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STUDY ON THE BIOACCUMULATION OF HEAVY METALS IN COMMERCIALLY VALUABLE AND EDIBLE MARINE SPECIES OF ENNORE CREEK, SOUTH INDIA

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ABSTRACT

A systemic study has been undertaken to establish a baseline data on the profiles of on the heavy metals (Cu, Cr, Zn, Ni, Pb and Cd) in the biota of Ennore Creek environment. Samples of fishes (*Oreochromis mossambica*, *Mugil cephalus, Clarias batrachus* and *Channos channos*), shrimps (*Penaeus monodon* and *Penaeus indicus*), crab (*Portunus pelagicus*) and mussels (*Perna viridis, Mytilus gravincia provincialis* and *Crassostrea madrasensis*) have been subjected to analyses. These selected biota have highly commercial value and are edible. The concentrations of Pb and Cd in the mussels (6.4 ± 0.52 $mg.kg^{-1}$and 3.9 ± 0.40 $mg.kg^{-1}$ respectively) exceeding the permissible limits recommended by FAO, USFDA and European Commission for food standards. The concentration of heavy metals (Cu (11.1 to 19.0), Ni (0.9 to 6.35), Cr (1.43 to 3.56), Cd (0 to 2.4), Pb (0.7 to 3.7) and Zn (4.6 to 24.0) $mg.kg^{-1}$) in the fish and crustaceans (Cu (15.9to 21.1), Ni (5.7 to 8.8), Cr (1.9 to 2.3), Cd (1.7 to 2.5), Pb (2.0 to 2.8) and Zn (47.8 to 56.7) $mg.kg^{-1}$) species also moderately higher and slightly exceeding the permissible limits. The bivalve mollusc, *Crassostrea madrasensis* have been identified to accumulate higher concentrations of non-essential (Cu (22.3 to 26.3), Ni (7.36 to 10.4), Cr (2.73 to 4.63), Cd (2.3 to 3.90) and Pb (5.2 to 6.40) $mg.kg^{-1}$) and essential (Zn (90.1 to 157) $mg.kg^{-1}$) heavy metals suggesting that they could serve as bioindicator of severe heavy metal pollution in the Ennore Creek environment.

KEYWORDS: **Ennore Creek; heavy metals; bioaccumulation; Biota**

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INTRODUCTION

In many countries, significant alterations in industrial development lead to an increased discharge of chemical effluents into the aquatic ecosystem, leading to damage of marine habitats. The estuary is an integral part of the coastal environment. It is the outfall region of the river, making the transitional zone between the fluvial and marine environs. The health status and the biological diversity of the Indian estuarine ecosystems are deteriorating day by day through man-made activities and dumping of enormous quantities of sewage into the estuary has drastically reduced the population of the aquatic biota. It has also caused considerable ecological imbalance and resulted in the large-scale disappearance of their flora and fauna. Further, introduction of untreated municipal waste-water, industrial effluents into these water bodies leads to serious water pollution including heavy metal pollution, which gets biomagnified and reaches man through food-chain implications (ENVIS 2002).

Heavy metals are considered to be the hazardous inorganic and organic pollutants in the coastal environment. Heavy metals may enter an aquatic environment from different natural and anthropogenic sources, including industrial or domestic sewage, storm runoff, leaching from landfills, shipping and harbor activities and atmospheric deposits. The Organisms can only accumulate the biologically available forms of pollutants that are always present in the environment thus enabling the continuous monitoring of pollutants (Akar and Tunali 2005; Obasohan 2007; Sivaperumal, 2007; Nair et al. 2006). Metals, such as Fe, Cu, Zn and Mn are essential since they play important roles in biological systems; whereas Hg, Pb, and Cd are toxic even in trace amounts. The essential metals can also produce toxic effects at high concentrations. According to European Union for hazardous metals (EC 2001), the three non-essential heavy metals such as Hg, Cd and Pb were proven hazardous nature and completely excluded in food for human consumption. On the other hand the USFDA has included a further three metals Cr, As and Ni in the list (USFDA 1993). In the view of the above, the present study was aimed to analyze Zn (essential metal) Cu, Ni, Cr, Cd and Pd (non essential metal) from the edible biota (samples such as Fishes *Oreochromis* mossambica, *Mugil cephalus, Clarias batrachus* and *Channos channos*), Shrimp (*Penaeus monodon* and *Penaeus indicus*), Crab (*Portunus pelagicus*) and Mussels (*Perna viridis, Mytilus gravincia provincialis* and *Crassostrea madrasensis*) of the Ennore Creek.

MATERIALS AND METHODS

Study area

Physiographic setting

Ennore Creek (latitude 13°15′ N and longitude 80°19′ E) is a fresh/brackish water system, which is nearly 800 m wide and elongated in a NE–SW direction (Fig.1). Ennore Creek is complex, the average depth rarely exceeding 5 m in the non-monsoon period, being fed by Koratalaiyar River and the Buckingham Canal. It is also connected to the Pulicat brackish water lake on the northern side, which once nurtured rich fauna and flora, including mangroves. The Ennore Creek flows from the west to east and open into the Bay of Bengal. It is located in the northeastern part of Chennai, Tamil Nadu, India and is spread over an area of 4 km^2 along the coast of Bay of Bengal. The Ennore Creek is the estuary of the river Kortaliar, which is an outlet for the excess water from the Poondi reservoir. The Ennore Creek flows from the west to east and opens into the Bay of Bengal at Ennore (Musthafa and Krishnamoorthy 2011).

Sample preparation and Analysis

Biota samples were collected from Ennore Creek Southern India, by using gill net of various sizes and they were stored at -20°C prior to further analysis. They thoroughly washed with Mili-Q water to prevent the soil and other dirties. Whole tissue was oven dried at

110°C, powdered with pestle and mortar and taken for heavy metal analysis. Exactly 2.5 g powdered sample was diluted with 10 ml of nitric acid-perchloric acid (10:4) at room temperature overnight and allow to cool to room temperature. The digested sample was filtered and made up to 50 ml with distilled water and the sample metal contents were analyzed using a Flame Atomic Absorption spectrophotometer (Perkin Elmer 800). The concentrate was expressed as ($mg.kg^{-1}$) wet weight of tissue (Kingston and Jassie 1988). The instrument was calibrated with standard chemical solutions prepared from commercially available chemicals (Merck, Germany).

RESULTS AND DISCUSSION

The concentrations of heavy metals in Fishes, Crab and bivalves from Ennore creek were presented in table 3-6. The concentrations of Copper in the samples analyzed ranged from 11.1 to 26. $mg.kg^{-1}$ with the highest concentration observed in bivalves (*Perna viridis*) (26.3 $mg.kg^{-1}$). But the concentrations in the samples were much below the toxic limit of 30mg/kg (FAO 1983The highest sources of copper are shellfish, especially Oysters and Crustaceans (Under wood 1977). Chromium and Nickel are group of hazardous metals noticed by the USFDA 1993a. Even though not covered by the EC regulations for fish and other aquatic products. Chromium was detected almost all the samples and the highest concentration (4.63 ± 0.65) was detected in *Perna viridis*. But the values were within the permissible limits of 12-13$mg.kg^{-1}$ (USFDA 1993a). Chromium is an essential element and it plays an important role in glucose metabolism. The Zinc content in the samples ranged between 16.0 ± 1.00 and 157.1 ± 1.25 $mg.kg^{-1}$, with a higher level of 157.1 ± 1.25 $mg.kg^{-1}$ in Oyster species. The nickel concentrations in the analyzed samples were ranged from 1.4 ±0.52 to 10.4 ± 0.51$mg.kg^{-1}$ with the highest concentration (10.4 ± 0.51 in *Perna viridis*. The concentration of lead ranged between 0.7 ± 0.20 and 6.4 ± 0.52 $mg.kg^{-1}$, with the maximum concentration of 6.4 ± 0.52 was observed in *Gravincia provinciailis*. All the values are above the recommended limits by EC 2001 (0.4 mg, kg^{-1}) and 0.5$mg.kg^{-1}$ (FAO 1983). The cadmium content in the analyzed samples was ranged between 0.7 ± 0.20 and 3.9 ± 0.40 mg. kg^{-1}. The maximum concentration was observed in *Perna viridis* the measured cadmium content values are above the recommended limits by EC 2001 (0.1 mg. kg^{-1}). In the fish samples, the concentration of Cr significantly correlates ($P < 0.05$) with Cu. Ni concentration significantly correlates ($P < 0.05$) with Cu. Ni concentration significantly correlates ($p< 0.05$) with Cu, Zn and strong significant correlation with ($P < 0.01$) with Cr was noticed. The Pb and Cd concentrations were strongly significant ($P < 0.01$) with Cd, Cr and Ni. There is no correlation with Cu, Zn and Cd (Table. 6). The concentration of heavy metals in the muscles of fish from the Middle Black Sea was low when comparing the data obtained from the present study (Tuzen, 2002). Similarly (Kwon and Lee 2001), measured concentrations of heavy metals in the muscles of different species from Mersan Bay were low when comparing to the present study. Tamira et al. (2001) reported heavy metal values for fishes from California lagoons and were nearly same and nickel (0.61-12 mg. kg-1) concentrations slightly higher than the present study (1.4 – 10.4 mg.kg-1). Lorenzing Glusti and Herozhang (2001) reported values of Zn and Cu for muscles from Murano, Italy was moderately higher than the present study.

Table 1
Atomic absorption spectrophotometer operating conditions

Operating conditions	Cr	Cu	Cd	Ni	Zn	Pb
Wavelength (nm)	357.9	324.8	228.8	232.0	213.9	283.3
Slit width (nm)	0.7	0.7	0.7	0.2	0.7	0.7
Flam type	Air-acetylene	"	"	"	"	"
Lamps	HCL	HCL	EDL	HCL	HCL	EDL
Linear Range (mg/l)	5.0	5.0	2.0	2.0	0.7	20.0
No. of Calibration Standards	5	5	5	5	5	5
Sample Volume (ml)	25	25	25	25	25	25

Table 2
Measured and certified values of heavy metal concentration, as mg.kg^{-1}dry weight, in standard reference material DORM-2 (dogfish muscle)

Reference material DORM-2	Certified values	Measured values	Recovery (%)
Cu	2.34	2.32 ± 0.14	99.1
Cr	34.7	33.8 ± 2.3	97.4
Cd	0.043	0.042 ± 0.004	99.5
Ni	19.4	19.33 ± 2.0	99.6
Zn	25.6	25.2 ± 2.2	98.4
Pb	0.065	0.065 ± 0.006	100

Table 3
Concentration of heavy metals in Commercial Fishes from Ennore creek

Species	Cu	Cr	Cd	Ni	Zn	Pb
Channos channos	11.1 ± 0.47	1.43 ± 0.51	0	1.4 ± 0.52	16.0 ± 1.00	0.7 ± 0.20
Mugil cephalus	14.0 ± 1.00	2.80 ± 0.75	0.7 ± 0.25	4.3 ± 0.61	24.0 ± 0.60	2.7 ± 0.17
Clarias batrachus	12.1 ± 0.65	2.56 ± 0.60	0.9 ± 0.25	0.9 ± 0.25	4.6 ± 0.40	1.90 ± 0.40
Oreochromis mossambica	19.0 ± 0.40	3.56 ± 0.40	2.4 ± 0.51	6.3 ± 0.35	23.5 ± 0.51	3.7 ± 0.75

Table 4
Concentration of heavy metals in Commercial Crustacean species from Ennore creek

Species	Cu	Cr	Cd	Ni	Zn	Pb
Shrimp						
Penaeus Monodon	16.4 ± 0.2	2.3 ± 0.7	1.7 ± 0.1	7.3 ± 0.6	52.0 ± 1.7	2.3 ± 0.3
Penaeus indicus	15.9 ± 0.6	1.9 ± 0.5	1.9 ± 0.1	5.7 ± 0.2	56.7 ± 2.6	2.0 ± 0.1
Crab						
Portunus pelagicus	21.1 ± 0.76	2.03 ± 0.41	2.5 ± 0.50	8.8 ± 0.85	47.8 ± 0.76	2.8 ± 0.35

Table 5
Concentration of heavy metals in Commercial Molluscans species from Ennore creek

Species	Cu	Cr	Cd	Ni	Zn	Pb
Crassostrea Madasensis	26.3 ± 0.60	4.63 ± 0.65	3.9 ± 0.40	10.4 ± 0.51	157.1±1.25	6.4± 0.52
Perna viridis	22.3 ± 0.20	3.9 ± 0.1	2.3 ± 0.10	8.1 ± 0.37	130.4±1.0	5.2± 0.30
Mytilus gravicia provincialis	24.3 ± 0.60	2.73 ± 0.3	2.9 ± 0.70	7.36 ± 0.30	90.1± 2.3	5.3 ± 0.90

Table 6
Pearson's moment Correlation coefficients between the heavy metals

Heavy metals	Cu	Cr	Zn	Ni	Pb	Cd
Cu	1					
Cr	0.89*	1				
Zn	0.37	0.75*	1			
Ni	0.83*	0.98**	0.81*	1		
Pb	0.92**	0.98**	0.65	0.94**	1	
Cd	0.94**	0.92**	0.53	0.92**	0.90**	1

****P < 0.05; **P < 0.01***

Figure 1
Map showing the study area

CONCLUSION

The somewhat high concentrations of Cu, Cr, Zn, Cd, Ni and Pb in the biota samples particularly in the bivalve species from Ennore Creek, South India may be resulted from anthropogenic influence particularly the Industrial effluents such as thermal outlet, Fertilizer Industrial effluent and Cement Industrial effluent. The result of this study reveals the valuable information about the metal contents in fish, crustacean and molluscan species from the Ennore Creek, South India. This can be considered as a bioindicator of the environmental contamination in this zone by estimating the bioavailability of metals to the marine biota. On the other hand Ennore creek is hardly polluted and surrounding fisherman community is severely affected by skin lesions and skin irritation due to consumption of marine species from Ennore creek and nearby localities, South India (Arunkumar and Hema achyuthan, 2007). Finally with our results, we have to recommend the authorities of the Ministry of Environment and Forest (MoEF) and Central Pollution Control Board (CPCB), Govt. Of India to implement the remedial measure particularly bioremedial measures to protect the water ecosystem and biodiversity of Ennore creek.

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