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AN INVESTIGATION ON THE HEAVY METAL CONTAMINATION IN ESTUARINE FISHES (ARIUS MACULATUS AND MUGIL CEPHALUS) OF COCHIN BACKWATERS, KERALA

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ABSTRACT

The study was conducted to investigate heavy metal contamination in estuarine fishes *Arius maculatus* and *Mugil cephalus.* Fish samples collected from Cochin backwaters and were analysed for heavy metals by using Hand Held X-ray Fluorescence (HHXRF). Heavy metals such as Fe, Zn, Cd and Mn were detected and metals such as As and Pd were below detection limits in all the samples collected. Concentration of metals shows variations with species and type of tissue. Metal concentrations were low in muscles when compared to liver except for Cd and Mn in *Mugil cephalus.* Highest concentrations of most metals were detected in the tissue samples of *Mugil cephalus*. The estimated daily intake and hazard quotient were calculated for all the elements detected. Cd had hazard quotient greater than one indicating that consumption of fish from this area can cause health problems.

KEYWORDS: Anthropogenic, Arabian sea, Benthopelagic, Consumption, Freshwater, Hazard, Monitoring Vembanad.

1. INTRODUCTION

A large number of industries were established and has contributed to all kinds of pollution in the last few decades. The metal contaminants are mixed in the aquatic system through smelting process, effluents, sewage and leaching of garbage which cause severe harm to the aquatic systems (Pandey and Madhuri; 2014). Industrial effluents can be considered as the main source of metal pollution in aquatic systems. With increasing heavy metals in the environment, these elements enter biogeochemical cycle leading to toxicity in animals, including fishes. Among all animal species, fishes are highly affected by these toxic pollutants, as these are not easily removed naturally from aquatic systems (Sardar *et al*; 2013).

Estuary is a semi enclosed costal body of water which has a free connection with the open sea, and within which sea water is measurably diluted with freshwater derived from land drainage (Pritchard; 1967). These bodies of water are adversely affected by anthropogenic activities such as industrialization, urbanization and overexploitation of resources (Lotze *et al;* 2006, Wolanski *et al*; 2019). Estuarine pollution can cause accumulation of pollutants in fishes and the rate of accumulation depends on various environmental factors. Pollutants entering the fish may be metabolized or stored in organs within the body, liver acts as main storage organ and also the site of detoxification.

Kochi known as Queen of Arabian Sea is enriched with lakes, backwaters and canals and these water bodies are inevitable in the geography and biological richness of Kochi (Haritha John; 2016). Cochin backwaters are being contaminated by heavy metals due to industrialization, and it has exceeded safety limits in some aquatic organisms (Anu *et.al*; 2014). Aquatic ecosystems are vulnerable to be polluted by dangerous heavy metals such as mercury, cadmium, copper, lead and zinc. These heavy metals can get accumulated in various tissues of fishes and cause poisoning of fish by affecting their vital metabolic functions. As fishes are exposed to heavy metal pollutants constantly they can be used as bio indicators for monitoring pollution (Authman *et al*; 2015). And can be used for practical bio monitoring of aquatic metal pollution (Zhou *et al*; 2008).

Thoppumpady is a region in Kochi and has numerous tourist destinations and industries associated with it. Cochin Fisheries harbour is located in the region and plays a major role in the fishing industry of the state. Urbanization and Industrialization has led to the exploitation of aquatic ecosystems by releasing of organic and sewage effluents in the region. Vembanad Lake flows through the region and people residing on the banks of the lake are dependent on it for their livelihood. Vembanad Lake joins the Laccadive Sea after flowing through regions of Kochi, including Thoppumpady. Various sources of pollution are associated with Vembanad Lake system and have adversely affected its water quality (Sajeev *et al*; 2020). *Arius maculatus* and *Mugil cephalus* differ in their feeding habits and this can have an impact on the heavy metal contamination in their tissues. *Arius maculatus* is considered as a good model organism to check heavy metal contamination due to its bottom feeding habits. They feed on detritus, crustaceans, polychaete worms and molluscs. It is generally marketed and consumed by people. *Mugil cephalus* are diurnal feeders, mainly consuming zooplankton and detritus. They are ecologically important as they take part in energy flow within estuarine communities through their feeding habits. They are marketed and consumed as food in different forms. So the present study was conducted to detect and quantify heavy metals present in estuarine fishes *Arius maculatus* and *Mugil cephalus*. So, the present study is an attempt to compare the amount of heavy metals in these fishes and understand, influence of the feeding habits in heavy metal contamination.

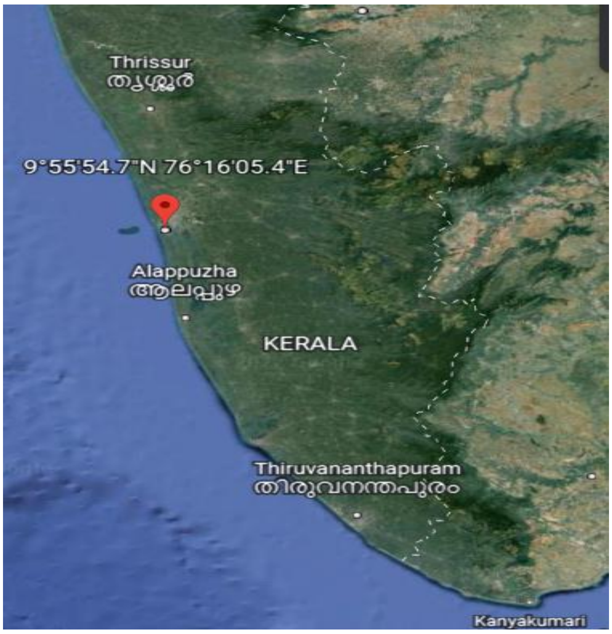

Fig. 1: Study area.

Fig. 2 A. ***Arius maculatus*** **B.** ***Mugil cephalus.***

2. MATERIALS AND METHODS

Fish samples were collected from Thoppumpady, Kochi, Kerala (9°55'54.7"N 76°16'05.4"E) from local fishermen, and the locations were geo-tagged. Samples were collected in ice packs, followed by washing and storing in freezer at the laboratory.

The collected fish species were dissected by standard protocols and tissues from liver and muscles were collected separately. The tissues were dried separately using hot air oven. The samples were placed at a temperature of 64°C in the hot air oven for 48 hours. Further drying of the samples was done at in 42°C for another 48 hours. Completely dried samples were powdered using mortar and pestle. Individual samples were collected in separate sample bottles.

The analysis of the prepared samples were conducted at Nuclear Physics Division, Baba Atomic Research Centre, Mumbai, Maharashtra by Hand held X-ray fluorescence (HHXRF) Spectrometry.

In a typical XRF spectrometer, the sample is excited by X-rays from an X-ray tube that has enough energy to liberate electrons from the inner shells of the sample's atoms. The electrons from the outer shells then fill the empty inner shell positions, leading to the emission of distinctive X-rays. These emissions are recorded and then used to determine the energy properties of the elements in the sample and can be quantified by the instrument or other software. It is called conventional X-ray fluorescence (XRF). Hand held XRF (HHXRF) is the need of the hour to analyse metals, powders and alloys, as other conventional XRF techniques are found to be cumbersome and difficult to handle. The finely powdered samples were irradiated by X-ray tube (Rhodium tube) in a cubical box. The spectrum of each was obtained in 30 seconds. The beam lines used were of (Beam 1 from 12 to 36 KeV) and beam 2 from 0-12 KeV).

3. RESULTS

Arius maculatus is a demersal fish and feeds on invertebrates as well as small fishes and *Mugil cephalus* is a benthopelagic fish and feeds on zooplankton. Heavy metals such as Fe, Zn, Cd and Mn were detected in fish samples. Concentration of metals showed variations with species and type of tissue. Metals such as As and Pd were below detection limits in all the samples collected. Metal concentration was low in muscles when compared to liver except for Cd and Mn in *Mugil cephalus.* In liver highest concentration of Zn was found in *Arius maculatus* and highest concentrations of other metals are detected in *Mugil cephalus.* In muscle tissue, concentrations of all the metals are found highest in *Mugil cephalus* except Fe which is present in equal concentration in both species. Concentration of Mn was below detection level in muscle of *Arius maculatus* (Table 1&2).

Table 1: Heavy metals concentration of *Arius maculatus* in ppm.

Metal	Concentration in liver	Concentration in muscle
Fe	576.5 ± 37	71 ± 22
Zn	134 ± 7.6	19 ±5
Cd	27 ± 20.6	26 ±16
Mn	29 ±23	BDL
As	BDL	BDL
Pb	BDL	BDL

Table 2: Heavy metals concentration of *mugil cephalus* in ppm.

Metal	Concentration in liver	Concentration in muscle
Fe	680.5 ± 42.25	71 ± 20
Zn	39 ± 5.75	21 ± 4
Cd	28 ± 16	31 ± 16
Mn	29.6 ± 25.3	36 ± 24
As	BDL	BDL
Pb	BDL	BDL

3.1 Human health risk assessment

The health risk in consuming heavy metal contaminated fish was determined by calculating Daily Dietary Intake (DDI) Estimated Daily Intake (EDI) and Hazard Quotient (HQ) (Zhang W & Wang W. X; 2012). These were calculated for every detected heavy metal in the fish samples. HQ greater than 1 it shows significant risk associated with the consumption of liver and muscle of *Arius maculatus* and *Mugil cephalus*.

3.2 Calculation of Daily Dietary Intake (DDI)

Daily Dietary Intake (DDI) was calculated by using the formula:

$$DDI = C_{fish} \times I_{fish}$$

C_{fish} = mean metal concentration in fish muscle (μg/g)
I_{fish} = daily fish consumption per capita (g/day)

Table 3: Daily Dietary Intake (µg/day) of *Arius maculatus.*

Element	DDI (muscle)	DDI (liver)
Fe	553.8	4496.7
Zn	142.2	1045.2
Cd	202.8	210.6
Mn	--	226.2

Daily Dietary Intake (DDI) intake was calculated for all metals detected by multiplying mean metal concentration in liver and muscle tissues (µg/g) of *Arius maculatus* and daily fish consumption per capita (g/day) (Table 3). In India average consumption of fish and fish products per capita per year is 2.85 kg and average daily fish consumption per capita per day will be 7.8 g. (Needham & Funge-Smith;2014).

Table 4: Daily Dietary Intake (µg/day) of *Mugil cephalus.*

Element	DDI (muscle)	DDI (liver)
Fe	553.8	5307.9
Zn	163.8	304.2
Cd	241.8	218.4
Mn	280.8	230.88

Daily Dietary Intake (DDI) was calculated for all metals detected by multiplying mean metal concentration in liver and muscle tissues (µg/g) of *Mugil cephalus* and daily fish consumption per capita (g/day) (Table 4). In India average consumption of fish and fish products per capita per year is 2.85 kg and average daily fish consumption per capita per day will be 7.8 g. (Needham & Funge-Smith; 2015).

3.3 Calculation of Estimated Daily Intake (EDI) and Hazard Quotient (HQ)

Estimated Daily Intake (EDI) was calculated by using the following formula:

$$\mathrm{EDI} = \frac{C_{fish} \times I_{fish}}{BW}$$

BW = Average body weight of population
Body weight of Indian population was taken as 70kg.

Hazard Quotient (HQ) was calculated by the following formula:

$$\mathrm{HQ} = \mathrm{EDI} \div \mathrm{RfD}$$

RfD = Reference dose established (Onsanit S *et.al*; 2010)

Table 5: Estimated Daily Intake (EDI) and Hazard Quotient (HQ) for muscle of *Arius maculatus.*

Element	EDI (µg kg BW^{-1} day^{-1})	RfD (µg kg BW^{-1} day^{-1})	HQ
Fe	7.91	700	0.0113
Zn	2.11	300	0.007
Cd	2.89	1	2.89
Mn	--	140	--

Estimated Daily Intake (EDI) and Hazard Quotient (HQ) were calculated for muscle of *Arius maculatus* (Table 5). Here, the HQ calculated is less than unity for all metals except Cd (HQ=2.89). This shows that comsumption of muscle of *Arius maculatus* can cause toxic effects due to higher concentrations of Cd in the tissue.

Table 6: Estimated Daily Intake (EDI) and Hazard Quotient (HQ) for muscle of *Mugil cephalus.*

Element	EDI (µg kg BW^{-1} day^{-1})	RfD (µg kg BW^{-1} day^{-1})	HQ
Fe	7.91	700	0.0113
Zn	2.34	300	0.0078
Cd	3.45	1	3.45
Mn	4.01	140	0.028

Estimated Daily Intake (EDI) and Hazard Quotient (HQ) were calculated for muscle of *Mugil cephalus* (Table 6). Here, the HQ calculated is less than unity for all metals except Cd (HQ=3.45). This shows that comsumption of muscle of *Mugil cephalus* can cause toxic effects due to higher concentrations of Cd in the tissue.

Table 7: Estimated Daily Intake (EDI) and Hazard Quotient (HQ) for liver of *Arius maculatus.*

Element	EDI (µg kg BW^{-1} day^{-1})	RfD (µg kg BW^{-1} day^{-1})	HQ
Fe	64.23	700	0.0917
Zn	14.93	300	0.0497
Cd	3.008	1	3.008
Mn	3.231	140	0.023

Estimated Daily Intake (EDI) and Hazard Quotient (HQ) were calculated for liver of *Arius maculatus* (Table 7). Here, the HQ calculated is less than unity for all metals except Cd (HQ = 3.008). This shows that consumption of liver of *Arius maculatus* can cause toxic effects due to higher concentrations of Cd in the tissue.

Table 8: Estimated Daily Intake (EDI) and Hazard Quotient (HQ) for liver of *Mugil cephalus.*

Element	EDI (µg kg BW^{-1} day^{-1})	RfD (µg kg BW^{-1} day^{-1})	HQ
Fe	75.827	700	0.108
Zn	4.345	300	0.014
Cd	3.14	1	3.14
Mn	3.29	140	0.023

Estimated Daily Intake (EDI) and Hazard Quotient (HQ) were calculated for liver of *Mugil cephalus* (Table 8). Here, the HQ calculated is less than unity for all metals except Cd (HQ = 3.14). This shows that consumption of liver of *Mugil cephalus* can cause toxic effects due to higher concentrations of Cd in the tissue.

In X-ray Fluorescence, samples are excited by X-rays and this will result in the ejection of inner shell electrons. A vacancy is created in the inner shells of atoms. Outer shell electrons fall into this vacancy by emitting photons according to the energy differences between the states. Each element has unique energy levels and this property is used to identify the elements present. Concentration of each element corresponds to the intensity of X-rays emitted. Spectral lines are obtained as a result of HHXRF, records the intensities of emitted X-rays. These are analysed to detect and quantify elements present in the sample. Such spectral lines were obtained by conducting HHXRF in tissue samples collected from *Arius maculatus* and *Mugil cephalus* (Fig.4 & 5) and were used to quantify heavy metals present in the samples.

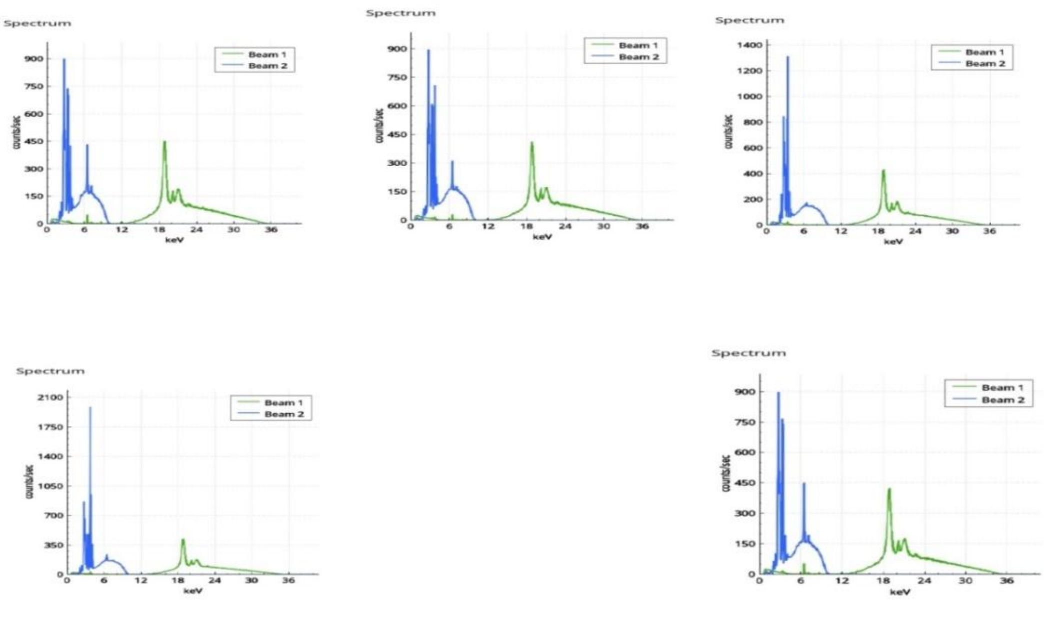

Fig. 3: Spectral lines obtained from samples of *arius maculatus.*

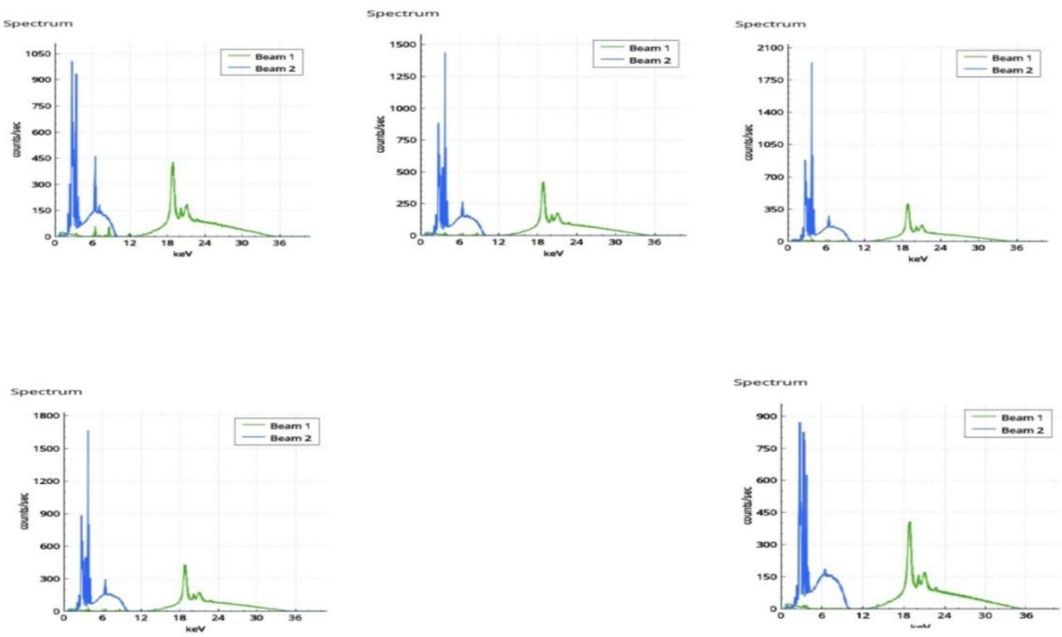

Fig. 4: Spectral lines obtained from samples of *Mugil cephalus.*

4. DISCUSSION

The present study showed that Heavy metals such as Fe, Zn, Cd and Mn were present in fish samples collected from the area of study. Heavy metals such as As and Pb were found below detection limits in all the samples. In contrary to the hypothesis; concentrations of metals was found to be highest in *Mugil cephalus*. Muscle tissues had lower concentrations of metals compared to liver except for Cd and Mn in *Mugil cephalus*. Varying concentrations of heavy metals in liver and muscle of these species may be due to the difference in their feeding habits.

4.1 Metal concentration study in *arius maculatus*

Arius maculatus is a demersal fish and feeds on invertebrates and small fishes. Metals such as Fe, Zn, Cd and Mn were detected in liver samples. In liver Fe was found in highest concentration (576.5 ± 37 ppm) followed by Zn (134 ± 7.6 ppm), Mn (29 ±23 ppm) and Cd (27 ± 20.6 ppm). Concentration of heavy metals in the liver samples followed the order: Fe> Zn> Mn> Cd. In muscle tissue samples Fe, Zn and Cd were detected and Mn was below detection limits. The concentrations of heavy metals in muscle samples followed the order: Fe (71 ± 22)> Cd (26 ±16)> Zn (19 ±5). As and Pb concentrations were below detection limits in all the samples collected. The Hazard Quotient (HQ) calculated for every metal found in liver and muscle showed that HQ of cadmium (Cd) was above unity. In liver HQ was 3.008 and 2.89 in muscle. This indicates that consumption of liver and muscle has potential to cause toxic effects in humans. Liver is more toxic to consume in comparison with the muscle tissue of *Arius maculatus.*

4.2 Metal concentration study in *mugil cephalus*

Mugil cephalus is a benthopelagic fish and feeds on zooplankton. Metals such as Fe, Zn, Cd and Mn were detected in tissue samples of *Mugil cephalus*. In liver samples Fe was found in highest concentration (680.5 ± 42.25) followed by Zn (39 ± 5.75), Mn (29.6 ± 25.3) and Cd (28 ± 16). In liver metal concentrations follows the order: Fe>Zn>Mn>Cd. In muscle tissue samples concentrations of metals were Fe (71 ± 20), Mn (36 ± 24), Cd (31 ± 16) and Zn (21 ± 4) and followed the order: Fe>Mn>Cd>Zn. As and Pb concentrations were below detection limits in all the samples collected. HQ was calculated for all heavy metals present in the samples of *Mugil cephalus*, it was found that HQ of all elements except Cd was below unity. HQ of Cd in muscle was 3.45 and 3.14 in liver samples. This indicated that consuming muscle tissue of *Mugil cephalus* can cause higher toxic effects than consumption of liver though the difference between HQ values is 0.315. Therefore consumption of liver and muscle of *Mugil cephalus* poses the risk of causing toxicity in human.

The heavy metals enter fish through water and get accumulated in the tissues. Liver take part in xenobiotic metabolism and removes toxic substances from blood. Heavy metals get accumulated in liver during such metabolic activities. This explains the presence of heavy metals in liver. Muscle tissue of fish is responsible for locomotion in fishes and it is developed by anabolic reactions. Accumulation of heavy metal in muscle tissue can occur if heavy metals are present in the blood stream of fish. Therefore, the presence of heavy metals in tissues of *Arius maculatus* and *Mugil cephalus* especially Cd shows significant pollution of water bodies by heavy metals and consumption of these fishes can cause toxic effects in human.

5. CONCLUSION

The study reported that various metals were present in liver and muscle tissues of the selected fishes in varying concentrations. Highest concentrations of metals were detected in liver except Mn, which was found in highest concentration in the muscle of *Mugil cephalus*. The HQ was below unity for Fe, Zn and Mn in both the species but HQ value of Cd was above unity for both species. HQ above unity shows potential toxic effects of Cd, due consumption of *Arius maculatus* and *Mugil cephalus.* Whereas, HQ values of Fe, Zn and Mn below unity shows that the concentration of metals are at safe limits for consumption. Regular monitoring is recommended and measures such as sewage and agricultural waste treatment, prevention of dumping E-waste near water bodies should be strictly implemented. Extensive studies can be conducted in various species and regions to evaluate the risk of heavy metal contamination and check possibilities of bioaccumulation and bio magnification in higher tropic levels.

Ethical standards

We declare that the experiments were conducted as per the guidelines of the institutional animals ethics committee.

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6. REFERENCES

1. Anu, P. R., Jayachandran, P. R., Sreekumar, P. K., & Nandan, S. B. A review on heavy metal pollution in Cochin Backwaters, Southwest Coast of India. *International Journal of Marine Science*, 2014; 4.
2. Authman, M. M., Zaki, M. S., Khallaf, E. A., & Abbas, H. H. Use of fish as bio-indicator of the effects of heavy metals pollution. *Journal of Aquaculture Research & Development*, 2015; 6(4): 1-13.
3. Elliott, M., Day, J. W., Ramachandran, R., & Wolanski, E. A synthesis: what is the future for coasts, estuaries, deltas and other transitional habitats in 2050 and beyond?. In Coasts and Estuaries, 2019; 1-28.
4. John, H. Once city lifelines now waste dumping yards: Kochi canals under severe threat. *The Newsminute*, 2016; 18(27). Retrieved from: https://www.thenewsminute.com/article/once-city-lifelines-now-waste-dumping-yardskochi-canals-under-severe-threat-51910
5. Lotze, H. K., Lenihan, H. S., Bourque, B. J., Bradbury, R. H., Cooke, R. G., Kay, M. C., & Jackson, J. B. Depletion, degradation, and recovery potential of estuaries and coastal seas. *Science*, 2006; *312*(5781): 1806-1809.
6. Needham, S., & Funge-Smith, S. J. The consumption of fish and fish products in the Asia-Pacific region based on household surveys. *RAP publication*, 2015; 12: 87.
7. Onsanit, S., Ke, C., Wang, X., Wang, K. J., & Wang, W. X. Trace elements in two marine fish cultured in fish cages in Fujian province, China. *Environmental Pollution*, 2010; 158(5): 1334-1342.
8. Pandey, G., & Madhuri, S. Heavy metals causing toxicity in animals and fishes. *Research Journal of Animal, Veterinary and Fishery Sciences*, 2014; 2(2): 17-23.
9. Pritchard, D. W. What is an estuary: physical viewpoint. *American Association for the Advancement of Science*, 1967.
10. Sajeev, S., Sekar, S., Kumar, B., Senapathi, V., Chung, S. Y., & Gopalakrishnan, G. Variations of water quality deterioration based on GIS techniques in surface and groundwater resources in and around Vembanad Lake, Kerala, India. *Geochemistry*, 2020; *80*(4): 125626.
11. Zhou, Q., Zhang, J., Fu, J., Shi, J., & Jiang, G. Biomonitoring: an appealing tool for assessment of metal pollution in the aquatic ecosystem. *Analytica chimica acta*, 2008; 606(2): 135-150.