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Eminence of heavy metal accumulation in fishes and crustaceans from the Gulf of Khambhat, India

Heavy metals are found naturally in micro quantities in all aquatic systems. In fact, some of them are essential micronutrients for living organisms. However, they became highly toxic to the organisms when present in higher concentrations[1,2]. These metal concentrations have been altered in the ecosystem by indiscriminate anthropogenic activities and dispersed into the water as well as sediment column[3]. The metal contaminants in aquatic systems usually remain either in soluble or suspension form and are taken up by the organisms living in them. The progressive and irreversible accumulation of these metals in various organs of marine organisms leads to metal-related diseases in the long run because of their toxicity, thereby endangering the aquatic biota[4–7]. Bioaccumulation of heavy metals in marine organisms leads to the bio-magnification process, which is a serious threat to the ecosystem and risk to its consumers. Various species of fish are used as bio-indicators of metal pollution[8]. The concentration of heavy metals in aquatic organisms can clearly depict the past as well as the current pollution status of the environment in which the organisms live[9].

The Gulf of Khambhat has its geographic proximity to two industrially progressive states of Gujarat and Maharashtra and hence acquires significant importance from the pollution point of view. It provides transportation avenues and effluent disposal sink for the industries in these two states. The unique geomorphology of the Gulf of Khambhat is its wide open around 230 km at southern side, reducing towards northeast reaching 5 km wide between Sabarmathi and Mahi river mouths (Figure 1). Its total length is about 250 km (ref. 10). Currents in the Gulf are mainly tidal and monsoonal in origin, dominated by barotropic tides[11]. Further, Gujarat coast has the highest tidal amplitude along the Indian coast and is located nearer to the Tropic of Cancer. This highly dynamic environment also includes oil exploration along the Tapi River basin (Figure 1). Hence a study was carried out to understand the metal profile in the body tissues of marine biota around the oil rigs area. The vibrant nature of the Gulf of Khambhat keeps these contaminants usually in suspension form as the bottom sediments are dispersed into the water column during major part of the year. This leads to high suspended matter load in the Gulf water than would occur in the open marine systems[12]. As a result, seafood, particularly fishes and crustaceans which have great local consumption and export value, is considerably affected[9]. In the present correspondence, we report the status of metal accumulation in some marine biota like fishes (*Harpodon* *nehereus*, *Arius platystomus* and *Scolinodon* sp.) and crustaceans (*Metapenaeus kutchensis*, *Penaeus monodon*, *Penaeus indicus*, *Panulirus polyphagus* and *Charybdis* sp.).

Fishes and crustaceans of equal size were collected with the help of standard trawl net hauled near the unmanned oil rigs (Figure 1). The collected samples were washed with distilled water, brought to the laboratory in an icebox and then frozen to –20°C. The samples were measured (size ~1 mm and weight ~1 g), dissected with clean equipment and then freeze-dried for 48 h. The muscles and soft tissues of all the fishes and crustaceans were pooled for each species respectively. These tissue samples were placed in small plastic vials. About 0.5 g of the homogenized samples of muscle was digested in triplicate with supra pure acids like HNO_3 (65% v/v) 7 ml and H_2O_2 (30% v/v) 1 ml using microwave oven digestive system (Multiwave 3000). Microwave digestion was used instead of classical methods because of the shorter duration of the process, less acid consumption, and ability to retain volatile compounds in the solutions[1,13–15]. The process of digestion transforms tissue samples from solid to liquid phase and leads to destruction of the organic components and extraction of metals into solution form suitable for spectroscopic analysis. These digested samples were suitably diluted to feed into inductively coupled plasma mass spectrometer (ICP-MS) to estimate the concentration of different heavy metals present in the respective samples. The concentration of metals like Cr, Zn, Mn, Ba, Pb, Co, Cu, Zn and Cd was estimated using ICP-MS[4,16]. Results are expressed in milligrams of metal per kilogram of tissue (mg/kg dry wt). All digested samples were analysed in triplicate. Analytical blanks were run in parallel during sample analysis and concentration was determined using standard solutions prepared in the same acid matrix. The accuracy of analysis was assured by carrying out spike tests.

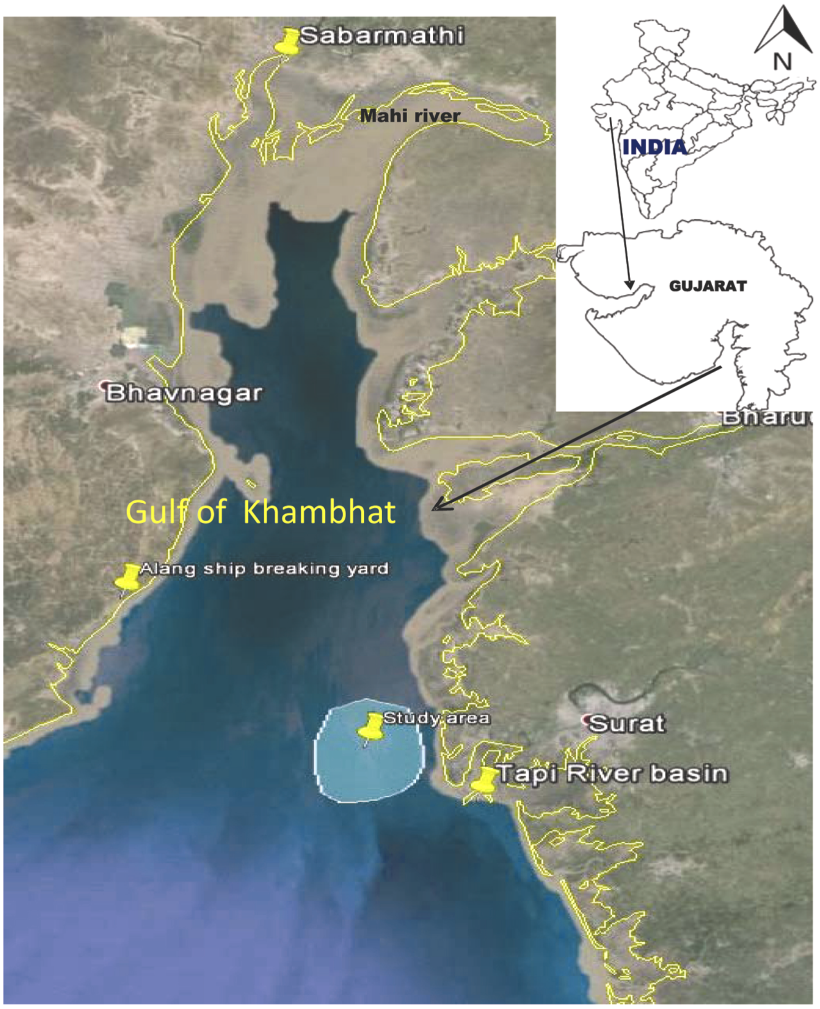

Figure 1. Location of the study area in the Gulf of Khambhat, India.

The concentration of metals (Cr, Zn, Mn, Ba, Pb, Co, Cu, Zn and Cd) in fishes and crustaceans is given in Table 1 and Figure 2. The data show that zinc has the highest concentration, followed by manganese and barium in fishes. Crustaceans also recorded the highest concentration of zinc followed by manganese and copper. Metal accumulation levels in crustaceans were high due to their bottom feeding nature. The degree of metal accumulation follows the orders: Zn > Mn > Cu > Ba > Ni > Cr > Cd > Co > Pb in crustaceans, and Zn > Mn > Ba > Cr > Ni > Cu > Pb > Co > Cd in fishes.

The highest mean Zn concentration in three fish species was 25.7 mg/kg dry wt, while in crustaceans species it was 33.9 mg/kg dry wt. The mean concentration of the essential elements Cu and Mn in fishes ranged from 1.4 to 2.37 mg/kg dry wt and 6.05 to 19.85 mg/kg dry wt respectively; in crustaceans it ranged from 3.26 to 22.04 mg/kg dry wt and 9.96 to 55.36 mg/kg dry wt respectively. Crustaceans exhibited slightly higher mean concentration of both Zn (33.9) and Mn (21.32) than that of fishes (Table 1). Overall, the concentration of Cd (twelve times), Co (two times), Cr (one time), Cu (five times), Ni (two times), Ba (two times) and Pb (one time) was found to be more in crustaceans compared to fishes, which may be due to the major functional differences in their body[17]. The study indicates that the accumulation of metals is relatively more in crustaceans than in fishes.

The concentration of some of the highly toxic metals (Cd, Cr and Pb)

Table 1. Heavy metal concentration (mg/kg dry wt) in commercial fishes and crabs collected from the Gulf of Khambhat

Heavy metals	Fishes	Crustaceans
Mn	11.2 ± 7.5	21.32 ± 19.3
Ni	2.43 ± 0.9	3.4 ± 0.9
Co	0.18 ± 0.07	0.36 ± 0.13
Cu	1.76 ± 0.52	8.86 ± 7.5
Zn	25.7 ± 15.49	33.9 ± 14.8
Cd	0.05 ± 0.02	0.61 ± 0.22
Pb	0.2 ± 0.06	0.23 ± 0.06
Cr	2.56 ± 1.2	2.3 ± 0.4
Ba	4.1 ± 1.14	7.25 ± 2.2

Table 2. Comparison of heavy metal concentration (μg g^{-1} dry wt) in muscles of fishes from the Indian coast and selected regions of the world

Species	Cr	Cd	Pb	Study area	Reference
Fishes	0.77 ± 0.054	0.23 ± 0.029	1.09 ± 0.071	*Gulf of Cambay, Arabian Sea	9
Crabs	2.075 ± 0.389	1.600 ± 0.566	2.775 ± 0.177	*Gulf of Cambay, Arabian Sea	9
Prawns	–	0.2 (0.1–0.4)	ND (0.01–0.02)	Thane creek, Arabian Sea	19
Prawns	–	0.1 (0.03–0.6)	0.3 (0.01–0.07)	Bassien creek, Arabian Sea	20
Crabs		0.3 (0.1–0.4)	0.03 (0.01–0.04)	Thane creek, Arabian Sea	19
Crabs		0.6 (0.4–0.7)	0.05 (0.02–0.07)	Bassien creek, Arabian Sea	20
Fishes	–	0.32 (0.19–0.73)	4.12 (2.4–16.0)	Arabian Sea, Pakistan	21
Fishes	–	0.59 (ND-3.24)	1.11 (1.0–3.43)	Northern Indian Ocean	22, 23
Crabs	–	0.61–1.12	<1.0–7.88	Northern Indian Ocean	22, 23
Tuna fish	0.38	0.16	0.53	Red Sea and Persian Gulf, Saudi Arabia	16
Crabs	0.1 ± 0.01	ND	ND	Cochin Kerala coast	24
Prawns	0.33 ± 0.05	ND	0.42 ± 0.03	Cochin Kerala coast	24
Fishes	–	1.39 ± 0.13	10.04 ± 0.43	Veraval coast, Gujarat	25
Fishes	0.95 ± 0.04	0.11 ± 0.03	0.48 ± 0.01	Cochin Kerala coast	24

*Gulf of Cambay also known as Gulf of Khambhat.

Table 3. Permissible metal levels in marine organisms utilized for food purposes from different countries

	Metals (ppm)									
Organization/country	Cd	Cu	Mn	Ni	Pb	Co	Cr	Ba	Zn	Reference
EC (European Community)	0.05	–	–	–	0.2	–	–	–	–	26
FAO (Food and Agricultural Organization)	–	10	–	–	0.5	–	–	–	30	27
Turkish guidelines	0.1	20	20	–	1	–	–	–	50	28
FAO/WHO (World Health Organization) limits	0.5	30	–	–	0.5	–	–	–	40	29
EU (Europian Union) limits	0.1	10	–	–	0.1	–	–	–	–	30
Saudi Arabia	0.5	–	–	–	2	–	–	–	–	31
MPEDA (Marine Product Export Developmental Authority), India	3.0	–	–	80	1.5	–	12	–	–	32

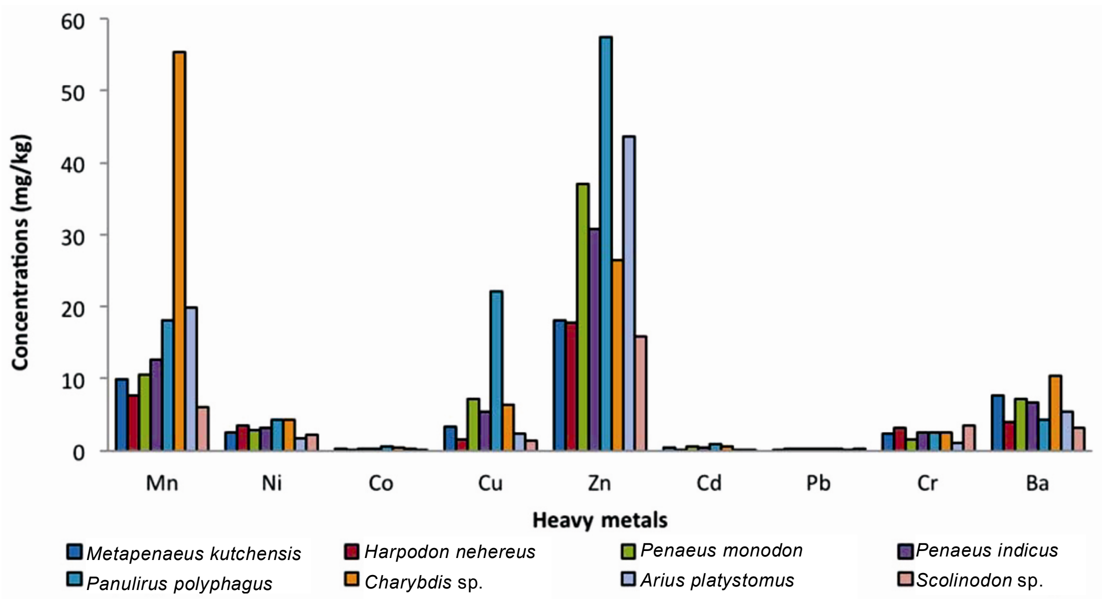

Figure 2. Bioaccumulation of heavy metals in fishes and crustaceans collected along the study area.

detected in organisms like fishes and crustaceans was compared with the reported values of biota from other regions (Table 2), in an effort to determine the degree of contamination in the study area. Pb accumulation is about 20 times less than that in the Arabian Sea along the Pakistan coast, and 11 times less than that in the Gulf of Khambhat study carried out along the Alang coast[9] (Table 2). Cd accumulation in fishes from the Gulf of Khambhat is about 12 times lesser than that in the northern Indian Ocean, and in the Veraval coast of Gujarat, it is about 28 times higher than that of the present study. However, it is six times lesser than that of the Gulf of Khambhat study conducted along Alang region[9] and Pakistan coast of the Arabian Sea. Cd accumulation in the crustacean species of the Gulf of Khambhat is about three times lesser than that of a previous study in the Gulf of Khambhat reported[9] along the Alang coast. In general, higher concentration of metals like Cd and Pb than in the case of the present study may be attributed to the proximity of the Alang ship breaking yard. Interestingly, the accumulation of Pb and Cd in the Gulf of Khambhat is comparatively lesser than that reported in the northern Indian Ocean, Thane and Bassien creeks as well as Pakistan coast of the Arabian Sea (Table 2). Cr accumulation in fishes from the Gulf of Khambhat was about three times higher than that of the Alang region in the Gulf of Khambhat[9], seven times greater than in the Red Sea, Persian Gulf and Saudi Arabia, and three times higher than the Cochin, Kerala Coast (Table 2). Cr accumulation in the crustacean species of the Gulf of Khambhat was about seven times higher than that in the Cochin Kerala coast and the same has been reported in the Gulf of Khambhat previously[9]. The high Cr concentration may be due to the spillage of drilling mud additives like chrome or ferrochrome lingosulphonate from the oil rigs[18].

The concentration of toxic metals like Pb and Cd in fishes is also similar to or less than the prescribed limits for India and other countries (Table 3). In the case of crustaceans, the concentration of Pb is within the limits, whereas Cd concentration is 12 times higher than that of the European Community, three times higher than that of England standards, six times higher than the Turkish standard and one time higher than that of FAO/WHO prescribed limits (Table 3).

Accumulation of heavy metals in some commercially important fish and crustacean species in the Gulf of Khambhat reveals that Pb and Cd are relatively higher than the standards prescribed in countries other than India. However, the concentrations were comparatively lower than the Marine Product Export Developmental Authority of India standards. The greater bioaccumulation of these metals may be due to anthropogenic activities, unusual physical oceanographic conditions and effluent discharges from the industries located in the vicinity. The conspicuous metal accumulation pattern among the fishes collected near oil rigs and ship braking yard indicates the presence of bioavailable toxic metals from these industries.

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