# STUDIES ON HEAVYMETAL POLLUTION IN ENNORE ESTUARY, SOUTH EAST COAST OF INDIA

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**Abstract**

Heavy metals are dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. In the present study in Ennore estuary, Concentration of metals shows significant variability and range from 1.7 to 3.7% for Fe, 284–460 μg $g^{-1}$ for Mn, 148.6–243.2 μg $g^{-1}$ for Cr, 385–657 μg $g^{-1}$ for Cu, 19.8–53.4 μg $g^{-1}$ for Ni, 5.8–11.8 μg $g^{-1}$ for Co, 24.9–40 μg $g^{-1}$ for Pb, 71.3–201 μg $g^{-1}$ for Zn and 4.6–7.5 μg $g^{-1}$ for Cd. The present study confirming that the concentration of metal from our result is comparatively high for lead, cadmium, and

cobalt. The concentration ranges will pose serious threat to the life of biota or man as a consumer.

Key words: ennore estuary, fish , pollution , water quality, heavy metals, Bioaccumulation.

**1.0 Introduction**

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals are used in many industries like automobiles, pharmaceuticals, paper industries, tanneries and so on. These metals are a cause of environmental pollution (heavy-metal pollution) from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain. Metals exert their biological influence only in solution as coordination complexes.Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc, iron, cobalt, manganese and molybdenum,) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Heavy metals are dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. One of the areas affected with heavy metal pollution is the Ennore estuary (Lat. 13.15'N and Long. 80.15E). Ennore estuary receives industrial effluents, domestic waste and agricultural waste containing substance varying in characteristic from high toxic compound to essential nutrients, their continuous flushing significantly altering the estuarine ecosystem. Following types of industries are located in and around Ennore estuary basin: Chemical, plastics, dye stuff, automobiles, aluminium, thermal power plant, manure, distilleries, dairy, leather tannery, battery and allied products. All the units release highly toxic effluents as untreated condition (Kuppusamy and Giridhar, 2005).

The impact of heavy metal on the aquatic environment can be assessed by monitoring their occurrence in the various component of the ecosystem. Their distribution among difference biotic compartment is controlled by their physical and chemical properties (Murray and Murray, 1973). The level of various water bodies in the world have been fairly documented (Braganca and Sanzgins, 1980, Matkar et al., 1981; Bryan, 1984; Jaffar and Ashraf, 1988; Song and Breslin, 1988; Senthilnathan and Balasubramanian, 1997).

Level of contamination in the estuarine environment is increasing as a consequence of anthropogenic activity and resulting in diminishing water quality reflects the status of aquatic resources. For this reason, there is an increasing need to develop method for identification, estimation, comparative assessment and management of risk pored by chemical pollutant discharge into aquatic environment. Therefore measuring the

biological effect of pollutant is essential for assessing the quality of an estuarine environment. The flat low land, moderate climate rich natural resources of the estuaries provides an excellent ecosystem as breeding ground for the crustaceans. Fishing activities are also carried out by the local fishermen in Ennore estuarine region. Due to consumption of those organisms there is an accumulation of pollutants through food chain. In this scenario, there is an urgent need to study at least the heavy metal pollution to assess the threat to the food chain. Ennore estuary is located north of Chennai and is surrounded by various industries which cause pollution. The polluted water is then drained in to the Bay of Bengal.

**1.1 Study area**

Ennore estuary is located north of Chennai and it comes under Kathivakkam municipality. Its exact location is Lat. 13 .15'N and Long. 80.15E. The average depth rarely exceeds 2 to 5 metres. It is being fed by Kortalaiyar, Buckingham Canal, and a number of small channels. The present study provides a history of accumulation of trace metals and their present level, and the data can be used as a baseline to monitor the estuaries and coast in future. Hence, the present research investigation on the sediments is imperative to assess the environmental degradation of the estuaries as well as the coast.

The Ennore Creek is dominated by coarse fraction of the sediments. There is no marked temporal variation in sediment texture. The mangroves present near the middle of the estuary promote the decomposition of organic matter by microbial activities. There are many industries in and around Ennore estuary which causes pollution to the river.

Pollution causes various problems to the fishermen like skin infections, changing of fishing ground, accumulation of silt and sand in the landing center etc.

Two stations were fixed to check the heavy metal load in the polluted site. 1st is near the landing centre at Kattukuppam. That is westward to the railway bridge. And the 2nd station was fixed in the creek that is right below the railway track. Water samples and sediment samples were collected from both the stations.

**1st sampling station**

**2nd sampling station**

## 1.2 Materials and methods

Two sampling stations were selected in Ennore creek to study the pollution load of cadmium, lead and cobalt in water, sediments and commercially important fishes. The selection of sampling stations was done on the basis of proximity of industrial areas and junction of tributaries which were expected to make significant contribution to heavy metal pollution. Commercially important fishes were taken for the heavy metal analysis.

White prawn (*P.indicus*) in shell fish and mullet in fin fish are caught more in Ennore estuary.

**Accumulation of sediments in landing center skin infection due to handling of fish caught in polluted water**

Heavy metal load in the water and the sediment samples were studied. Bioaccumulation in commercially important estuarine organisms including fin & shell fish is studied. And create awareness to the fishermen community about the heavy metal poisoning and their impacts.

### 1.3 Sample preparation

#### 1.3.1 Heavy metal preparation from water sample- Solvent extraction method

1 gram of Ammonium Pyrulidine Dithio Carbamate (APDC) was added with 100ml of water sample and is then treated with 100ml of purifying agent (Methyl Iso Butyl Ketone). The solution was mixed well, the aqueous layer was collected**.** Water

samples were collected in acid washed containers, filtered and acidified with the concentrated nitric acid to bring the pH approximately to 2. Acidification minimizes precipitation and absorption of metal on the walls of the container. Samples were stored frozen until further analysis. Sediments samples was collected in a clean shovel, stored in a polythene bags and after drying, was stored in a cool place. The estimation of metal in different organisms was done by ash drying technique modified by Middleton (1973). The whole body of the organism was taken for metal analysis. All the analysis was carried out in the laboratory.

### 1.3.2 Determination of heavy metals in estuarine water

1 liter of water sample is taken and the pH is adjusted to 4.0 ±0.1 by addition of nitric acid. Then the sample is taken in a separating funnel, 10 ml of APDC solution is added to the sample, then it is shaken for 5 minutes, after shaking the sample is allowed for 10 minutes while the phase was separated. Aqueous layer was drained off and organic layer was collected. Further 40 ml of MIBK was added and re-extracted it for 5 minutes. Again the phase is separated and the aqueous layer is separated and the organic layer is drained out. The preconcentrated metals in the aqueous layer was directly aspirated it to an Absorption Spectroscopy (AAS) and quantified against the known standards.

### 1.3.3 Determination of heavy metal from sediments and biological samples

**Mullet – *Mugil cephalus***

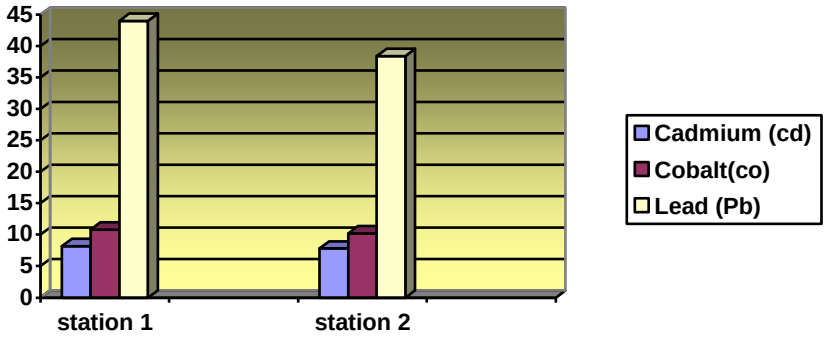
**White shrimp- *Penaeus indicus***

20 ml of concentrated nitric acid was added to the 0.5g of dried and powdered sample. Mixture was left for 24 hours then the sample was evaporated to dry ness on a hot plate at 120˚C until the residue turns yellow. After drying 10ml of 4:1 ratio of nitric acid (16ml) and perchloric acid (4ml) was added and placed in hot plate and evaporated to dryness. After 10 minutes, 10ml of 10% nitric acid was added. After 2 hours it is filtered through Millipore filter unit and made up to 20 ml with double distilled water. The samples are then analyzed by Atomic Absorption Spectroscopy (AAS).

### 1.4 Results

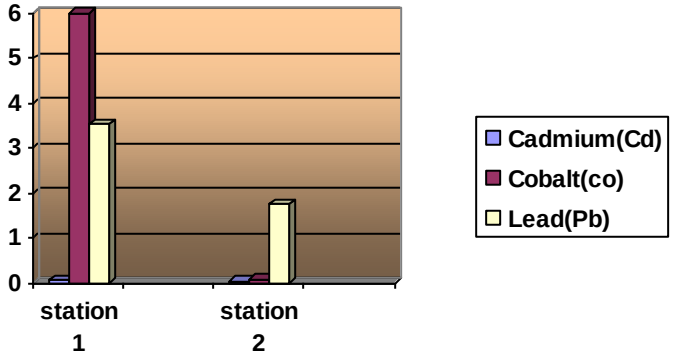
**Water sample (µg)**

| **Sampling station** | **Cadmium (Cd)** | **Cobalt (Co)** | **Lead (Pb)** |
|---|---|---|---|
| Station 1 | 8.2 | 10.8 | 44 |
| Station 2 | 7.8 | 10.2 | 38.4 |



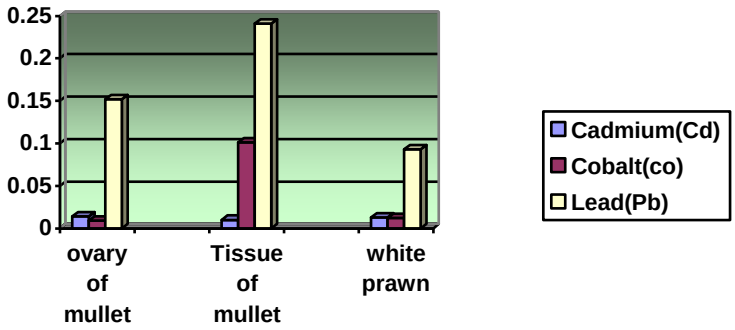

**Sediment sample**

| Sampling station | Cadmium (Cd) | Cobalt (Co) | Lead (Pb) |
|---|---|---|---|
| Station 1 | 0.081 ppm | 0.239 ppm | 3.526 ppm |
| Station 2 | 0.048 ppm | 0.100 ppm | 1.751 ppm |




**Biological samples**

| Biological sample | Cadmium (Cd) | Cobalt (Co) | Lead (Pb) |
|---|---|---|---|
| Ovary of mullet | 0.014 ppm | 0.009 ppm | 0.152 ppm |
| Tissue of mullet | 0.010 ppm | 0.101 ppm | 0.241 ppm |
| White Shrimp (whole body) | 0.013 ppm | 0.012 ppm | 0.093 ppm |




**1.5 Discussion**

Various works has been done on heavy metal pollution in many estuaries. The value of the heavy metals for our work done in Ennore estuary is discussed below. The load of heavy metal is comparatively high in the water, sediments and biological samples due to high concentration of pollutant which is being drained from the industries situated in and around Ennore estuary.

In order to avoid the pollution of trace metals in marine environment, it is necessary to establish the data and understand the mechanisms influencing the distribution of trace metals in marine environment. The concentrations of heavy metals (Fe, Mn, Cr, Cu, Ni, Pb, Zn, Co and Cd) were studied in sediments and water of Ennore

estuary, to understand the metal contamination due to heavily industrialized area of Ennore, south-east coast of India. Concentration of metals shows significant variability and range from 1.7 to 3.7% for Fe, 284–460 μg $g^{-1}$ for Mn, 148.6–243.2 μg $g^{-1}$ for Cr, 385–657 μg $g^{-1}$ for Cu, 19.8–53.4 μg $g^{-1}$ for Ni, 5.8–11.8 μg $g^{-1}$ for Co, 24.9–40 μg $g^{-1}$ for Pb, 71.3–201 μg $g^{-1}$ for Zn and 4.6–7.5 μg $g^{-1}$ for Cd. For various metals the contamination factor (CF) and geoaccumulation index ($I_{geo}$) has been calculated to assess the degree of pollution in sediments and water sample. The geoaccumulation index shows that Cd, Cr and Cu moderately to extremely pollute the sediments. This study shows that the major sources of metal contamination in the Ennore shelf are land-based anthropogenic ones, such as discharge of industrial wastewater, municipal sewage and run-off through the Ennore estuary. When compare to previous work our result seemed to have little higher concentrations of heavy metal. This shows the pollution load which is drained from the industries are increasing day by day.

Concentration of trace metals like Hg, Cd, Pb, Zn, Fe, Mn, Cr, Co, and Ni were determined in squid. *Loligo duvauceli* and *D*orytruthis *sibogae* collected from Mangalore. The mean value of highly hazardous metal in the muscle of the two species was: Hg= 0.05-0.07; Cd= 0.55-0.89; Pb=0.99-0.89; Cr=0.72-0.45, Ni=0.45-0.19 ppm and co =0.42, all with in the international safety limits. However elevated level of some metals, particularly Cd, Zn and cu were some tine observed. The liver the major site of accumulation is probably as complex as metaallothioneins. Gills and ink also significantly concentrate metals. Cadmium level in the muscle increase with growth in *L. duvauceli* and liver concentration of Cd, Cu, and Zn significantly correlated with total length. Geographical variations in metal were observed in these species. The

concentration of metal from our result is comparatively high for lead and cadmium, and the value of and value of cobalt is comparatively lower. This may be due to the source for lead and cadmium pollution is more around Ennore estuary.

Concentrations of Fe, Cu, Zn and Pb in molluscs studied were influenced by season. Highest concentrations of these metals were found during low salinity and low pH of the habitat water (monsoon period). Metal concentration decrease in these species in summer month- the period of high salinity and pH. Nearly all four metals were positively correlated in clams. *V.cyprinoides and M.casta.* In *P.viridis* only a few combinations (Cu/Zn, Cu/Pb, Zn/Pb) were significantly correlated. The mean values are as follows.

***V.cyprinoides:*** Lead (Pb): 0.6873, Copper (Cu): 0.8744, Iron (Fe): 0.6359

***M.casta:*** Lead (Pb): 0.9465**,** Copper (Cu): 0.906, Iron (Fe): 0.5796

***P.viridis:*** Lead (Pb): 0.6771, Copper (Cu):0.8548, Iron (Fe):0.3859

Bivalves being filter feeding organism the values of heavy metals are comparatively higher than the values of metals detected from the biological sample from Ennore estuary.

The level and distribution of cadmium, lead, copper, zinc and cobalt in five commercially important fishes, water and sediments at three locations (downstream, midstream and upstream) in lake Kainji, Nigeria were determined using standard methods. The ranges of heavy metals (micro g/g) in fishes were: Cd 0.04-0.20, Pb 0.00-

1.12, Cu 0.23-2.93, Zn 15.5-36.8, and Co 0.04-0.27. The levels of heavy metals (micro g/g) in most water samples for the three studied locations fall within following ranges: Cd 0.004-0.015, Pb 0.004-0.015, Zn 0.050-0.060 and Cu 0.01-0.04. Concentration (micro g/g) ranges of metals in sediments were: Cd 0.02-0.05, Pb 9.33-16.00, Cu 4.26-24.00, Zn 35-42, Co 8.69-15.00. Generally, there was correlation between the levels of heavy metals in sediments, fish and water. The highest concentrations of these heavy metals were observed in the downstream followed by upstream and midstream. The concentrations of the tested heavy metals were within the acceptable standards of WHO (1984). The concentration ranges will not pose any serious threat to the life of biota or man as a consumer (Amoo et al., 2005). The concentration of metal from our result is comparatively high for lead, cadmium, and cobalt. The concentration ranges will pose serious threat to the life of biota or man as a consumer.

Concentrations of cadmium, iron, lead, zinc, copper, manganese, nickel, chromium, cobalt and aluminum were determined in three commercially valuable fish species, *Saurida undosquamis*, *Sparus aurata*, *Mullus barbatus* from Iskenderun Bay. The concentration of metals was measured by atomic absorption spectrophotometry (AAS). Concentrations of the heavy metals in examined fish species ranged as follows: Cd 0.01-4.16; Fe 0.82-27.35; Pb 0.09-6.95; Zn 0.60-11.57; Cu 0.04-5.43; Mn 0.05-4.64; Ni 0.11-12.88; Cr 0.07-6.46; Co 0.03-5.61; Al 0.02-5.41 mg kg-1 dry weight, respectively (Turkmen *et al.,* 2005). The accumulation of metal comparatively low which shows the pollution causing industries are more in Ennore estuary. Advanced study for other pollutants are also should be introduced by the government and there should be

thorough study about the heavy metal for all the commercial edible organisms which are in need of this hour.

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