industrial waste and sewage from the city as it faces the open Arabian Sea, unlike the other docks that face the creeks. Although the levels of heavy metals such as lead, copper, cadmium, and arsenic were within permissible limits, continuous exposure and bioaccumulation in seafood can have unwarranted impact on the ecosystem and the consumer.

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