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Assessment of Heavy Metal Contamination in Water, Sediment and Fishes Tissue from Ennore Ecosystem, South East Coast of India

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Abstract: The study of the trace metals and heavy metals present in the Ennore ecosystem plays a vital role in determining the extent of pollution in the study area. In the present study results showed that higher level of heavy metal concentration in the water, sediments and fish tissues, has a high potential to concentrate heavy metals like Cd, Hg, Pb and Cr though the observed concentrations are above the permissible limits except two metals (Cu and Zn) are within the permissible limits. Based on these results there is serious heavy metal pollution in the Ennore mangrove ecosystem. There is an urgent need to control the industrial pollution and save the above water bodies for the welfare of the present and future generations.

Keywords: Ennore ecosystem, heavy metal, fishes, AAS.

Introduction

Pollution of heavy metals in an aquatic ecosystem is growing at an alarming rate and has become an important worldwide problem [1]. Heavy metals may enter an aquatic ecosystem from different natural and anthropogenic sources, including industrial or domestic sewage, storm runoff, leaching from landfills, shipping and harbor activities and atmospheric deposits [2]. The toxic heavy metals entering the ecosystem may lead to geo-accumulation, bio accumulation and biomagnifications. Heavy metals like Fe, Cu, Zn, Ni, Cr, Pb, Cd and other trace elements are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders. The mixing of toxic heavy metals into the water bodies deteriorates the

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quality of water, sediment and aquatic organisms [3]. It is a threat to the several endemic fish species due to the heavy metal pollution of rivers and lakes. Further, the heavy metals could also pass to human beings through the food chain and create various health hazards.

Heavy metal toxicity can result in various ill health effects in humans. Inorganic arsenic is carcinogen and can cause cancer of skin, lungs, liver and bladder. Ingestion of very high levels may result in death. Cadmium and cadmium compounds are also known human carcinogens. Breathing high levels of cadmium may cause severe damage to the lungs. Ingestion of high level severely irritates the stomach causing vomiting and diarrhea. Long term exposure to Chromium can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation. Exposure to high levels of Mercury can permanently damage the brain, kidneys, and developing fetuses. Exposure to high levels of lead can severely damage the brain and kidneys and ultimately cause death [4]. In order to study the industrial pollution, the sediments of Ennore ecosystem which were found very close to the industrial area of Manali of Tamilnadu, India have been chosen to assess the concentration of heavy metals.

The Ennore mangrove ecosystem comprises of lagoons, with salt marshes and backwaters, which are submerged under during high tide and form an area of the sea opening in to the Bay of Bengal. The total area of the creek is 2.25 sq km and is nearly 400 m wide. Its channels connect it to the Pulicat Lake to the north and to the Kortalaiyar River in the south. Increasing pressure on mangrove forests due to urbanization, industrialization and intensive aquaculture in this area poses a threat to this ecosystem. Ennore mangrove ecosystem receives sewage from in and around the Ennore town area, Royapuram and industrial effluents from Manali. The treated effluents of the Madras Refinery Ltd., through the Buckingham canal and the Madras Fertilizers Ltd., through the Red Hills surplus channel, reach the Ennore backwater. In view of the above, the present study was undertaken to assess the heavy metal parameters in Ennore ecosystem, Tamil Nadu, India.

Materials and Methods

The Ennore creek (Latitude 13°15□ N and Longitude 80°19□E) spreads over an area of 4 sq.km is located approximately 24 km in the northeastern part of Chennai city, South East Coast India. The creek formed at the mouth of the river kortaliyar is an outlet for the excess water from the Poondi reservoir, the average depth rarely exceeding 5 km in the non- monsoon period. Ennore creek fed by Kortaliyar River and Buckingham canal. The Korttalaiyar is a 136 km long river that originates in Kaveripakkam in Vellore, flows through Thiruvallur, enters Chennai through the Cooum River and drains into the Bay of Bengal at Ennore Creek. It is bordered on sides by the Bay of Bengal on the eastern end, Buckingham canal on the western end, Pulicat Lake on the northern end and Ennore town on the southern end. The Ennore Creek flows from the west to east and open in to the Bay of Bengal (Figure 1a and 1b)

The water, sediments and fishes samples were collected during summer, pre monsoon and monsoon in year of 2014 from six locations of Ennore ecosystem. The sampling of biota was carried out by professional fishermen using a nylon gill net. For each location, the liver, gills and muscle were dissected from fish and a compound sample was prepared. The samples were frozen

in an ice box at 20^0C and brought to the laboratory for further analysis. The tissue samples were crushed to uniform particle size before analysis. Water samples were collected in an acid washed polyethylene bottles and immediately preserved by the addition of a few drops of concentrated nitric acid. Sediment samples were collected by a grab sampler and placed in pre-cleaned polyethylene bags. The samples were transferred to the laboratory in an icebox and were processed within 18–24 h. Before analysis, the sediment samples were dried, ground, sieved with 100-mesh sieve and stored in acid washed (1:1 HCl and 1:1 HNO_3) plastic containers.

Processing of water sample

25ml of acid preserved water samples was taken in a 100 ml beaker Then 5 ml of concentrated nitric acid (HNO_3) was added and the sample was evaporated in the hot plate for 15 to 20 minutes. After evaporation again 5ml of concentrated nitric acid and 10 ml of concentrated sulphuric acid was added. Again the sample was evaporated until a dense white flame appears and then sample was cooled and diluted with de-ionized water up to 50 ml. A blank was also digested using the de-ionized water as a reference material [5]. The digested samples were analyzed for six metals by atomic absorption spectrophotometer using flame atomization.

Processing of Sediment sample

Sediment samples were oven dried at 105ºC for at least 10-16 hours until a constant dry weight. Afterwards the dried samples were homogenized with a pestle and mortar in order to normalize for various in grain size. The homogenized samples were sieved through a 250 mm screen and kept in clean plastic container for further analysis. For each sample a known quantity (1 g) of sediment was digested with a solution of concentrated $HClO_4$ (2 ml) and HF (10 ml) to near dryness. Subsequently, a second addition of $HClO_4$ (1 ml) and HF (10 ml) was made and the mixture was evaporated to near dryness. Finally, 1 ml $HClO_4$ alone was added and the sample was evaporated until white fumes appeared. The residue was dissolved in 12 N HCl and diluted to 25 ml (6). Heavy metal concentrations Cr, Cu, Cd, Hg, Pb, and Zn were measured using a flame atomic absorption spectrophotometer (Perkin-Elmer AA700) equipped with a deuterium background corrector. Suitable internal chemical standards (Merck Chemicals, Germany) were used to calibrate the instrument. All the reagents used were analytical grade of high purity. The results of the heavy metal concentrations were determined on a dry weight basis ppm g-1.

Processing of fish samples

The fish samples were collected from Ennore, sacrificed in the field and it was immediately kept in -4°C with the transport box and it was transported to the laboratory, stored at -20°C in the deep freezer until further analysis. During the course of analysis, fish samples were washed thoroughly with distilled water to remove the sediments and debris. Then the fishes were dissected and the organs like liver, muscles and gills were removed and then oven dried at 95ºC. The dried fish's organ samples were powdered with a pestle and mortar. In each fish powder samples were weighed and digested in 8-10 ml of concentrated acid (60 per cent nitric acid (HNO_3): 70 per cent perchloric acid ($HClO_4$). The digested samples were heated slowly to 180°C on hot plate, till the sample volume was reduced to 2-3 ml. The resulting colorless solution filtered through Whatman

filter paper No.1 and made up to 50 ml distilled water and the sample metal contents were analyzed by Atomic absorption spectrophotometer [7].

Results and discussion

During the present study, the results showed that the accumulation of heavy metals from water were concentrated more than the sediment. The mercury (Hg) concentrations in the analyzed samples were ranged from 8.65 ± 0.02 ppm/g to 10.45±0.20 ppm/g followed by the cadmium (Cd) concentrations was ranged from 4.56± 0.06 ppm/g to 8.93± 0.13 ppm/g, the chromium (Cr) was concentrations ranged from 6.55± 0.19 ppm/g to 13.9± 0.16 ppm/g, the copper (Cu) concentrations was ranged from 1.41 ± 0.20 ppm/g to 4.92± 0.30 ppm/g, the lead (Pb) concentrations was ranged from 14.9 ± 0.51ppm/g to 20.93± 0.26 ppm/g and the zinc (Zn) concentrations was ranged from 1.45± 0.05 ppm/g to 2.95± 0.25 ppm/g and the highest concentrations of all metals were observed at location 4. The heavy metals (Cd, Hg, Pb and Cr) though the observed concentrations are above the permissible limits (Cd: 2ppm/g, Cr: 1ppm/g, Pb: 5-6 ppm /g and Hg: 0.5 ppm) except two metals (Cu and Zn) are within the permissible limits (Cu: 10 ppm/g and Zn: 50 ppm/g). Copper concentration was high in the summer season [8].

The overall heavy metals accumulations in the water samples were represented in the following order Pb (14.9 ± 0.51ppm/g to 20.93± 0.26) > Cr (6.55± 0.19 ppm/g to 13.9± 0.16 ppm/g) > Hg (8.65 ± 0.02 ppm/g to 10.45±0.20 ppm/g) > Cd (4.56± 0.06 ppm/g to 8.93± 0.13 ppm/g) > Cu (1.41 ± 0.20 ppm/g to 4.92± 0.30 ppm/g) > Zn (1.45± 0.05 ppm/g to 2.95± 0.25 ppm/g) (Fig. 2). Most of the heavy metals concentrations high in the water samples during the monsoon season due to the addition of heavy metals by soil erosion and run off during the rainy season [9].

Fig 1a. Map showing the sampling points of study area in Ennore Creek

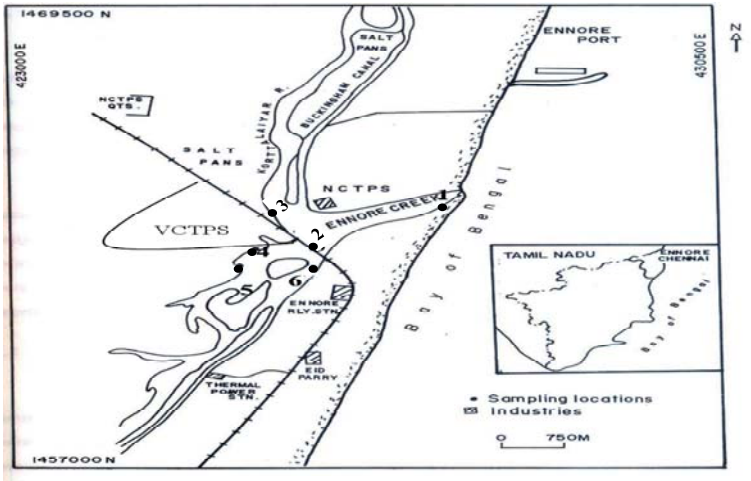

Fig 1b. Map showing the sampling points of study area in Ennore Creek (Satellite view)

Fig 2: Bioaccumulation of heavy metals (Hg, Cr, Cd, Pb, Cu & Zn) (ppm) in Water from Ennore ecosystem.

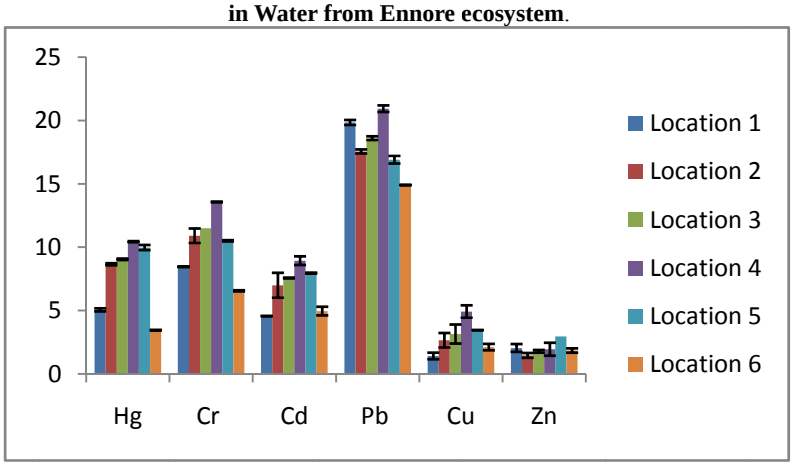

Table 2 and figure 3 shows the overall heavy metals accumulations in the sediment samples, were represented in the following sequential order Pb (11.6 ± 0.46 ppm/g to 48.5± 1.44 ppm/g) > Hg (6.56± 0.19 ppm/g to 10.54± 0.05 ppm/g) > Cr (2.95± 0.28 ppm/g to 10.3± 0.69 ppm/g) > Cd (3.60±0.17 ppm/g to 8.95± 0.25 ppm/g) > Cu (1.94± 0.03 ppm/g to 5.95± 0.11 ppm/g) > Zn (0.94± 0.09 ppm/g to 4.36± 0.10 ppm/g). The highest heavy metals concentration was observed in the sediment during post-monsoon season and this may be attributed due to the settlement of heavy metals from the water [10]. The four heavy metals (arsenic, cadmium, chromium and lead) concentrations of the sediment samples were maximum in the Ennore by discharge of untreated effluent from various industries located near Ennore [11].

Fig 3: Bioaccumulation of heavy metals (Hg, Cr, Cd, Pb, Cu & Zn) (ppm) in Sediment from Ennore ecosystem

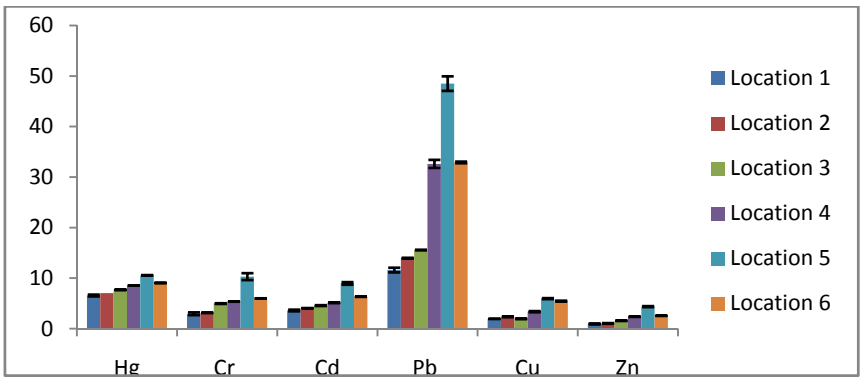

Table 1, 2 and 3 shows the heavy metal concentrations in fishes tissues i.e., liver, gills and muscles. The heavy metals concentrations in fishes were detected almost all the samples and the highest concentration was detected in the following sequential order, in liver samples Zn (14.71±0.40ppm/g) > Hg (9.87±0.27 ppm/g) > Cd (7.67±0.56 ppm/g) > Cr (5.96±0.27 ppm/g) > Pb (2.32±0.35 ppm/g) > Cu (0.65±0.02 ppm/g) / *Channos channos* > *Arius* sp. > *Chanos chanos* > *Arius Sp* > *Oreochromis mossambicus* > *Siganus javus*. In muscles Pb (11.08±0.04 ppm/g) > Cd (10.80±0.05 ppm/g) > Zn (10.60±0.23 ppm/g) > Cu (9.21±0.12 ppm/g) > Hg (7.22±0.26 ppm/g) > Cr (6.33±0.19 ppm/g) / *Siganus javus* > *Chanos Chanos* > *Arius Sp.* > *Siganus javus* > *Arius Sp.*> *Siganus javus*. In gills Cd (15.60±0.63 ppm/g) > Hg (10.82±0.46 ppm/g) > Zn (10.82±0.04 ppm/g) > Cr (10.31±0.02 ppm/g) > Cu (6.80±0.10 ppm/g) > Pb (5.90±0.03 ppm/g) / *Liza melanoptera* > *Oreochromis Mossambica* > *Arius* sp. > *Siganus javus* > *Arius* sp.> *Arius* sp. The high concentration of metals depending upon the anthropogenic sources such as waste incineration, vehicle operations, combustible consumption, fertilizer use, which likely come from the upper basin of the lotic system that flow into the wetland and there is no correlation between the metals from the present data [12]. This study shows that the water, sediments and selected fish species, has a high potential to concentrate heavy metals though the observed concentrations are above the recommendation limits of FAO guidelines [13].

Table1: Bioaccumulation of heavy metals (Hg, Cr, Cd, Pb, Cu & Zn) (ppm) in commercial fish species Liver from Ennore mangrove ecosystem

Sampling Locations	Heavy metals Concentration in ppm/g					
	Hg	Cr	Cd	Pb	Cu	Zn
L.melanoptera	9.32±0.18 [a]	5.96±0.27 [a]	7.56±0.08 [a]	2.14±0.80 [a]	0.31±0.03 [a]	14.56±0.55 [a]
C. channos	9.80±0.69 [a]	5.31±0.18 [a]	7.67±0.56 [a]	2.24±0.15 [a]	0.58±0.04 [c]	14.71±0.40 [a]
M. cephalus	8.76±0.15 [a]	5.32±0.10 [a]	7.44±0.81 [a]	2.10±0.80 [a]	0.40±0.04 [ab]	13.91±0.53 [a]
O.mossambica	9.59±0.32 [a]	5.43±0.23 [a]	7.51±0.28 [a]	2.32±0.35 [a]	0.62±0.04 [c]	14.55±0.20 [a]
S. javus	9.31±0.15 [a]	5.65±0.20 [a]	7.38±0.21 [a]	2.18±0.09 [a]	0.65±0.02 [c]	14.40±0.23 [a]
Arius Sp	9.87±0.27 [a]	5.96±0.14 [a]	7.63±0.17 [a]	2.24±0.06 [a]	0.52±0.04 [bc]	14.51±0.28 [a]

The result shown above is the mean value of duplicate experiments along with standard deviation. The p is<0.05 at 95% confidence level.

Table 2: Bioaccumulation of heavy metals (Hg, Cr, Cd, Pb, Cu & Zn) (ppm) in commercial fish species Gills from Ennore mangrove ecosystem

Sampling Locations	Heavy metals Concentration in ppm/g					
	Hg	Cr	Cd	Pb	Cu	Zn
L.melanoptera	10.70±0.28 [a]	10.11±0.31 [a]	15.60±0.63 [a]	5.67±0.06 [ab]	6.45±0.05 [ab]	10.56±0.17 [ab]
C. channos	10.50±0.45 [a]	10.11±0.06 [a]	15.05±0.02 [a]	5.74±0.02 [ab]	6.68±0.10 [bc]	10.62±0.06 [ab]
M. cephalus	09.86±0.17 [a]	09.85±0.25 [a]	14.95±0.14 [a]	5.42±0.12 [a]	6.19±0.04 [a]	10.40±0.08 [a]
O.mossambica	10.82±0.46 [a]	10.20±0.08 [a]	15.10±0.19 [a]	5.80±0.20 [ab]	6.66±0.08 [bc]	10.70±0.10 [ab]
S. javus	10.50±0.14 [a]	10.31±0.02 [a]	15.12±0.04 [a]	5.86±0.20 [ab]	6.71±0.10 [bc]	10.78±0.04 [ab]
Arius Sp	10.80±0.12 [a]	10.16±0.04 [a]	15.14±0.27 [a]	5.90±0.03 [b]	6.80±0.10 [c]	10.82±0.04 [bd]

The result shown above is the mean value of duplicate experiments along with standard deviation. The p is<0.05 at 95% confidence level.

Table 3: Bioaccumulation of heavy metals (Hg, Cr, Cd, Pb, Cu & Zn) (ppm) in commercial fish species Muscles from Ennore mangrove ecosystem

Sampling Locations	Heavy metals Concentration in ppm/g					
	Hg	Cr	Cd	Pb	Cu	Zn
L.melanoptera	6.50±0.16 [a]	5.67±0.28 [a]	10.40±0.22 [a]	10.74±0.13 [a]	8.56±0.07 [a]	10.34±0.26 [a]
C. channos	7.01±0.06 [ab]	5.98±0.55 [a]	10.80±0.05 [a]	11.01±0.04 [a]	9.10±0.04 [b]	10.42±0.24 [a]
M. cephalus	6.71±0.26 [ab]	6.04±0.09 [a]	10.21±0.33 [a]	10.98±0.50 [a]	9.04±0.17 [b]	10.09±0.25 [a]
O.mossambica	7.13±0.30 [ab]	6.21±0.08 [a]	10.30±0.27 [a]	10.86±0.15 [a]	9.02±0.11 [b]	10.54±0.17 [a]
S. javus	7.20±0.11 [b]	6.33±0.19 [a]	10.13±0.07 [a]	11.08±0.04 [a]	9.21±0.12 [b]	10.36±0.05 [a]
Arius sp.	7.22±0.26 [ab]	6.30±0.23 [a]	10.36±0.15 [a]	10.92±0.25 [a]	9.08±0.04 [b]	10.60±0.23 [a]

The result shown above is the mean value of duplicate experiments along with standard deviation. The p is<0.05 at 95% confidence level

Conclusion

In the present study results showed that higher level of heavy metal concentration in the water, sediments and fish tissues, have a high potential to concentrate heavy metals like Cd, Hg, Pb and Cr. Though the observed concentrations are above the permissible limits except two metals (Cu and Zn) are within the permissible limits. Based on these results there is serious heavy metal pollution in the Ennore mangrove ecosystem. The Ennore mangrove ecosystem is heavily contaminated by pollutants from rapid urbanization and industrialization to release untreated industrial effluents and domestic sewages to this ecosystem. However urgently need the regular biological monitoring of water and fish for safety in seafood consumption from Ennore area. So avoid such kind of problem in the Ennore ecosystem to practicing safe disposal mechanism of

industrial effluents and domestic sewages. Also, there must be continuous environmental pollution monitoring and check heavy metals hazard by state and central Government to take remedial measure for protection of Ennore mangrove ecosystem.

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