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Investigation of heavy metal concentrations in sea food from three selected landing centers of Chennai coast

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Abstract

A polluted marine environment may end in food chain and pose risk to public health. A study was undertaken to analyze the level of heavy metal concentrations chromium (Cr), copper (Cu), Iron (Fe), zinc (Zn), Lead (Pb), nickel (Ni), manganese (Mn), lithium (Li) and titanium (Ti) in sea foods harvested from fish landing centres Ennore, Royapuram and Pattinapakkam located in Chennai. The samples were analyzed using inductively coupled plasma optical emission spectrometry method (ICP-OES). The highest average concentration of heavy metals was recorded from Ennore (10.70 mg kg $^{-1}$) and in crabs (11.7 mg kg $^{-1}$) among the sea foods. Ni was highest and Fe was lowest recorded from all the study sites. Chi square analysis revealed no significant difference (P > 0.05) between the study areas and seafood varieties. Cr, Mn, Ni and Zn exceeded and Cu, Fe and Pb were within the permissible limits of WHO (1989) for human consumption.

Keywords: heavy metals, sea foods, landing centres, icp-oes, safety, public health

Introduction

Heavy metal is a metallic element with high atomic weight which can damage living things at low concentrations and tend to accumulate in the food chain [1]. Some heavy metals have essential roles for human health and forms an integral part of numerous enzymes. Heavy metal pollution has become a worldwide concern due to the increasing levels of pollution and its obvious impacts on human health. These are of great concern from the public health point of view, and being environmental pollutants it can occur naturally in the environment and can come from industrial (e.g. mining, metallurgical, incineration, pesticide etc.) or agricultural sources (e.g. pesticide and fertilizers use). Almost all pollutants find their ways finally to sea as the ultimate sink. These contaminants are highly toxic and may accumulate in seafood, whose consumption can represent an important route of human exposure to these harmful substances and ultimately threaten human health. Marine coastal ecosystems could therefore be endangered by pollutants, such as heavy metals, pesticides and antifoulants that could be easily detected in the water column or in the sediment of harbours and estuaries [2].

Heavy metals, in general, are not biodegradable, have long biological half lives and also have the potential for accumulation in the different body parts leading to unwanted side effects [3]. Untreated urban and industrial wastewater effluents cause a variety of health and environmental concerns, when released into receiving water bodies. Coastal belts are highly populated and urbanized with industries.

Marine food such as fish, prawn, crab and mussel are delicacies and form an important staple part of daily food. The tendency of heavy metals to get accumulated in marine animals is of scientific interest in heavy metal chemistry. The bioavailability of trace metals is the key factor determining tissue metal levels in the marine biota. Trace metal uptake occurs directly from surrounding marine water across the permeable body surface and from food along with the seawater to the gut [4]. Fish, crab, prawn and squids form an important link as possible transfer media to human beings. Information on the level of heavy metal pollution in coastal environment is important as they cause serious environmental health hazards [5, 6, 7].

Fishery harbour complex generate wastes of varying degrees and types. These wastes, if not properly handled, will lead to contamination of the product and degradation of the harbour environment due to pollution. Problems related to chemical contamination of the aquatic environment are nearly all manmade. Industrial effluents, sludge from sewage treatment plants, agriculture run-offs and raw untreated sewage from urban populations and industry-all these contribute to chemical contamination of the environment.

Although considerable work has been carried out on heavy metal levels in various media and marine animal species, there is a paucity of information in the heavy metal concentrations in the food web along the coast of chennai, India. Hence a detailed study on the assessment of heavy metals in sea foods becomes inevitable. Evaluation of heavy metals along the food chain may throw light on the heavy metal input to the human body from sea food. The extensive persistence of heavy metals infectivity in bioaccumulation and biomagnification are a serious threat of the food chain and these heavy metals will automatically transfer into the body while people consumes seafood. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation.

There are about 12,000 industries in Tamil Nadu out of these 5,500 industries are located in coastal districts and 2,500 are situated near the coasts. The major congregation of industries along Chennai coast where 1500 industries are located [8]. The domestic and municipal wastes from many coastal cities in Tamil Nadu are discharged directly into the coastal waters untreated. In the city of Chennai alone, there are more than 10million people living along the coast, and as a result more than 75 million gallons /day of sewage get discharged into adjoining sea. The major part of the sewage is released into Coovum, Adyar rivers and Buckingham canal which finally drains into the sea.

The main objective of this present study was to determine the heavy metal concentrations (Cu. Cr, Fe, Zn, Pb, Ni, Mn, Li and Ti in different sea foods viz crabs, fishes, prawns and squids harvested from three different fish landing centres Ennore, Royapuram and Pattinapakkam located in Chennai. The results obtained will provide information on levels of heavy metals in the sea food harvested from different parts of Chennai for effective monitoring of safety of the sea food consumed and safe guard the public health.

Materials and methods Study area

Royapuram fishing harbour, also known as Chennai fishing harbor or Kasimedu fishing harbor located in latitude: 13°06'14.51"N and longitude: 80° 17' 37.18" E of Chennai is one of the major fishing grounds for fishes and crustaceans located at Kasimedu in the Royapuram area of Chennai, India [9]. Ennore creek is a backwater located in Ennore, located in latitude: 13.2146° N longitude: 80.3203° E of Chennai along the Coromandel Coast of the Bay of Bengal. It has been estimated that about 4, 49, 000 litres / day of industrial effluents carrying heavy metals are let out in this estuary by the industrial establishments $^{[10]}$. The study area is also surrounded by three industrial belts namely the Manali, Ennore-Tiruvottiyur and Ambattur padi complexes [11]. Pattinapakkam latitude: 13.0301° N longitude: 80.2771° E is prominent fishing locality located along the beachfront near Mylapore, abundant with wide variety of sea food. The fresh catch is marketed near the beachfront and it is also in the close proximity to road way often with heavy traffic. This

place is frequently affected with discharge of domestic and industrial effluents draining from the rivers and several episodes of oil spillage from cargo ships.

Sample collection

Assorted sea food samples which include fishes, prawns, crabs and squids were collected every month over a period of 14 months from October 2018 to December 2019 from three different landing centres of Chennai city viz. Royapuram, Ennore and Pattinapakkam. A total number of forty five samples were analyzed which include fifteen from each landing centre. Upon collection the samples were stored in sterile polythene zip lock covers. Samples were brought to the laboratory, thoroughly washed with distilled water to remove the external debris and sediments and were preserved at -20°C until analysis.

Estimation of the level of toxic metal / chemical concentrations from the sea food Samples

The frozen samples thawed at room temperature and processed for analysis. 2g of sample was weighed and homogenized manually using mortar and pestle.

Digestion of samples (Wet digestion procedure)

2 g of sample was placed in a digestion tube and pre digested in 10ml of concentrated HNO $_3$ at 135° C until the liquor was clear. There after 10 ml of HNO $_3$, 1 ml of HCLO $_4$ and 2ml of H $_2$ O $_2$ was added and temperature was maintained at 135° C for one hour until the liquor becomes colourless. Product of digestion was allowed to slowly evaporate to near dryness. It was cooled and digested in 10 ml HNO $_3$. The digests subsequently filtered through whatmann filter paper No. 1 and diluted to 25 ml in 1M HNO $_3$ [12]. The digested samples were stored under refrigerated conditions until analysis.

Inductively coupled plasma optic emission spectrometry (ICP-OES)

To cover optimum emission working range 0.001 to 5.00mg/ml serial dilutions was prepared. Freshly stored standard curves in the system software was used. Blank solutions were also prepared accordingly. The external standard methods of the Inductively Coupled Plasma Optical emission Spectrometry method (ICP-OES) were used for the determination of heavy metals [13]. The (Perkin Elmer ICP-OES 7000 DV) operational with SVS auto sampler was used for the determination of heavy metals. Samples were analyzed under the instrumental operating conditions. RF power 1.3 KW, outer argon flow 15.0 L/min, intermediate and inner argon flow 1.0 L/min and the nebulizer uptake rate (ml/min) 1.0 sample run were performed in replicate and integrated computer results of determinations will be recorded.

Table 1: Wave lengths for determination of heavy metals (nm)

Element	Wave length (nm)			
Chromium	267.716			
Copper	327.393			
Iron	238.204			
Lithium	670.784			
Manganese	257.610			
Nickel	231.604			
Lead	220.353			
Titanium	334.940			
Zinc	206.20			

Statistical analysis

Data have been entered in to MS office 2007 excel spread sheet, coded and analyzed by SPSS version 24. One way ANOVA was performed to assess whether heavy metal concentrations varied significantly between sites and different sea foods and chi-square test to measure the association between study centers and different sea foods. (P < 0.05) considered as statistically significant.

Results and discussion

The heavy metal concentrations in the study areas was, highest average concentration of heavy metals recorded from Ennore (10.70 mg kg⁻¹), followed by Royapuram (10.63 mg kg⁻¹) and Pattinapakkam (10.56 mg kg⁻¹). (Fig.1). Similar trend observed by [14, 15] in their study where metal concentrations in fish tissues collected from Ennore estuary were much higher than those from the Kovalam estuary and offshore areas. The concentrations of Hg, Cd, Cu, Zn, Ni, Pb and Fe in various tissues of *Liza macrolepis* inhabiting the Ennore estuary were found to be above the permissible safe levels [16]. The high metal concentrations in the tissues of fish inhabiting the Ennore estuary are probably related to a high influx of metals as a result of pollution from the surrounding industries thereby increased bioavailability to the fish.

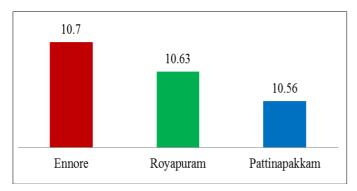


Fig 1: Heavy metal concentrations in the sampling sites (mg kg⁻¹)

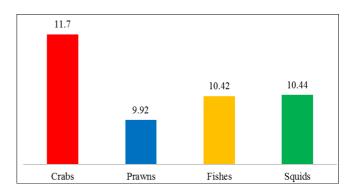


Fig 2: Heavy metal concentrations in the sea food varieties (mg kg⁻¹)

Information about heavy metal concentration in different sea food types is important with respect to both the ecosystem management and human consumption. The aquatic organisms are sensitive to heavy metals when the concentrations of the metals reach a significant level in the water and sediment. In the present study remarkable diferences of metal concentrations are observed in the muscle of crab, prawns, fishes and squid. The presence of heavy metal concentrations on an average was highest in crabs (11.7 mg kg⁻¹) and lowest in prawns (9.9 mg kg⁻¹) and similar concentrations were recorded from fishes and squids (10.4 mg kg⁻¹). (Fig.2) Similar findings were reported by [17, 18] where, crabs showed higher mean heavy metal concentrations than shrimp and lobster who collected from the coast of Bangladesh. Crabs and shrimps tend to accumulate more heavy metals than fish as a result of differences in the evolutionary strategies adopted by various phyla [19]. In contrast [20] mentioned that shrimp samples heavy metal concentrations were higher than the crab heavy metal concentrations in southern Gulf of Mexico. Crustaceans, particularly crabs, may be a good indicator for measuring the contamination level in the surface sediment. Crustaceans may act as a typical benthic organism which live on sea floor, and it may be considered as an absolutely discrepant aquatic species [21]. The hepatopancreas of crabs has the capability of accumulating more trace metals and is one of the most important organs that play vital role in metal detoxification [22].

Table 1: Mean heavy metal concentration in crab samples at different landings in Chennai

S. No	Heavy metals	Ennore		Royapuram		Pattinapakkam	
		Mean (mg/Kg)	SE	Mean (mg/Kg)	SE	Mean (mg/Kg)	SE
1.	Chromium	1.9509	0.171	2.4255	7.697	2.0725	0.284
2.	Copper	3.6676	0.749	3.1970	0.388	2.2900	0.235
3.	Iron	0.0009	0.000	0.0015	0.000	0.0011	0.000
4.	Lithium	0.2698	0.070	0.3321	0.050	0.3175	0.022
5.	Manganese	16.6220	6.823	8.8308	1.973	8.0094	1.843
6.	Nickel	56.1889	2.004	83.2850	16.460	70.4563	11.195
7.	Lead	0.2113 ^a	0.041	1.5904 ^{ba}	0.467	0.5166 ^a	0.106
8.	Titanium	1.0015	0.299	1.5918	0.586	1.1496	0.289
9.	Zinc	8.3965	0.503	20.9538	7.663	12.2694	1.506

Mean values with different superscripts for each element differ significantly (p<0.05)

Table 2: Mean heavy metal concentration in fish samples at different landings in Chennai

S. No	Heavy metals	Ennore		Royapuram		Pattinapakkam	
		Mean (mg/Kg)	SE	Mean (mg/Kg)	SE	Mean (mg/Kg)	SE
1.	Chromium	2.169	7.531	2.079	0.002	2.205	6.251
2.	Copper	2.186	0.582	2.743	0.490	1.670	0.135
3.	Iron	0.001	0.000	0.001	0.000	0.001	0.000
4.	Lithium	0.186^{a}	0.033	0.346 ^b	0.018	0.332 ^b	0.019
5.	Manganese	6.782	1.212	8.286	2.485	5.802	0.287
6.	Nickel	66.068 ^a	6.843	64.075 ^a	1.138	71.593 ^b	1.009
7.	Lead	0.340	0.083	0.476	0.231	0.398	0.044
8.	Titanium	0.779	0.057	1.541	0.476	0.744	0.123
9.	Zinc	10.591	1.390	12.086	0.439	11.643	1.187

Mean values with different superscripts for each element differ significantly (p<0.05)

Table 3: Mean heavy metal concentration in prawn samples at different landings in Chennai

S. No	Heavy metals	Ennore		Royapuram		Pattinapakkam	
		Mean (mg/Kg)	SE	Mean (mg/Kg)	SE	Mean (mg/Kg)	SE
1.	Chromium	2.102	9.035	2.043	0.056	2.293	0.125
2.	Copper	3.132	0.734	1.524	0.285	3.306	1.662
3.	Iron	0.001	0.000	0.001	0.000	0.001	0.000
4.	Lithium	0.311	0.104	0.514	0.130	0.533	0.232
5.	Manganese	13.000	4.576	6.828	1.928	13.805	7.624
6.	Nickel	59.100	3.399	59.267	1.758	67.379	4.600
7.	Lead	0.231a	0.025	0.602^{b}	0.235	0.337a	0.023
8.	Titanium	0.827	0.149	0.743	0.055	0.571	0.199
9.	Zinc	9.366	1.526	11.603	2.350	8.635	0.662

Mean values with different superscripts for each element differ significantly (p<0.05)

Table 4: Mean heavy metal concentration in squid samples at different landings in Chennai

S. No	Heavy metals	Roya	Pattinapakkam		
S. NO		Mean (mg/Kg)	SE	Mean (mg/Kg)	SE
1.	Chromium	2.011	8.914	2.175	8.039
2.	Copper	2.706	0.952	0.769	0.056
3.	Iron	0.002	0.001	0.001	0.000
4.	Lithium	0.274	0.133	0.553	0.093
5.	Manganese	10.048	4.293	9.2	0.995
6.	Nickel	60.600	0.545	70.498	7.348
7.	Lead	0.305 ^a	0.044	0.467 ^b	0.031
8.	Titanium	1.627	0.708	0.690	0.021
9.	Zinc	11.243	1.216	10.715	1.237

Mean values with different superscripts for each element differ significantly (p<0.05)

Depending upon the average over all mean value of the metal accumulation in the assorted sea food samples collected from study sites the accumulation pattern of metals was in the order of Ni > Zn > Mn > Cu > Cr > Ti > Pb > Li > Fe in Royapuram, Ni > Mn > Zn> Cu > Cr > Ti > Pb > Li > Fe at Ennore and Ni > Zn > Mn > Cr > Cu > Ti > Li > Pb > Fe at Pattinapakkam. In samples from all the stations the highest recorded heavy metal accumulated is Nickel, which is similar to the study of $^{[23]}$ in the selected edible fishes harvested from fishing harbour, Visakhapatnam. The lowest metal recorded was Fe in the study which is contrast to the studies of $^{[24]}$ in fishes from north east coast of India, Kalpakkam $^{[25]}$ and in Mumbai harbour $^{[26]}$.

Nickel: The elevated Nickel concentrations observed in the present study from all the study sites is due to petroleum industries, stainless steel industries, electroplating plants, smelting plants, nickel-cadmium battery plants and nickel smelters in this particular geographical region. Nickel is also used in jewelry, ceramics, disinfectants and batteries and found to be elevated in populated areas [27]. In the present study the maximum mean concentrations of Ni was 69.9 mg kg⁻¹ from Pattinapakkam and minimum of 60.4 mg kg⁻¹ from Ennore. The measured values are higher than the values of [23] (1.63 mg kg⁻¹) in edible fishes of Vishakapatnam harbour and in fishes of Western Australia (7.5 mg kg⁻¹) [28]. The mean concentrations of Ni differ significantly between Pattinapakkam and other two centres (P < 0.05) in fishes. (Tab. 2). The estimated maximum guideline for Ni is 70-80 mg kg⁻¹ as per USFDA, 1993 guidelines. The concentrations of Ni was below the stipulated limit.

Zinc: Zinc recorded highest accumulation next to Ni at a maximum concentration of 13.9 mg kg⁻¹ at Royapuram and minimum concentration of 9.45 mg kg⁻¹ at Ennore. Similar findings were reported in marine fishes of bay of bengal ^[28], in selected fishes of Gulf of mannar ^[29] and in different sea foods available at Selangor, Malaysia ^[30]. The main sources of zinc

in the present geographical locale are galvanization units, paint manufacturing units and pharmaceutical processes. Zn is used as galvanized metal paint to prevent corrosion of boats ^[31]. Higher levels of Zn in harvest from Royapuram is may be due to more number of fishing boats and trawlers docked along side of jetty for a longer time which may favour the leaching of Zn from the paints from outer of fishing boats. The results of the present study showed that sea food tested from all the study sites were within the permissible limits of WHO (1989) which is 30-100 mg kg⁻¹.

Manganese: Mn concentration in the samples from all the study sites is above the detection levels of WHO, 1989 (1 mg kg⁻¹). Higher concentration reported from Ennore (12 mg kg⁻¹) followed by Pattinapakkam and Royapuram. The major sources of Mn are reported to be from iron, steel and alloy industries and to the lesser extent from production units of dry cell batteries, fertilizers and fungicides. Ennore is a hub of a range of industrial projects which let their untreated waste water flow in to the Ennore creek. A survey along the coast particularly Buckingham canal indicated the presence of above small scale manufacturing industries acting as a source of this metal at different places of Chennai ^[25] and coovum river connects Buckingham canal to the bay of bengal at center of Chennai which is an important contributing for detection of this metal in Royapuram and Pattinapakkam.

Chromium: Chromium is one of the priority metals which is of great health significance. The increased levels in the food chain is a consequence of human activities like mining, improper waste disposal and fuel combustion. The chromium values in this study were above the detection level permitted by WHO, 1989 for human consumption (1mg kg⁻¹) but lower than the maximum allowable chromium content level in fish (12-13 mg kg⁻¹) set by USFDA, 1993. The range of Cr levels recorded in this study were (2.05-2.19 mg kg⁻¹), which was higher than measured (0.65-0.92 mg kg⁻¹) in Parangapettai [32], (0.47 mg kg⁻¹) in Calicut [33], 0.2-0.8 mg kg⁻¹ by in Kalpakkam

^[25]. Higher values were reported in California ^[34]. 80-90% of tannaries around the world use salts of trivalent chromium for tanning ^[35]. 40% of total tanneries in India are located in Tamil Nadu. The major production centres of leather and leather products are located in Chennai. As of 2019 more than 2000 leather and tanning factories exist in Chennai and largest leather tannery in chromepet ^[36]. All the liquid wastes are dumped in to the sewage lines then led to one of the lakes or empty into the river then to the sea. This might be one of the attribute to higher chromium levels recorded in this study. Most of the studies proved that chromium is the predominant heavy metal in chrome tanning effluent 200 mg l⁻¹ of Cr in effluent from leather processing units of Bangladesh ^[37].

Copper: Cu is an micronutrient is required for proper growth development and maintenance of bone, connective tissue, brain, heart and many other organs. Copper is commonly found in aquatic systems as a result of both natural and anthropogenic sources. Natural sources of copper in aquatic systems include geological deposits, volcanic activity, and weathering and erosion of rocks and soils. Anthropogenic sources of copper include mining activities, agriculture, metal and electrical manufacturing, sludge from publicly owned treatment works, pesticide use. A major source of copper in the marine environment is antifouling paints, used as coatings for ship hulls, buoys, and underwater surfaces, and as a contaminant from decking, pilings and some marine structures that used chromated copper arsenate treated timbers [38]. The mean average values of cu in all the study centers is within the limits of WHO, 1989 (30 mg kg⁻¹). The highest concentrations recorded from Ennore (2.9 mg kg⁻¹) followed by Royapuram and Pattinapakkam. The levels were similar to the findings of [39, 26]. The observed values were lower than those reported by²⁹ (6.27 mg kg⁻¹) and higher than the values reported by $^{[23, 40]}$ (0.29 mg kg⁻¹ and 0.39 mg kg⁻¹). The mean concentration values in this study were within the permissible levels recommended by WHO (1989) which is 30 mg kg⁻¹.

Lead: Lead is a non essential trace metal and the adverse health effects from Pb are familiar. It has adverse effect on both marine biota and humans. The highest concentration reported from this study is from the samples of Royapuram (0.74 mg kg⁻¹). Antifouling paints used to prevent the growth of marine organisms at the bottom of the boats and trawlers contain Pb as an important component. Presence of large number of boats and trawlers in Royapuram may be a reason for increased levels. Pb also enters to oceans and coastal waters both from terrestrial sources and atmosphere in the form of lead aerosols [41]. This may be a contributing factor for high levels of Pb in sea food obtained from Pattinapakkam (0.42 mg kg⁻¹) as the landing centre is in close proximity to the road way with near shore automobile activity. The values obtained in the present study were higher than reported by [42] which is 0.12 mg kg⁻¹. Even though Pb was detected in samples from all the study centres, the mean concentration was within the permissible level for human consumption set by WHO (1989) for human consumption (0 to 0.15 mg kg⁻¹). The mean values of Pb differ significantly (P < 0.05) for crabs, prawns and squids between the study centres. (Tab.1, 2 and 4). A significant difference of P < 0.01 in lead reported between the different stations of study in Sunderbans [41]. Higher mean values of Pb is recorded from crabs (1.59 mg kg 1) and prawns (0.231 mg kg⁻¹) from Royapuram and in squids

(0.467 mg kg⁻¹) from Pattinapakkam.

Titanium: Titanium is classified as possible carcinogen. Metallic titanium is mainly used in the aircraft industry and in the production of high strength corrosion resistant alloys. Titanium dioxide is extensively used in white pigment in paints, enamels and plastics. The main source of contamination in environment is combustion of fossil fuel and incineration of titanium containing wastes. Ti was detected in samples from all the sampling sites, with a mean concentration of 1.37 mg kg⁻¹ from Royapuram, 0.86 mg kg⁻¹ from Ennore and 0.78 mg kg⁻¹ from Pattinapakkam. The concentrations recorded from all the sites were highe. The maximum detectable limits in the fish which is 0.025 mg kg⁻¹ ⁴³. High levels of Ti in sediments reported from different regions of Chennai coast, which was as high as 4100-20,000 mg 1-1 [44], which is an substantial evidence for higher concentration for Ti in sea food harvested along the coast in our study.

Lithium: Lithium is clearly important to modern man. Lithium materials are important in ceramics, glass industry, aluminium production, pharmaceuticals, batteries, nuclear reactor coolants, hot spring spas and swimming pools. The highest Li mean concentrations were reported from Pattinapakkam (0.43 mg kg⁻¹) followed by Royapuram and Ennore. Pattinapakkam and Royapuram recorded higher than Ennore. Our present values were higher than the values reported by [45] in North Chile, where they have analyzed nine shell fish and eight fish types. All had high levels of Li which corresponds to high levels of Li in ground water which is >1500 pbb. They obtained a range of 18.2 to 110.6 mg kg⁻¹ in their study. Li at a concentration of 0.27 to 1.42 mg kg⁻¹ in Cauvery river basin, Tamil Nadu [46]. Literature on Li is available on industrial uses, medical uses and in water but not much published data available on levels of Li in sea foods. Desirable limits or permissible limits were unavailable for foods to make a comparison with the present study. The mean values of Li differs significantly between Ennore and other two study centres (P < 0.05) for fishes. (Tab.2). Pattinapakkam and Royapuram recorded higher than Ennore.

Iron: The major source of Fe in coastal waters is due to decrease in grain size and an increased input of organic matter and anthrapogenic metals from industrial pollution and also due to direct discharge of sewage and hospital waste in to the water bodies [47]. The mean concentrations of Fe recorded in the present study is 0.0009 to 0.001 mg kg⁻¹ which is within the permissible levels of WHO (1989) that is 0.004 to 0.0048 mg kg⁻¹. The results obtained were in contrast to studies (240 mg kg⁻¹), (59.6 to 73.4 mg kg⁻¹) in mediterranaian sea [26, 48]. In the present study highest concentrations of Fe (0.0012 mg kg⁻¹), Mn (14.2 mg kg⁻¹), Ni (69.8 mg kg⁻¹), Pb (0.77 mg kg⁻¹ ¹), Ti (1.24 mg kg⁻¹) and Zn (13.8 mg kg⁻¹) were recovered from crab samples. Cr (2.15 mg kg⁻¹) and Cu (4.4 mg kg⁻¹) were highest in fish samples, prawns has the highest concentrations of Li (0.45 mg kg⁻¹). Out of all the sea foods studied squids recorded less concentrations of all the heavy metals. The mean concentration of Pb is higher in crabs and prawns of Royapuram, whereas in squids it is in Pattinapakkam. Lithium concentration is highest in fishes from Royapuram and Ni concentration is high in fishes of Pattinapakkam.

Table 5: Association of study areas and sea food varieties

Study area	Number of complex		Sea food va	Chi Canana taat	Cionificance		
	Number of samples	Crab	Prawn	Fish	Squid	Chi Square test	Significance
Ennore	15	5 (33.3)	5 (33.3)	5 (33.3)	0 (0.0)		
Royapuram	15	5 (33.3)	3 (20.0)	2 (13.3)	5 (33.3)	8.727	0.190
Pattinapakkam	15	2 (13.3)	3 (20.0)	5 (33.3)	5 (33.3)		

(P < 0.05)** statistically significant (P > 0.05) no significance

Statistical analysis using chi square revealed no significant difference (P > 0.05) between the study areas and seafood varieties from these areas. (Tab. 5)

Conclusion

This study was undertaken to provide the information on metal accumulation in sea foods harvested from three landing centres of Chennai. Metal concentrations showed variability between the study sites and between different types of sea Ennore showed highest mean heavy metal concentrations followed by Royapuram and Pattinapakkam which could be related to high contamination of water through industrial and anthrapogenic activities. Crab samples showed the maximum mean heavy metal concentrations followed by fishes, squids and prawns indicating distinct accumulation capacity for each type. The present study reveals the concentrations of Cu, Fe and Pb were within the permissible limits of WHO (1989) for human consumption whereas, Cr, Mn, Ni and Zn were above the permissible limits. Li and Ti were also detected in samples from three study sites which is a matter of public health concern.

References

- 1. Environmental Protection Agency, 2000. http://www.epa.gov/305b.
- 2. Antizar-Ladislao B. Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. Environ Int. 2008; 34(2):292-308.
- 3. Sathawara NG, Parikh DJ, Agarwal YK. Essential heavy metals in environmental samples from western India bulletin of environmental contamination and toxicology. 2004; 73:756-761.
- 4. Depledge MH, Rainbow PS. Models of regulation and accumulation of trace metals in marine invertebrates: A mini-review. Compar. Biochem. Physiol. 1990; 97:1-7.
- 5. Nitta T. Marine pollution and sea life (Ed.: M. Ruivo). Fishing News (Books) Ltd., Farmharm, 1992, 77.
- 6. Gupta Pallavi, Neera Srivastava. Effects of sub-lethal concentrations of zinc on histological changes and bioaccumulation of zinc by kidney of fish, Channa punctatus (Bloch). J Environ. Biol. 2006; (27):211-215.
- Shukla Vineeta, Monika Dhankhar, Jai Prakash, Sastry KV. Bioaccumulation of Zn, Cu and Cd in Channa punctatus. J Environ. Biol. 2007; 28:395-397.
- 8. GoTN. Tamil Nadu Annual Fisheries Statistics 1994-95 (Endeavour and Achievement), Department of Fisheries, Chennai, 1995.
- Mohanraj G, Shoba Joe Kizhakudan, Vivekanandan Kasim HM, Lakshmi Pillai S, Joe K Kizhakudan SN *et al.* Quantitative changes in bottom trawl landings at Kasimedu, Chennai during 1998-2007. Jmbai. 2012; 54(20):01727-08.
- Shanthi V, Gajendran N. The impact of water pollution on the socio-economic status of the stakeholders of Ennore Creek, Bay of Bengal (India): Part Indian Journal of Science and Technology, 2009, 2(3).

- 11. Jayaprakash M, Kumar RS, Giridharan L, Sujitha SB, Sarkar SK, Jonathan MP. Bioaccumulation of metals in fish species from water and sediments in macrotidal Ennore creek, Chennai, SE coast of India: A metropolitan city effect. Ecotoxicol. Environ. Saf. 2015; 120:243-255.
- 12. Fredeen KJ. Inductively coupled plasma atomic emission Spectroscopy: an overview. 2014; 4(8):470-477.
- 13. Belton PS. Trace element analysis of food and diet rsc food analysis monographs royal society of chemistry, Thomos Graham House Science park, Milton road Cambridge, CB4 0WF, UK, 2006.
- 14. Padmini E, Vijaya Geetha B. A comparative seasonal pollution assessment study on Ennore Estuary with respect to metal accumulation in the grey mullet, *Mugil cephalus*. International Journal of Oceanography and Hydrobiology. 2007; 36(4):91-103.
- 15. Lourduraj Arockia Vasanthi, Peranandam Revathi, Jayaprakash Mini, Natesan Munuswamy. Integrated use of histological and ultrastructural biomarkers in *Mugil cephalus* for assessing heavy metal pollution in Ennore estuary, Chennai. Chemosphere. 2013; 91:1156-1164.
- Nammalwar P. Fish bioassay in the cooum and adyar estuaries for environmental management, In K.P. Singh & U.J.S Singh (Eds), Tropical ecosystems Ecology and management Delhi, India: Wiley Eastern, 1992, 359-370.
- 17. Mohammad Abdul Bakia, Md. Muzammel Hossaina, Jhuma Aktera, Shamshad B, Quraishib, Md. Fajlul Haque Shojiba *et al.* Concentration of heavy metals in seafood (fishes, shrimp, lobster and crabs) and human health assessment in Saint martin island, Bangladesh. Ecotoxicology and environmental safety. 2018; 159:153-163
- 18. Raknuzzaman M, Ahmed MK, Islam MS, Habibullah-Al-Mamun M, Tokumura M, Sekine M *et al.* Trace metal contamination in commercial fish and crustaceans collected from coastal area of Bangladesh and health risk assessment. Environ. Sci. Pollut Res. 2016; 23:17298-17310.
- 19. Prabhu Dass Batvari B, KamalaKannan S, Shanthi K, Krishnamoorthy R, Lee KJ, Jayaprakash M. Heavy metals in two fish species (*Carangoidel malabaricus* and *Belone stronglurus*) from pulicat lake north of chennai, and southeast coast of India. Environ. Monit Assess. 2008; 145:167-175.
- 20. Taft MK, Hosein ZZ, Mehrizi SMT. The relation between financial literacy, financial wellbeing and financial concerns. Int. J Bus. Manag. 2013; 8:63.
- 21. Ololade IA, Lajide L, Olumekun VO, Ololade OO, Ejelonu BC. Influence of diffuse and chronic metal pollution in water and sediments on edible seafoods within Ondo oil-polluted coastal region, Nigeria. J Environ. Sci. Health Part A. 2011; 46:898-908.
- 22. Reinecke AJ, Snyman RG, Nel JAJ. Uptake and distribution of lead (Pb) and cadmium (Cd) in the freshwater crab, *Potamonautes perlatus* (crustacea) in the eerste river, south Africa. Water air soil pollut. 2003; 145:395-408.

- 23. Sanchari Biswas, Ramakrishna CH, Avasn Maruthi Y. Heavy Metal Concentrations In selected edible fishes from fishing harbour of Visakhapatnam, Andhra Pradesh, India. International Journal of Engineering Sciences & Research Technology. 2017; 6(10):570-578.
- 24. Kumar PJS, Delson PD, Babu PT. Appraisal of heavy metals in groundwater in Chennai city using a HPI model. Bulletin of Environmental Contamination and Toxicology. 2012; 89:793-798.
- 25. Smita Achary M, Satpathy KK, Panigrahi S, Mohanty AK, Padhi RK, Sudeepta Biswa et al. Concentration of heavy metals in the food chain components of the near shore coastal waters of Kalpakkam, southeast coast of India Environment & Safety Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, TN, India. Food Control. 2017; 72:232-243.
- Velusamy A, Satheesh Kumar P, Anirudh Ram, Chinnadurai S. Bioaccumulation of heavy metals in commercially important marine fishes from Mumbai Harbor, India, Marine Pollution Bulletin. 2014; 81:218-224.
- 27. Eisler R. Cadmium hazard to fish, wildlife and invertebrates: a synoptic review. US Fish Wildl. Serv. Biol. Rep. 1985; 85:1-30.
- 28. Saha N, Mollah MZI, Alam MF, Safiur Rahman M. Seasonal investigation of heavy metals in marine fishes captured from the Bay of Bengal and the implications for human health risk assessment, Food Control, 2016.
- 29. Karunanidhi K, Rajendran R, Pandurangan D, Arumugam G. First report on distribution of heavy metals and proximate analysis in marine edible puffer fishes collected from gulf of mannar. Marine Biophere Reserve, South India. Toxicol. Rep. 2017; 4:319-327.
- 30. Abdulali KA, Taweel M, Shuhaimi-Othman, Ahmad AK. Analysis of heavy metal concentrations in tilapia fish (*oreochromis niloticus*) from four selected markets in selangor, peninsular Malaysia. Journal of Biological Sciences. 2012; 12:138-145.
- 31. Lakshmanan R, Kesavan K, Vijayanand P, Rajaram V, Rajagopal S. Heavy metals accumulation in five commercially important fishes of parangipettai, southeast coast of India. Advance Journal of Food Science and Technology. 2009; 1(1):63-65.
- 32. Raja P, Veerasingam S, Suresh G, Marichamy G, Venkatachalapathy R. Heavy metal concentration in four commercially valuable marine edible fish species from Parangipettai coast, south east coast of India. Journal of Animal and Veterinary Advances. 2009; 1(1):10-14.
- 33. Shankar BS. A critical assay of heavy metal pollution index for the ground waters of Peenya Industrial Area, Bangalore, India. Environ Monit Assess. 2009; 191:289.
- 34. Moeller A, Mac Neil, Ambrose SD, Hee RF. Elements in fish of malibu creek and malibu lagoon near Los Angeles, California. Mar. Pollut. Bull. 2003; 46:424-429.
- 35. Leathersmithe. Tanning methods and the danger of using chromium-tanned leathers, 2016. http://www.leathersmithe.com. September, 2016.
- 36. Ramalingam D. Growth of Leather Industries in Tamil Nadu under the British A study International Journal of Humanities and Social Sciences. 2017; 7(1):61-65.
- 37. Manjushree Chowdhury, Mostafa MG, Tapan Kumar Biswas, Abul Mandal, Ananda Kumar Saha. Characterization of the effluents from leather processing Industries. Environmental Processes. 2015; 2:173-187.

- 38. EPA-HQ-OPP-2015-0349 at https://www.regulations.gov.
- 39. Sankar TV, Zynudheen AA, Anandan R, Viswanathan Nair PG. Distribution of organochloride pesticides and heavy metal residues in fish and shellfish from Calicut region, Kerala, India. Chemosphere. 2006; 65:583-590.
- 40. Akan J, Mohmoud S, Yikala B, Ogugbuaja V. Bioaccumulation of some heavy metals in fish samples from river benue in vinikilang, adamawa state, Nigeria. Am J Anal Chem. 2012; 3:727-36.
- 41. Abhijit Mitra, Kakoli Banerjee, Subhasmita Sinha. Shrimp tissue quality in the lower Gangetic delta at the apex of Bay of Bengal, Toxicological & Environmental Chemistry. 2011; 93(3):565-574.
- 42. Burger J, Gochfeld M. Heavy metals in commercial fish in New Jersey. Environ. Res. 2005; 99:403-412.
- 43. Environmental Health Criteria. 24 International programme on chemical safety, 1982.
- 44. Tholkappian M, Ravisankar R, Chandrasekaran A, Prince Prakash Jebakumard J, Kanagasabapathy KV, Prasad MVR *et al.* Assessing heavy metal toxicity in sediments of Chennai coast of Tamil Nadu using Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) with statistical approach. Toxicology Reports. 2018; 5:173-182
- 45. Figueroa LT, Razmillic B, Zumeata O, Aranda GN, Barton SA, Schull WJ *et al.* Environmental lithium exposure in the north of Chile--II. Natura Biol Trace Elem Res, 2013.
- 46. Vetrimurugan E, Brindha K, Elango L Osman Muzi Ndwandwe. Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta. Applied Water Science. 2017; 7:3267-3280.
- 47. Satheeshkumar P, Senthilkumar D. Identification of heavy metals contamination by multivariate statistical analysis methods in Pondicherry mangroves, India. Journal of Environment and Earth Science, 2011, 1(1).
- 48. Kalay M, Ay O, Canil M. Heavy metal concentrations in fish tissues from the Northeast Mediterranean sea. Bull. Environ. Contam. Toxicol. 1999; 63:673-681.