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A STUDY ON THE ACCUMULATION OF HEAVY METALS ON THE SEDIMENTS AND SHRIMPS OF COCHIN ESTUARY

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ABSTRACT

Cochin backwater is facing serious threat due to pollution caused by rapid urbanization and industrialization. Effluents from industries are the major cause of pollution in and around the Cochin estuary of Vemaband Lake system. Water and sediment samples were collected from four sites along estuary region of Ezhikkara Grama Panchayath and physicochemical analysis were carried out. The results of the analysis reveals that water and sediment in the study area is highly polluted and can affect the aquatic ecosystem, probably due to the untreated effluent from the shrimp processing unit located near the sampling sites. Three species of prawns were collected and analysed for heavy metals. Zn and Pb were detected from all the shrimp species. The quantities of heavy metals are within the limits of permissible level for human consumption prescribed by WHO. Study shows the potential of analysed species as bio indicators of heavy metal contamination in the Lake.

KEYWORDS: Cochin Estuary, Heavy Metals, Bioaccumulation, Metal Contamination

Vembanad Lake, part of the Vembanad-Kol Wetland Ramsar site of Kerala, having an area of 151,250 ha, is the largest wetland ecosystem in the peninsular India. This wetland is of extraordinary importance for its hydrological function, rich biodiversity, support for huge fish population and its link with the Arabian Sea through Cochin estuary. The Lake receives large quantity of Industrial discharge of hazardous pollutants like phosphates, sulphides, ammonia, fluorides, heavy metals and insecticides through the downstream reaches of the Periyar river. It is estimated that, every day nearly 260 million litters of industrial effluents reach the Periyar River from Kochi industrial belt (Ramasamy *et al*., 2012; Sowmya *et al*., 2014, Jayasooryan *et al*., 2011). Heavy metals may consistently retain within the water bodies or may be taken up by organisms such as plankton, benthos or fish and finally be transferred to humans. Several studies were conducted on the heavy metal contamination and heavy metal accumulation in the fishes from Cochin estuary. Studies have also been conducted on the health risk assessment on the industrial belt situated in the shores of Cochin estuary (Harikumar *et al*., 2007). Eutrophication, metals contamination, and bacterial pollution are among the major problems and stresses of the aquatic environment and have been receiving global attention and interest (Malik and Ahmad 2002; Parnell 2003; Jonas and Millward 2010; Reopanichkul *et al.,* 2010; Shin *et al.,* 2012)

The present study aims to analyse the heavy metal accumulation in the sediments and edible prawns collected from the Ezhikkara Grama Panchayath region of Cochin estuary.

MATERIALS AND METHODS

Sampling Location

Samples were collected from Ezhikkara region(10°6′0″N, 76°13′0″E) situated close to cochin township. Ezhikkara is famous for its pokkali (a type of rice) fields and prawn farms. Fishing and rice farming are the main source of income for the people in the location. A shrimp processing unit located near the sampling site is the major source of pollution in the region.

Collection of Water and Sediment Samples

The surface water samples were collected from four sampling sites using water sampler at depth of 25 cm below and three random sub samples were also collected from each sites. The sediment was collected using grab sampler. The samples were transported to the laboratory and stored under freezed condition without any contamination. Physical and chemical characteristics of water were analysed following standard method of APHA.

Analysis of Heavy Metals from the Sediment

Aquaregia Extraction

Accurately weighed 1.0 g of air dried soil/sediment and placed inside a kjeldahl flask. 15 mL of Aqua regia was added to the sediment and placed in a heating block and digested for 30 minutes. Then it was filtered through Whatman no. 541 filter paper and made up to 5 mL with0.25 M HNO3. Digested samples were analysed for heavy metal using ICP-AES (Maiti,2011). The heavy metal concentrations were compared with USEPA and WHO guideline.

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Heavy Metal Analysis of Prawn Species

Three species of prawns, *Metapenaeus monocerous, Penaeus indicus, Penaeus Semisculatus* were collected using fisher net. The samples were identified in the laboratory and preserved without any contamination. The edible parts of the prawns ere dissected with stainless steel apparatus, dried in a hot air oven at 50^0C for till constant weight. Then powdered and kept in borosilicate vials. 0.5 g each of samples were taken into clean dried beaker (100 mL), 5 mL of aqua regia HCl and HNO3 (3:1) was added to the sample for digestion. Few drops of H2O2 were then added to clear the solution to pale yellow. The samples were allowed to be evenly distributed in the acid by stirring with a glass rod digested for 3 hours. The digested sample was filtered through Whatman filter paper No 541 into a graduating cylinder and the filtrate was made up to 50 mL using deionized water and analysed for heavy metals using ICP – AES (Maiti, 2011).

RESULTS AND DISCUSSION

The water quality parameters were analysed and the results are showed in the table 1.

Table 1: Physicochemical characteristics of water sample

Parameters	Site-1	Site-2	Site-3	Site-4
Turbidity(NTU)	3.0	3.0	3.0	3.0
pH	7.5	6.6	7.6	7.5
conductivity	35057.0	35027.4	36077.0	32057.0
Acidity (Mg/L)	13	15	12	12
Alkalinity	70	72	62	60
Sulphate (Mg/L)	380.5	283.6	379.6	370.0
Total Dissolved Solids (Mg/L)	18600.0	18500.0	18900.0	18800.0
Total Hardness (mg/l)	4856.0	4845.0	7695.0	8215.0
Calcium (mg/l)	248.6	342.7	190.4	186.7
Magnesium (mg/l)	1523.2	969.6	1754.5	878.0
Chloride (mg/l)	15676.0	13566.0	16116.0	18760.0
Iron (mg/l)	0.19	0.15	0.26	0.28
Nitrate (mg/l)	0.8	0.8	0.8	0.8
Total Organic Carbon (mg/l)	4.9365	5.5375	4.739	3.997
Biological Oxygen Demand (mg/l)	7	7.5	8.5	8.0

According to the guide lines of WHO typical pH range for polluted surface waters is 3.0-12.0. In the present study the pH of the water sample were in between 6.6-7.6. The minimum pH values in surface water required for survival of fauna is 6.0, in the present study S -2 has pH 6.0 which may lead to the death of snails and crustaceans. is the low pH in the samples might be due the discharge of waste from the shrimp processingindustry. Conductivity increases with the increasing mineral content of the water sample. According to the water quality guidelines conductivity of waste water is>10,000. In the present study conductivity is higher than 10,000 in all sampling stations. According to the WHO guidelines BOD values for much polluted water is in between 4.0-10.0 range. In the present study the BOD values are in 7.0-8.5 range (S -1 to S -4). The levels of $NH4^+$ and $NO3^-$ are often below 1 Mg/L in unpolluted fresh water and it can limit the plankton growth. However in some areas nitrate and ammonium ions have risen to potentially harmful levels mainly due to the discharges of waste water and agriculture runoff.

The permissible limit of Fe in river water is 0.7 mg/l in the present study 0.28 mg/l of Fe is reported from S-4 site.

Heavy Metal Analysis of Sediment Sample

Analysis of heavy metals shows that the Site -4 has chromium as (0.62 ppm) and Pb (0.7-0.18ppm). The concentrations of Zn were high in site 4 and site 2 (0.59 ppm and 0.38 ppm). The presence of Cadmium was not detected from the study sites. The heavy metal concentration in the sediments were in the following order Cd<Pb<Cr<Zn.

Table: 2. Heavy metals in sediment samples

Parameters (ppm)	**Site1**	**Site2**	Site 3	Site 4
Chromium	0.48	0.50	0.41	0.62
Lead	0.13	0.07	0.11	0.18
Zinc	0.52	0.38	0.42	0.59
Cadmium	ND	BDL	BDL	ND

ND; Not Detected, BDL; Below Detection Level

Levels of Cr in sediment originating from parent material rich in chromite can be relatively high. Average concentrations of Chromium in sediment tend to be 100-1000 mg/kg. Lead was detected from the study site but not exceed the permissible limits. Major anthropogenic source of lead include petrol additive and sewage sludge. The presence of Zn was higher than the other heavy metals. Zn concentration in the soils typically ranges 1 to 2000 mg/kg.

This comply with Fianko *et al*. (2007) who reported that sediments contain more sand and lower values of organic matter exhibit low metals enrichment. Also, the concentrations of heavy metals in sediment increase as the amount of organic material increase. Sediment has certain limited capacity to absorb different ions from waters percolating through it. This capacity is lowest for carbonate-sandy fractions of sediments (Lake-sea area), and highest for clayey organic matter rich sediments (Sharma *et al*., 1998).

By comparing the accumulation of heavy metals in water and sediments, it can be concluded that the heavy metals are highly accumulated in sediments than water, since the sediments act as reservoir for all contaminants and dead organic matter descending from the ecosystem above (Forstner *et al*., 1989; Graham *et al*., 2008)

Heavy Metal Analysis of Shrimp Species

Table: 3 heavy metals in shrimp samples

Test specimens	**parameters**	Concentration (ppm)
Metapenaes monocerous	Chromium	ND
	Lead	0.51
	Zinc	0.34
	Cadmium	ND
Penaeus semisulcatus	Chromium	ND
	Lead	0.53
	Zinc	2.15
	Cadmium	ND
Penaeus indicus	Chromium	ND
	Lead	0.46
	Zinc	1.51
	Cadmium	ND

ND - Not Detected

Results of the heavy metal analysis in shrimp samples are showed in Table 3. Concentration of lead and zinc in *Metapenaes monocerous,* were 0.51 and 0.34 ppm respectively. In *Penaeus semisulcatus,* Pb and Zn was in the order of 0.53ppm 2.15 ppm and in*Penaeus indicus* was 0.46 ppm 1.51 respectively. All the body parts of invertebrates have a high tendency to accumulate zinc possibly due to the presence of a sulphide-transporting protein with zinc at its active site and also due to acting as a precursor in most enzymatic activities (Islam *et al*., 2004; Jones *et al*., 2001). Moorthi and Nair, 1971, reported Pb and Zn concentration in *Penaeus indicus* from Thane Creek, Maharashtra as 0.02-0. 09 ppm and 41.9-72.0 ppm respectively. According to USEPA 1989, the permissible limit of Pb is 2 ppm in prawns whereas in Seafood Standards, maximum allowable limits for Pb accumulation of shrimps were 0.5 ppm. The present study results shows that the contamination of heavy metals in shrimps has not reached hazardous levels for human health at present, but may cause potential impacts on biota and human beings in the near future, if the resent condition persists. It is essential to conduct a further monitoring and

risk assessment on heavy metal contamination of the Lake for proper management and conservation of the ecosystem.

CONCLUSION

In the present study sediment and 3 prawn species were collected from Cochin estuary and analysed for selected heavy metals. Water samples were also collected for analysing for physico chemical characteristics. Cr, Pb and Zn were detected from the sediment samples of study area. Heavy metals in the sediments samples were low compared to the previous reports from the Cochin estuary because the sampling locations were confined to the northern part, which is not affected by the industrial pollution from the Udyogamandal region. Three species of shrimps were collected and analysed for heavy metals, Cr and Lead were detected from the prawns but within the limits of permissible level for human consumption prescribed by WHO. Shrimps are one of the most commercially important species collected form Cochin estuary and consumed by the large population daily their daily diet. So the study recommends further monitoring and risk assessment of edible shrimps in the lake.

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