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A Study on Total Mercury Content in Surface Water and Backwater Fishes of Periyar

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Abstract:- Aquatic systems are extensively contaminated with heavy metals released due to anthropogenic activities. Mercury is one of toxic elements and its toxicity to humans has been established. The concern about mercuric pollution in the environments started with the incident of 'Minamata' in Japan in 1950's. During the study period, flowing mercury electrode was used for the preparation of caustic at Travancore Cochin Chemicals Ltd (TCC), Eloor and effluents of small industries at Edayar were the sources of mercuric pollution. Surface water samples were collected from 1Km apart from TCC, near to Indian Rare Earth Ltd (IRE), Muttinakam and Mannamthuruth and fishes (male and female) were collected from this region with the help of local fishermen. This study implies the amount of mercury in aquatic system and its influence in different body components of three fishes. Total mercury content in both the samples analysed using cold vapour atomic absorption using Mercury Analyser MA-5840 and loss on mercury on heating processes (fishes) was decreased by the use of Bethge Apparatus. Fishes were *Oreochromis mossambicus* (Thilapia), *Mugil cephalus* (Mullet) and *Arius arius* (Cat fish) which were living in surface to near shore, middle of the river and bottom. The proximate composition (AOAC, 2000) of fishes showed that they were low fat (0.57-4.24%) with high protein content (18.4-21.96%). The total mercury content in surface water varied from 1.667- 3.334ng/ml and it was above tolerance level (1ng/ml) while in fishes followed the order *A. arius*> *M. cephalus*> *O. mossambicus*. Relatively higher concentrations of mercury were noticed in gut and liver than muscle, and also male fishes predominated over female. This study shows that mercury cycle in the habitat water did not influence to any hazardous level in these three fishes.

Keywords:- *Mercury, Pollution, Periyar, Water and Fishes.*

I. INTRODUCTION

Mercury is one of toxic elements and its toxicity to humans has been established. The concern about mercury pollution in the environments started with the notorious incident of 'Minamata'in Japan wherein the 1950'sof several people died or became terminally sick after consuming fish and shellfish containing relatively high concentrations of mercury and methyl mercury (Kurland, 1960).In Kerala, the first reported mercuric pollution was from the Chaliyar River, near Calicut owing to the effluent discharge contained high levels of mercuric pollutants from the Mavour Gwalior Ryons factory. Many health problems have been reported in people from Vazekattu village, near to the factory, probably indicated by mercury and other heavy metal poisoning (India Today dated 16th April 2003). Water is an essential for existence of life on earth for all forms of living organisms. Drinking water is a basic need for human development, health and well being, and it is also an internationally accepted human right. Water is a major component in most of the organisms ranged from micro to macro. Rivers has been witness to the evolution of human civilization. Over consumption and improper handling of river water leading to the death of many rivers. Periyar River in Kerala which is bearing the brunt of effluent discharge from the numerous factories situated on its banks. Periyar is a major source of water for the residents of Cochin. Pollutant in the lower reaches of Periyar River declining the biodiversity and fish production.

In general, the natural aquatic systems are extensively contaminated with heavy metals released due to anthropogenic activities. Mercury (Hg) cause serious health problems in various life forms. Mercury, due to its trans boundary nature, possess threat to many ecosystems worldwide, where it was never expected before (Loux 1998). An increased incidences of ailments like asthma, cancer and congenital malformations, which have link to mercury pollution. Chronic mercury toxicity is difficult to diagnose because initial symptoms are vague comprising headache, paraesthesias, amnesia and depression (Mohapatra *et al.*, 2012). Its accumulation in sediments and other non-biological materials are estimated to have increased up to five times pre-human level, primarily as a result of man's activities (Brim et al. 1994). In aquatic ecosystems, major sink of heavy metals are sediments, where they can be transformed into toxic forms. The transformation of inorganic mercury to organic form of mercury (mainly methyl mercury) through biotic or abiotic processes is the most important among them (Lawrence and Mason 2001). The half-life of elimination of mercury is in the order of 2 years from the fish tissues due to the covalent bond with protein sulphahydryl groups (UNEP 2002). As a consequence, mercury may get more time to get magnified in food chains. The backwaters of Kerala, south west coast of India, support as much biological productivity and

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diversity as tropical rain forests. They are supporting the rich fisheries potential of Kerala. Unfortunately, these backwaters, especially the Cochin backwaters, are highly polluted with metals due to the discharges from industries, urban and agricultural sectors (Menon *et al.*, 2000). Earlier studies have reported a high concentration of mercury in the water and sediments of Cochin backwaters (Omana and Mahesh 2008; Ouseph 1992, 1996).

Mercury from either natural or anthropogenic sources enters the environment mainly as mercury vapor, is converted to organic form in aquatic environments by bacteria and phytoplankton (WHO, 1991). It was found that total mercury found in fish tissue is chiefly present as methyl mercury (MeHg) (Windom and Cranmer, 1998 and Kehrig et al., 2002). MeHg is soluble, mobile, and quickly enters the aquatic food chain. It absorbed by fish when they eat smaller aquatic organisms and its binds to proteins in the fish tissue. MeHg then becomes biomagnified in the food chain through passage from bacteria, plankton, macro invertebrates, herbivorous fish, piscivorous fish and finally, to humans (WHO, 1991). Fish appear to accumulate MeHg from both food sources and the water column as it passes over the gills during respiration. MeHg can also be produced within the fish's gastrointestinal tract and on the external slime layer but the amount of MeHg contributed to tissue concentrations by these processes has not been quantified and is assumed to be insignificant. However, food was found to be the predominant source of Hg uptake in fish (Hall et al., 1997). More than 240 industrial units operating in Edayar village of Eloor panchayath make this part of the river into a cesspool of chemical pollutants. The volume of industrial effluents from Eloor- Kalamasery belt is about 2.6 million litres per day (Menon et al., 2000; Greenpeace, 2003), much of which is discharged directly into the Periyar River from where it is emptied into Cochin backwaters.

Fish is one of the major sources of protein for a large human population.Methyl mercury is 100 times more toxic to organisms than inorganic mercury. High toxicity of methyl mercury is attributed to its rapid absorption by tissues, lipid solubility and low rate of elimination. Aquatic burden of methyl mercury is derived mainly from chemical and biological conversions and anthropogenic activities (Hutzinger O., 1980).The chlor-alkali plants are one of the biggest polluters of mercury. Travancore Cochin Chemicals (TCC) had the chlor-alkali plant situated in the banks of Periyar River, Eloor industrial area. Along with large number of small industries in the Edayar industrial areamaking electricalapparatus and control instruments, paints, pulp, paper and recovery of metals (amalgamation) like Zinc, Copper, Silver etc. These industries contribute high mercury pollution in the Periyar River. Smaller amounts of mercury are used in plastics industries as heat transfer agent. The objective of the present study was to find the level of mercury (total mercury) in surface water and three species of fishes *Oreochromis massambicus*, *Mugil cephalus* and *Arius arius* which are living on the surface near to the shore, middle of the river and bottom. An attempt was also made to find out the variation of mercury with different body components of the above three species. Along with the biochemical composition of all the species were carried out.

II. MATERIALS AND METHODS

A. Materials

Cochin backwaters, situated at the northern part of the Vembanad Lake is a tropical estuarine system extending between 9°40′ and 10°12′ N and 76°10′ and 76°30 E.The major sources of mercury in water as well as in fishes were the industries located on the banks of Periyar River, which drain in to the Cochin estuary. Cochin alone account for more than 60% of industries in Kerala (Ouseph 1996). Fishes belonging to two different feeding habits were also collected from Varapuzha, Cochin backwaters (Table 1) with the help of local fishermen (Fig. 1). The sampling was done during post-monsoon season (January). Eight numbers of each species viz., *Mugil cephalus* (mullet), *Arius arius* (cat fish), and *Oreochromis mossambicus* (tilapia) were collected. Mean length and weight of fishes were given Table 1.All these fishes are edible and form major part of the diet of a large population living on the banks of these backwaters. The collected fish samples were sealed in polythene bags and kept in ice to reach the research lab. Fishes were filleted, deskinned and different body parts were separated, homogenised to a paste for the analysis. The surface water samples were collected using niskin sampler in acid cleaned glass bottles, the latitude between 9º 03.999'to 9º 0.502N and 076º 16.924' to 076º17.049'1from the middle of the river (Eloor industrial area). The water sample acidified with concentrated nitric acid to pH below 2.

Table 1 Physical Characteristics of Back Water Fishes.

Si. No.	Species	Length in cm	Weight in g	Food habits
1	*Oreochromis massambicus*	18.5 ± 0.8	100.6 ± 1.9	Detritus, decaying plants, waste products including rice ban, pea nut cake.
2	*Mugil cephalus*	18.5 ± 0.9	68.33 ± 2.5	Decaying macro vegetation, higher algae like myzophyceae, chlorophyceae, mud.
3	*Arius arius*	18.5 ± 0.7	150 ± 4.1	Insects, zooplankton, fish eggs, small fishes, larvae, mud and detritus.

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B. Methods

- *Proximate Composition of Fish*

Proximate composition is the approximate of moisture, protein, lipid and ash content. The proximate composition of fishes was determined by using AOAC, 2000.

- *Determination of Total Mercury Content in Fish*

An aliquot of 10±0.5g homogenized samples were pre digested with conc. HNO_3 and continue the digestion with conc. H_2SO_4. Digestion was continued till fumes of sulphur dioxide evolved and the solution become colourless. Loss on mercury on heating processes was decreased by the use of a Bethge Apparatus (AOAC, 1990). The concentrations of mercury in fishes were quantitated by cold vapour atomic absorption using Mercury analyser MA-5840. An aliquot of sample containing ionic mercury was treated with stannous chloride (20%) to get elemental mercury. The liberated mercury was drawn into the absorption cell which is irradiated by low pressure mercury lamp and absorbs the radiation at 253.7nm, which can be related to mercury concentration in the sample (directly proportional to the mercury concentration). Mercuric chloride was the standard used for calibration.

- *Determination of Total Mercury Content in Water*

Take a suitable aliquot of the sample containing not more than 1.0µg/ml in a beaker. The water samples wet oxidation were carried out using acid solutions and freshly prepared potassium persulphate solution (AOAC, 1990). The level of mercury in the samples was determined by as mentioned above.

III. RESULTS AND DISCUSSIONS

The proximate composition of three species was given in Table 1 and they were similar in composition and a wide variation was observed in lipid and moisture content of *Oreochromis mossabicus*. Based on fat content, fishes with fat content less than 5% is lean, fat between 5 – 10% is medium fat fish and above 10% is fatty fish (Bennion, 1997).Among these species, the fat content varied from 0.57 to 4.24% and, *Mugil cephalus* and *Arius arius* belongs to the medium fat category. According Feeley *et al.*, (1972) the low fat fish have higher water content and, as a result their meats are white in colour. The present finding was resembled in the case of *O.mossabicus.* The fatty fish instead stores fat in muscle tissue and the flesh is yellow, pray, pink or another colour (Gurr, 1992). Generally the protein content of fish muscle ranges between 16 – 22%. Fishes with protein content below 15% signifies as a low protein food. Most of the marine fishes are a good source of protein and it was high in these species. The protein content varied from 18.4 to 21.98% (*M.cephalus*).Comparatively high ash content in mullet followed by *A. arius* and *O.mossabicus* (Table 2).

Water resources get polluted with waste materials including heavy metals from various sources which accumulate in sediments. The content of mercury in water bodies are very critical due to its non-degradable nature and toxicity even at low concentrations, can be accumulated and magnified in biota and converted to methyl mercury- a toxic bomb. Also metals like Hg, Cd, Pb etc are not removed from the water by self purification, due to its high ecological significance. The total mercury content in water samples varied from 1.667 to 3.334ng/ml comparatively high values obtained at stations 1 and 2 (near to the chlor - alkali plant) and its concentration was decreased at stations 3 and 4 (Table 3). The results showed that the concentration was above the permissible limit in all the stations. Among the water samples collected from the Kochi estuary and Periyar River, mercury concentration was found greater in the bottom water than in surface water in all the seasons. During the post monsoon season the concentration of mercury ranged from 50 to 450ng/ml in surface water (CESS Annual report 2010-2011). According to Mahapatra *et al.*, 2011, the mean level of mercury was found to be 30 ng/ml in Periyar River, which was 30 times more than the permissible level in the drinking water. Mercury levels are higher at 1m depth as compared to the surface.

Table 2 Proximate Composition of Fishes.

Species name	Moisture (%)	Protein (%)	Fat (%)	Ash (%)
Oreochromis massambicus	78±0.68	19.82±0.24	0.57±0.10	0.88±0.11
Mugil cephalus	73.1±0.64	21.96±0.33	4.24±0.19	1.27±0.20
Arius arius	75.7±0.59	18.4±0.28	3.22±0.16	1.04±0.19

Table 3 Total Mercury Content in Water Samples

SI No.	Sampling location	Concentration in (ng/ml)
1	1Km apart from TCC	3.33±0.22
2	Near to IRE	3.33±0.28
3	Muttinakam	2.083±0.19
4	Mannamthuruth	1.67±015

Mercury content was not detected in well water samples collected from Eloor industrial area. A total of 25 sample each during 4 different seasons, viz. summer, pre-monsoon, monsoon and post-monsoon (Thomas *et al.*, 2011). Periyar River for drinking purposes and for this programme, samples collected from 4 stations namely Kanakkankadavu, Purappallikavu, Pathalam and Manjummal. Mercury was detected in the months of January and March at Kanakkankadavu (Ashraf and Mukundan, 2007). Online edition of India's national newspaper "The

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Hindu" dated September 8, 2009 reported that the heavy metal pollution in Vembanad lake and the river and the rivers emptying into it. The maximum concentration of total mercury in the lake water varied from 10ng/ml during the monsoon to 20ng/ml in the post monsoon period. The total mercury concentration in the water samples varied from 50ng/ml to a maximum of 130ng/ml. Robin *et al.*, 2012 studied the heavy metal contamination in the marine environment of Arabian Sea, along the Southwest coast of India. Six transects were established for the study along southern Kerala coast and collected samples were surface water, particulate matter, sediment and zooplankton. The result showed that mercury was in lowest concentration in all samples and its concentration in surface water ranged from 7 to 65ng/ml. Results revealed that the mercury content in all the species were within the permissible limit. The total mercury content was comparatively high in *Arius arius*, followed by Mugil *cephalus* and *Oreochromis mossambicus*. The variation between Mullet and Tilapia was very less. The mercury content in Tilapia ranged from 0.050 to 0.072µg/g, Mullet 0.067 to 0.092µg/g and cat fish 0.200 to 0.282µg/g. (Table 4). High content of mercury was found in the gut and liver compared to flesh and also the sex wise difference observed was comparatively less, except cat fish. Methyl mercury is soluble, mobile and quick to enter to the aquatic food chain. It gets bio-accumulated and biomagnified due to its high lipid solubility and long biological half life (USPHS 1997). High content of mercury in cat fish might be due to its food habits and its high lipid content. The total mercury content in fish samples of Vembanad Lake ranged from 0.50 to 1.75µg/g and a maximum concentration was obtained in Ophiocephallus (Omna and Mahesh, 2008).

Table 4 Total Mercury Content in Fishes

No.	Species name	Body Parts	Total Mercury content in (µg/g)
1	*Oreochromismassambicus* (M)	Muscle	0.050±0.005
		Gut & Liver	0.063±0.007
2	*Oreochromismassambicus* (F)	Muscle	0.058±0.006
		Gut & Liver	0.073±0.008
3	*Mugil cephalus* (M)	Muscle	0.067±0.006
		Gut & Liver	0.080±0.008
4	*Mugil cephalus* (F)	Muscle	0.075±0.007
		Gut & Liver	0.092±0.009
5	*Arius arius* (M)	Muscle	0.250±0.14
		Gut & Liver	0.282±0.15
6	*Arius arius* (F)	Muscle	0.200±0.11
		Gut & Liver	0.220±0.12

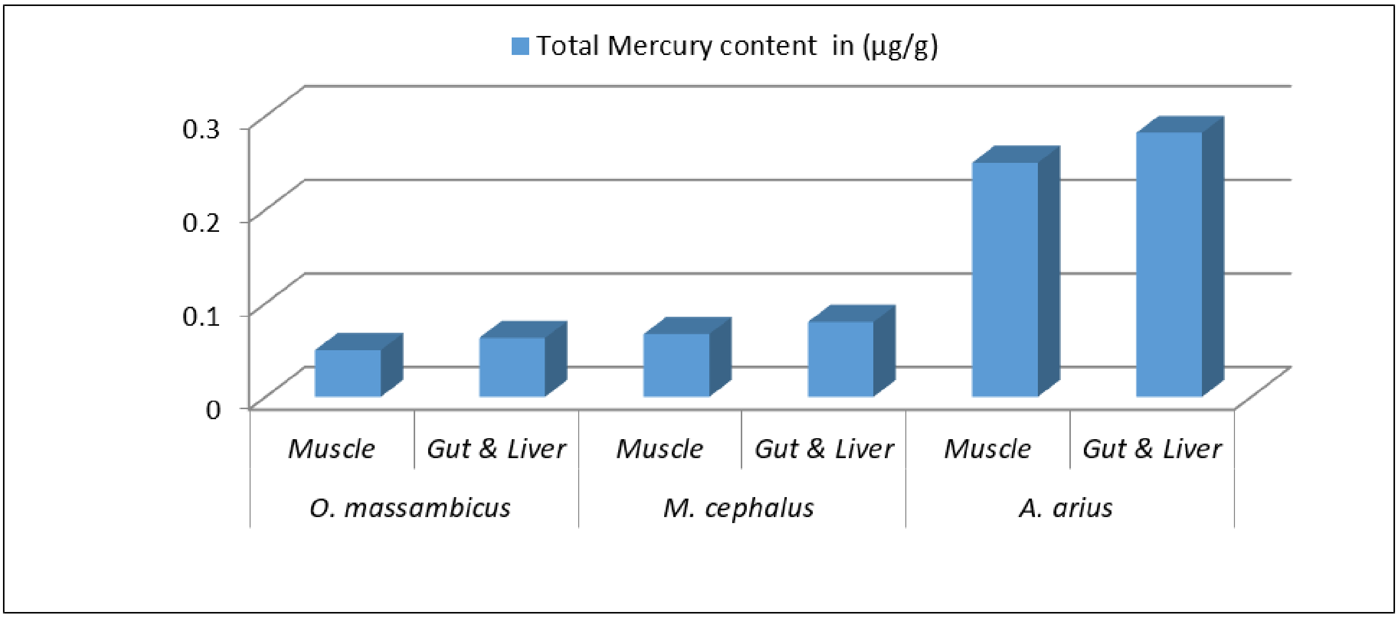

Fig 1 Total Mercury Content in Male Fishes.

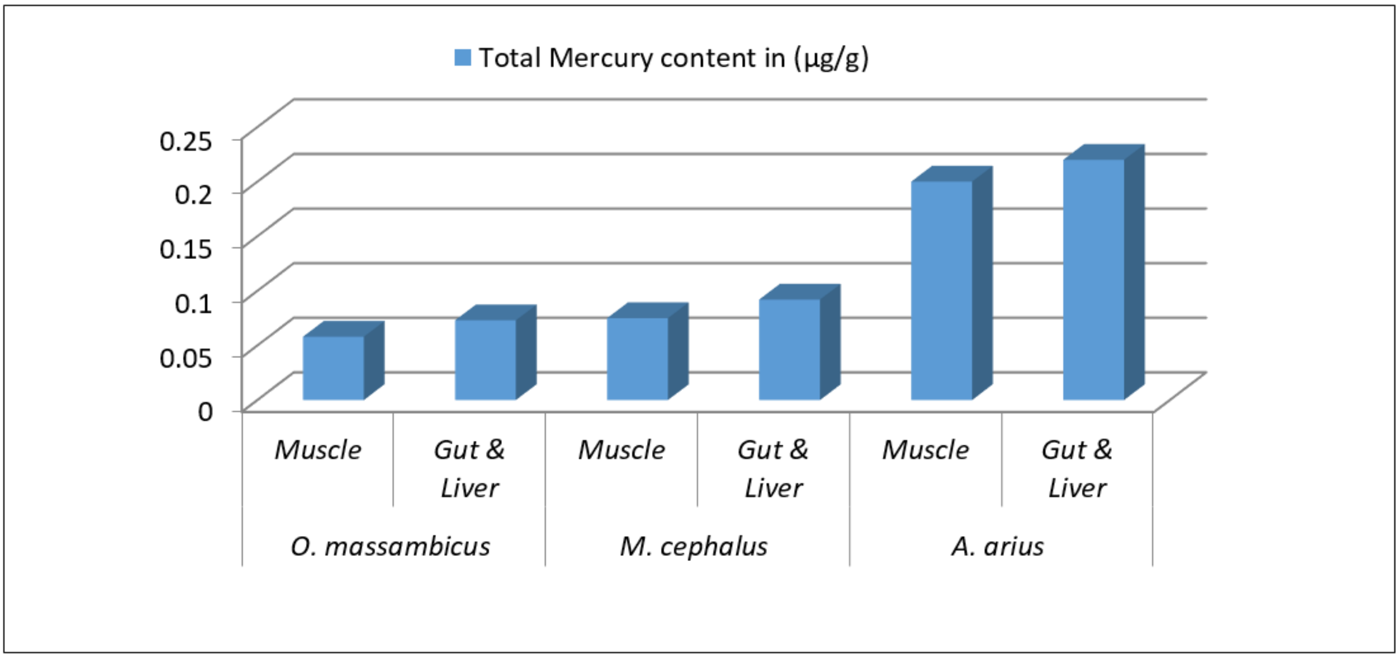

Fig 2 Total Mercury Content in Female Fishes

Mercury content was observed in fishes such as *Arius arius* and *Etroplussuatensis*, which are bottom feeders and omnivores. The maximum concentration was found in the alimentary canal, gills and flesh (The Hindu 8th September 2009). This result resembled with the findings given in the case of *Arius arius* and comparatively high concentration of mercury observed in the gut and liver of all species. Bhupander *et al.*, 2012 studied the distribution of heavy metals in valuable coastal fishes from northeast coast of India. 54 samples of 9 commercially valuable fish species were collected from different counters of the fish landing station of Digha, and the fishes were the commercially important species consumed by the people. The concentration of mercury in muscle tissues varied from 0.050 to 0.160µg/g. The highest concentration was observed in *Trichiurustrichiurus* and lowest in *Formioniger*. The mercury content in *Arius arius* species varied from 0.42 to 0.57µg/g. Mercury levels in fish muscles of some fish species from Dique channel, Colombia was measured t assess the water pollution with mercury (Olivero *et al.*, 1997). In the Tapajos River, an Amazon water body highly exploited by gold mining activities, the average value for mercury in muscle carnivore fish was 690µg/Kg, almost ten times greater than those found in the Dique channel (Malm*et al.*, 1997).

IV. CONCLUSION

Water, the most vital resources for all kinds of life on this planet is also the resource, adversely affected both quantitatively and qualitatively by all kinds of human activities. Today most rivers of world receive millions of litre of sewage, domestic wastes, industrial and agricultural effluents varying in characteristic from simple nutrients to highly toxic substances. Mercury is one of such parameters which are present in effluents from chemical industries. In this study, the mount of mercury in surface water samples of Periyar were has been estimated. The tolerance limit given for the mercury in surface water is 1.0 ng/ml and its concentrations were higher than the permissible limit in all the stations. Fish flesh provides an excellence source of protein for human diets. The proximate composition of three species of fishes reveals that they were a good source of protein and not contain high levels of fat. This study also indicates that the three species did not contain toxic mercury to any hazardous levels. Among the three species of fishes studied, mercury cycle in the habitat water seemed to have more influence on cat fish (*Arius arius)* than the other two species. Mercury content in the three species were in the order Cat fish (*Arius arius*)>Mullet (*Mugil cephalus*)>Tilapia (*Oreochromis massambicus)*

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