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ASSESSMENT OF THE CONCENTRATION LEVELS OF HEAVY METALS IN FISH AND SEA WATER OF ENNORE AND KALPAKKAM

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ABSTRACT

Ecological degradation has been mainly contributed by pollution and the many types of pollutants resulting from natural and anthropogenic activities. Certain heavy metals are essential for human health and are required components of numerous enzymes. Heavy metal poisoning has become a global issue as pollution levels rise and its negative effects on human health deteriorate. From the viewpoint of public health, they are extremely concerning. The test was carried out on two sampling sites, Ennore and Kalpakkam from Seawater and Fish tissues on four heavy metals (Ni, Pb, Cr and Mn). The heavy metal analysis showed low concentration levels in water compared to high concentration levels in fish tissue due to bioconcentration and bioaccumulation of heavy metals.

Key words: Water toxic, Heavy metals, Fish tissue, Chromium

INTRODUCTION

In recent times, Environmental pollution and its adverse effects have continued to increase and has posed a great threat to the ecosystem as well as to all living beings (Kumar C.S *et al.*, 2013). It is a consequence of rapid industrialization and urbanization that pose a significant threat to ecosystems and human well-being worldwide.

Pollution is caused by pollutants which are synthetic or chemical compounds (Shetty,S.S *et al.,2023*). The Pollutants can be naturally occurring compounds and foreign compounds which are further classified as inorganic, organic and biological pollutants. Organic pollutants include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), pesticides, petroleum and organochlorine pesticides (OCPs) and also human waste, food waste. Biological pollutants are bacteria, viruses, moulds, mildew, animal dander and cat saliva, house dust, mites, cockroaches and pollen which are the resultant of the activities of humans.

Inorganic pollutants are sourced from Industrial, agricultural and domestic wastes. Some of the inorganic pollutants are mineral origin, metals, salts and other minerals which occur naturally in environment but, are altered by humans for high production numbers which eventually invades the environment through anthropogenic activities such as mine drainage, smelting, metallurgical and chemical processes, as well as natural processes.

These inorganic pollutants are life threatening as well as toxic as they are capable of accumulating in the food chain (Masindi, V., & Muedi, K. L.,2018).

Among the Inorganic pollutants, heavy metals have also been a major cause of impact to the ecosystem and biological health of the organisms. Heavy metals are naturally occurring elements with a high atomic weight and density that is five times more than that of water, despite the fact that the term is not specifically defined (Bánfalvi, 2011). Because of their toxicity, environmental chemists have focused a great deal of emphasis on heavy metals among all other contaminants. Natural waterways typically include minimal levels of heavy metals, but many of them are hazardous even in extremely low doses. Even in trace amounts, metals including arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc, and selenium are extremely poisonous. (Masindi, V., & Muedi, K. L.,2018).

The ocean serves as a final sink for almost all contaminants since most heavy metals are introduced into the sea through Urban and Industrial activities. (Supriya *et al.*, 2020). These toxins are highly hazardous and can accumulate in seafood, which can cause humans to be exposed to such harmful compounds and ultimately endanger human health. (Antízar-Ladislao, 2008).

The accumulation of heavy metals in marine organisms has prompted scientific interest in heavy metal chemistry. The bioavailability of trace metals is crucial for estimating tissue metal levels in marine biota. (Depledge and Rainbow, 1990).

Fish and shellfish such as prawns, mussels, and crab are delectable and play a vital role in people's daily diets. Heavy metal endorsement has been observed to occur directly from adjacent marine water through the permeable outer body surface, as well as from food and seawater to the muscle and hepatopancreas through the gut (Patra *et al*., 2020). Fish, prawns, and crab form an important bond as potential transfer media to animals and humans, as they play a crucial role in the food chain. The high nutritional value of fish makes it an essential component of the human diet (Sioen *et al*., 2007).

When heavy metals are not metabolized by the body and accumulate in soft tissues, they become toxic. When they come in contact with humans, they may enter the human body through food, water, air, or absorption through the skin (Masindi, V., & Muedi, K. L.,2018). Heavy metal accumulation can occur due to contaminated food, water, air, or soil exposure. Certain metals have been associated with an increased risk of lung, bladder, liver, and kidney cancer. The body requires non-carcinogenic heavy metals like iron, copper, and zinc (Qian *et al*., 2016b). Numerous studies have discussed exposure and toxicity levels using the toxic equivalent factor (Jiang *et al*., 2014).

Most of the chemical pollution in the aquatic environment is caused by humans. Industrial effluents, sludge from sewage treatment facilities, agricultural runoff, and raw untreated sewage from urban populations and industry all contribute to chemical pollution of the environment. There is limited information available on heavy metal concentrations in the food chain along the coast of Chennai, India, despite extensive research on heavy metal levels in various media and marine animal species. The assessment of heavy metals in the food chain may pay way to the heavy metal input to the human body from seafood. Heavy metals pose a significant concern to the food chain due to their persistence in bioaccumulation and biomagnification.

Several coastal cities in Tamil Nadu release residential and municipal trash directly into the coastal waterways without treatment. More than 10 million people live along the coast of Chennai, and as a result, over 75 million gallons of sewage are dumped into the sea each day. The majority of the sewage is discharged into the Coovum, Adyar river, and Buckingham Canal, which eventually empties into the sea. (Supriya *et al*., 2020).

Materials and Methods

Study site:

The fish and water samples were collected from the coast of Ennore and Kalpakkam respectively. The Thazhankuppam (latitude 13° 13' 24.94236" N, Longitude 80° 19' 42.58344" E) in Ennore is one of the main fishing spots where the livelihoods of local fishermen and sellers is dependent on and it also has a booming market for seafood, bought and consumed by the local population. The Kosasthalaiyar river's mouth drains into the coastal waters near Ennore which passes the Ennore creek. The water carries debris and other chemicals, pesticides and effluents from nearby industries, factories and also by anthropogenic activities.

The Meyyurkuppam situated in Kalpakkam(12° 31' 44.83236" N, 80° 10' 0.87528" E) is also an important site for fishing where many fishermen practice traditional methods of fishing. Situated along the coast is the atomic power station where there might have been effluents discharged from nuclear power plants, anthropogenic activities of nearby population and from backwaters. Therefore, these locations were preferred to study on the heavy metal concentration. The sites are mentioned in (Figure 1) below.

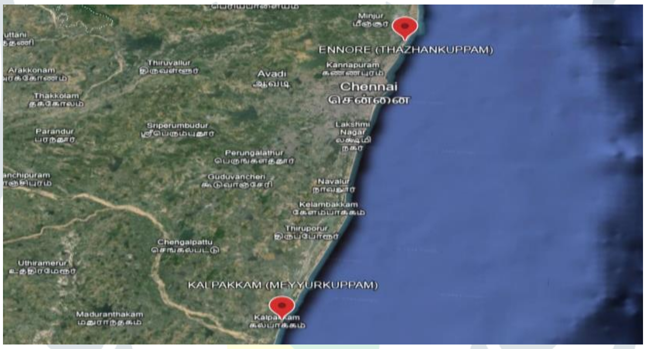

Figure 1: Map showing the sampling sites (Closer view)

Sample collection:

The Samples were collected over a period of five months from August 2023 to December 2023 from two different fishing centers, Ennore and Kalpakkam.Water samples were collected in clean storage bottles and were kept in a polythene bag.

Fresh fish samples *Mugil cephalus* (Grey mullet) and *Deveximentum insidiator* (Pugnose Ponyfish) was stored in an ice box below 10°C and transported safely to the laboratory for analysis. The samples were immediately transported to the laboratory.

Analysis of Heavy Metals:

Analysis of Heavy metals in water sample and Fish

The water sample collected was filtered using filter paper to remove debris and sand particles. Then 50 ml of the sample was transferred to a prewashed beaker. The beaker was pre-rinsed with dilute HNO3. An aliquot of water sample was taken and 1 ml of HNO3 was added to it, to inhibit biological activity and verify that all chemicals in the water column were present. Then the sample was transferred to a Digestion tube and was placed in the Hot block digester at 80°C for 45 minutes. After the digestion process, the sample was allowed to cool down. Then the water sample was diluted to make up 50 ml volume using ultra-pure water and kept at 4°C before analysis. The sample was analyzed for the presence of heavy metals (Ni,Cr,Pb,Mn) using Inductively Coupled Plasma Mass Spectrometry (ICPMS), followed by Calibration Standards of Heavy metals. A Method Blank was also processed simultaneously.

The fish samples were thawed at room temperature before the test. Then the fish tissues (skin and muscle) were cut into small pieces and oven dried at 60°C.The dried samples were grind using porcelain mortar to homogenize the tissue samples. 0.5g of the homogenized tissue sample was transferred into a microwave digestion tube.The sample was analysed by ICPMS method.

Calculation for Heavy Metal Analysis in water sample:

Water (Liquid) - (mg/L)

$$\frac{\text{(Sample Concentration in Solution µg/L - Blank Concentration in Solution µg/L) X Made Up Volume (ml)}}{\text{Volume of sample taken (ml) X 1000}}$$

3.3.4 Calculation for Heavy Metal Analysis in Fish tissue sample:

Fish (Solid) - (mg/kg)

$$\frac{\text{(Sample Concentration in Solution µg/L - Blank Concentration in Solution µg/L) X Made Up Volume (ml)}}{\text{Weight of sample taken (g) X 1000}}$$

RESULT AND DISCUSSION

Heavy Metals in water samples:

The sea water analysed showed higher amounts of Mn (0.087 mg/L), Cr (0.008 mg/L) but, Ni and Pb was below the detectable range at Ennore. The Concentration of heavy metals from the analyzed water sample at Kalpakkam showed higher levels of Mn (0.047 mg/L) whereas, Ni, Cr and Pb were found to be at below detectable range. The range of Heavy metals present in water at both sampling sites are given in (Table 1).

Heavy Metals in Fish Tissues:

Our study revealed that higher levels of Mn was present in tissues of both the fishes followed by high levels of Cr was also observed. In Ennore, the concentration level of Mn was found to be (0.857 mg/kg) whereas in Kalpakkam the concentration level of Mn was (0.529 mg/kg), which is observed to be lesser than from Ennore. Similarly, the concentration level of Cr was found to be (0.455 mg/kg) in Ennore whereas, in Kalpakkam the concentration level of Cr was found to be (0.201mg/kg), which is observed to be less than Ennore. The size of the fish (*Mugil cephalus*) in Ennore is much larger when compared to the size of the fish (*Deveximentum insidiator)* in Kalpakkam. Ni and Pb were found to be in below detectable range (BDL). (Table 2)

Manganese: Mn concentrations in samples from all sampling sites were found to be below WHO's 1989, detection threshold (1 mg kg-1). The highest concentration was observed from Ennore, followed by Kalpakkam. 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 (Achary *et al.*, 2017) and coovum river connects Buckingham canal to the bay of bengal at center of Chennai which is an important contributing of this metal.

Chromium: The chromium values in this study were below the detection level permitted by WHO, 1989 for human consumption (1 mg kg-1) but lower than the maximum allowable chromium content level in fish (12-13 mg kg-1) set by USFDA, 1993.80-90% of tanneries worldwide make use of trivalent chromium salts for tanning (Leathersmithe,2016).

Nickel: In the present study the concentrations of Ni were found to be below detectable level in both sampling sites. The estimated maximum guideline for Ni is 70-80 mg kg-1 as per USFDA, 1993 guidelines. The concentration of Ni was below the stipulated limit.

Lead: The concentration levels of Pb from both sampling sites were found to be below detectable range. The permissible level of Pb for human consumption set by WHO (1989) is (0 to 0.15 mg kg-1).

The bioconcentration factor (BCF) describes how a certain element is concentrated in organisms compared to their surroundings. BCF is used to assess an aquatic organism's capacity to acquire chemicals from its surrounding environment. (Table 3).

$$BCF_{fish} = \frac{C_{fish}}{C_{water}}$$

where, C_{fish} is the chemical concentration in fish (test organism) in mg/kg (preferably wet weight), C_{water} is the chemical concentration in water, in mg/l, and BCF_{fish} is the bioconcentration factor for the test organism. The observed BCF of Cr (56.8) in Ennore and Mn (9.8) in Ennore and (11.2) in Kalpakkam remained >1 which suggested that the fish has strong ability to accumulate metals effectively (Table 3). However, it is not considered as significant unless BCF exceeds 100 (USEPA., 1991). According to (Potipat *et al.*,2015), heavy metal BCFs are classified as BCF>1000, very high, BCF 100-1000, high, BCF 30- 100, moderate, and BCF<30, low. Therefore, in this study, all heavy metal BCFs were less than 100 (BCF<100) according to the category, indicating no possibility. But, the BCF for other heavy metals (Ni, Pb and Cr from Kalpakkam) were unable to find since they were estimated to be below the detectable range.The bioconcentration factors of the tissue analysed is much below the Organisation for Economic Co-operation and Development guidelines (OECD, 1997). in the present investigation, increased bioaccumulation of heavy metals in fish tissues was reported during the pre-monsoon period due to an increase in temperature due to depletion of dissolved oxygen, energy demand, and the increased amount leads to an increase in the rate of respiration in the fish body, resulting in rapid waste assimilation (Salem *et al*., 2014). Furthermore, the rise in water temperature during the pre-monsoon period increases fish metabolic rate and predation activity, resulting in increased metal absorption and accumulation in tissues (Obasohan., 2008). Such seasonal trends in tissue bioaccumulation of heavy metals were supported by the findings of (Khaled., 2004); (Bahnasawy and Khidr., 2011) and Ibrahim and Omar., 2013). Heavy metal concentrations in water samples (Ennore and Kalpakkam) and different fish tissues (*Mugil cephalus* and *Deveximentum insidiator*) were compared with the maximum allowable limit (MPL) for human consumption set by different organizations (US EPA 1976, FAO 1983, WHO 1984, 2008/2011). The results showed that heavy metal concentrations in the water samples and fish tissues were found to be satisfactorily below the standard limit.

Low concentration of metals in edible tissue i.e. muscle was observed during the present study, so consumption of fish from Ennore and Kalpakkam is still safe. But if metal concentration goes on increasing in the seawater, it may cause an impact on human beings in the near future. So, in order to be precautious and safe, periodic monitoring and evaluating the ecological condition of fishes and water conditions is necessary, such measures can be helpful and can prevent heavy metal toxicity in humans as well as marine biota.

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Table 1: Heavy Metals concentration range in Sea Water

Heavy Metals	**Concentration levels of Heavy Metals in water (mg/L)**	
	Ennore	**Kalpakkam**
Ni	BDL	BDL
Cr	0.008	BDL
Pb	BDL	BDL
Mn	0.087	0.047

BDL- *Below Detection Level*; DL*(Detection Level) - 0.001*

Table 2 : Heavy Metals concentration range in Fish Tissue

Heavy Metals	**Concentration levels of Heavy Metals in Fish Tissue (mg/kg)**	
	Ennore (*Mugil cephalus*)	**Kalpakkam** (*Deveximentum ruconius)*
Ni	BDL	BDL
Cr	0.455	0.201
Pb	BDL	BDL
Mn	0.857	0.529

BDL- *Below Detection Level*;

DL *(Detection Level) - 0.001*

Table 3 : Bioconcentration factors in fish tissues

S.No	Heavy Metals	Bioconcentration Factor	
		Ennore	Kalpakkam
	Ni	0	0
	Pb	0	0
	Cr	56.8	0
	Mn	9.8	11.2

Plate I : Fish sample from Ennore - *Mugil cephalus*

Plate II : Fish sample from Kalpakkam - ***Deveximentum insidiator***

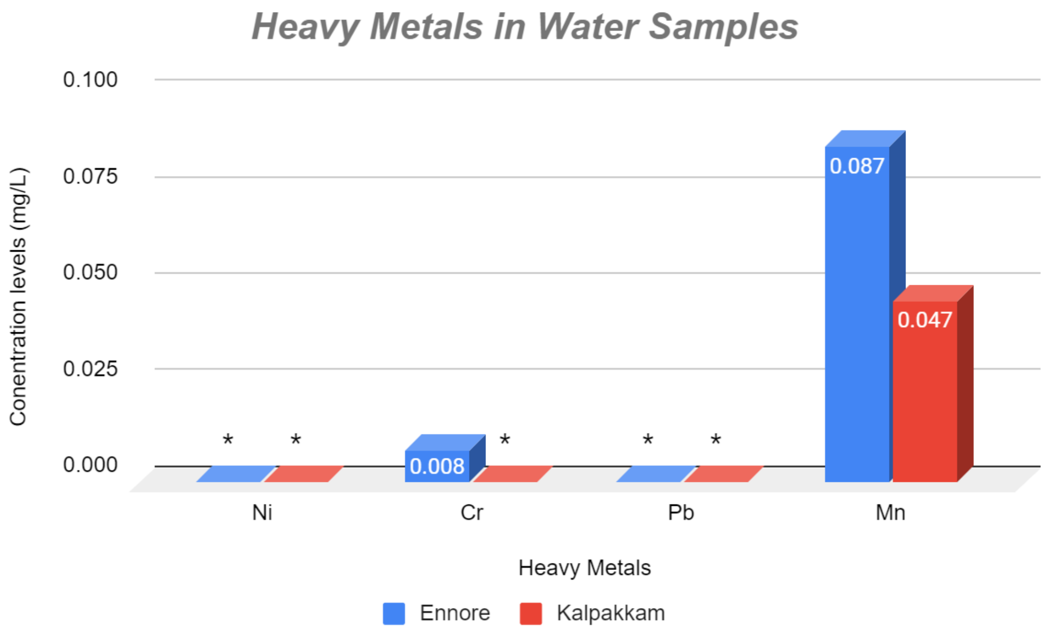

Plate III: Concentration levels of Heavy Metals in Seawater from Ennore and Kalpakkam

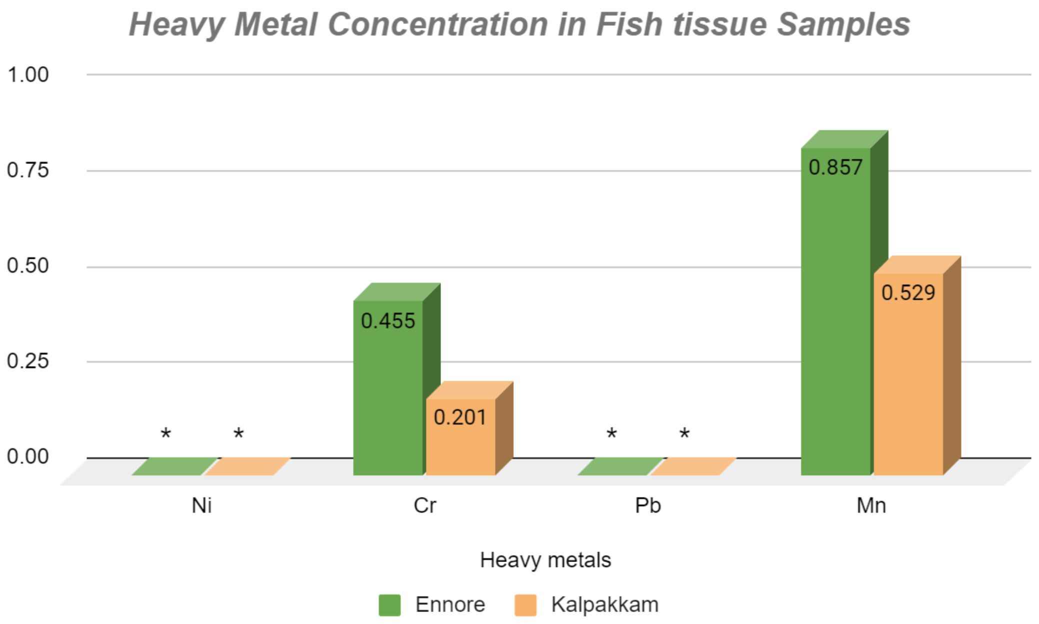

Plate IV: Concentration level of Heavy Metals in Fish Tissue from Ennore and Kalpakkam