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Heavy Metal Concentration In Edible Bivalve *Meretrix Meretrix* From Two Estuaries Of Uttara Kannada, Karnataka

[1]Sujal K. Revankar, [2]J.L.Rathod

Department of Studies in Marine Biology, Karnatak University Post Garduate Centre,Karwar, Karnataka

*Corresponding author: *sujalrevankar97@gmail.com*

ABSTRACT

Analysis of heavy metals like Cadmium(Cd), Chromium(Cr), Nickel(Ni), Zinc(Zn), Lead(Pb) and Arsenic(As) in commercially important edible bivalve *Meretrix meretrix* was carried out from September 2021 to October 2022 in two estuaries of Karnataka. The samples were collected from Kali ($14^0$80’58”N & $74^0$14’26.2”E) and Aghanashini Estuary ($14^0$52’25.6”N& $74^0$36’67.5”E) during low tide. Heavy metals were analysed by using ICP-OES OPTIMA 8000(Perkin Elmer). During the present investigation on *Meretrix meretrix,* highest concentration of Chromium 103.10 ppm at Aghanashini was observed, which are much higher than permissible limits (12 ppm) as per Indian standards. Permissible limit of Zinc is 40 ppm, whereas higher concentration of 110.90 ppm at Kali was observed, which was much higher than the permissible limit. Nickel 20.84 ppm at Kali was observed which is higher than permissible limit (0.5 to 0.6 ppm). Whereas, 2.53 ppm of Cadmium was observed in Kali estuary which was a slightly higher than permissible limit (2.0 ppm). 7.61 ppm of Arsenic was observed at Aghanashini which was in low concentration than permissible limit (86.0 ppm).From above findings it is concluded that bivalves (*Meretrix meretrix*) from these two estuaries are not safe for consumption.

Keywords: Heavy metals, Marine Biology, *Meretrix meretrix*, Kali, Aghanashini

INTRODUCTION

Heavy metals are defined as metallic elements that have a relatively high density compared to water [1]. There is no scientific classification and grouping for the term heavy metals as it has never been defined by an authoritative body like International Union of Pure and Applied Chemistry (IUPAC). Different literature's have listed different metals under the umbrella term heavy metals [2]. They include metals such as mercury (Hg), cadmium (Cd), arsenic (As), thallium (Ti), zinc (Zn), nickel (Ni), copper (Cu) and lead (Pb) [3]. These metals occur naturally on earths crust, environmental contamination and exposure to humans are usually caused by Anthropogenic activities [4]. In recent years there has been an increasing concern over the use and disposal of heavy metals. There is the potential ecological and public health impacts, which

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are now important for the research. Heavy metals are the natural source of pollution in the environment. Natural emission of heavy metals in environment occurs through environmental processes like volcanic eruptions, weathering of metal bearing rocks, forest fires, sea-salt sprays, biogenic processes and air-borne soil particles. Heavy metals naturally found in environment as hydroxides, oxides, phosphates, silicates, sulphates and organic compounds. Some of the most naturally occurring heavy metals in environment are Lead, Copper, Cadmium, Arsenic, Zinc, Chromium and Nickel [5].

India has an estuarine expanse of 0.29 million hectares and more than 55 major estuaries [6]. Inland fishing sector is major contributor to India's annual fish production and estuaries are ideal environments for commercial fishing activities and fish culture. In 2017-18 India reported a total annual fish production of 12.59 million tonnes, of this 8.9 million tones came through inland fisheries. Some of the major species exploited in Indian estuarine system are fishes like Pearl Spot, Mullet, Seabass and shellfishes include species of shrimps, bivalves like mussel and clam(*Meretrix sp.*), oyster and crabs [7].Hence, the health of estuarine ecosystem is extremely important to the heath of the estuarine fishery resources of India. Estuaries are described as semi-enclosed bodies of water, situated at the interface between land and ocean, where sea water is diluted by the inflow of the fresh water [8]. Estuaries are most dynamic and diverse ecosystems in the world characterised by their high productivity. Many coastal species spend their juvenile stage in estuarine marshes, as it provides them necessary food and shelter. They also provide a direct resources for commercially important estuarine species of fish and shell fish.

Worlds population lives in and around estuarine watersheds, as a result many commercial and industrial activities happen in and around estuarine areas. This has led estuarine ecosystems becoming extremely vulnerable to contamination from anthropogenic sources. Natural introduction of metals to the estuarine environment is due to the weathering of rocks and erosion processes. Metal contamination through anthropogenic sources in estuarine and coastal environments is mainly a result of industrial, agricultural and urban activities like municipal wastes and pesticide run offs [9].

Water is the universal solvent; it can dissolve organic and inorganic contamination for the environment. The presence of trace metals in water can be extremely harmful to organisms due to its ability to bioaccumulate in organisms and biomagnifies through the food chain. As the word heavy metals which means they are denser so they settle at the bottom. The accumulation of heavy metals on the soil sediments is the major problem. The accumulated metals in the soil can be quickly cycled to food chain through various processes and this leads to the process of accumulation in organisms though the food chain. Heavy metal contamination of water and sediment can lead to bioaccumulation of metals in tissues and organs of aquatic organisms [10]. The metals enters the blood of the organisms through skin, gill and by feeding and the metals gradually accumulate in their tissues [11, 12]. Excess concentration of metals entering the body of animals, will impair their ability to remove metals from the body through excretion, this leads to the bioaccumulation of metals [13]. Bioaccumulation of heavy metals in commercially important fishes and shell fishes can be threat to human health [14]. Shellfishes such as bivalves are used as bioindicators to check for environmental pollution due to their ability to accumulate environmental pollutants quickly in their bodies. As they are the filter feeders, they feed from particulate organic matter and plankton through bronchial filtration. They can tolerate high

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concentrations of contaminants without significant metabolic damage [15].

Heavy metals toxicity can include many adverse health effects in human body. Accumulation of heavy metals in the body can alter and damage the functions of organs such as brain, liver, kidney and lungs. Long term exposure can lead to physical and neurological disorders which are similar to multiple sclerosis, muscular dystrophy and Alzheimer's disease. Chronic long-term exposure may lead to cancer [16]. The threat of heavy metal pollution to humans gained worldwide attention with the outbreak of Minamata disease in Japan. Minamata disease was officially discovered in 1956 and was due to the environmental contamination of Shiranui sea by Methyl mercury (MeHg) through the waste water discharge from a local industrial plant. The disease occurred in humans who ingested fish and shellfish contaminated with MeHg from Minamata Bay. Typical symptoms of this disease are sensory disturbance, ataxia, dysarthria, constriction of visual field and tremors. Further, foetus of mother affected by the disease were also poisoned by MeHg.

Shell fishes are considered as poor mans rich protein food of majority of inhabitants of coastal area. Bivalves are usually consumed by local public and even it is transported to different places. In the present study an attempt is made to analyse the concentration of some of the heavy metals from one of the important edible bivalve *Meretrix meretrix* from two estuaries of Uttara Kannada district Karnataka.

MATERIAL AND METHODS

Study Area

Two estuaries of Uttara Kannada district Karnataka i.e. Kali Estuary and Aghanshini Estuary selected for present work. Kali Estuary ($14^0$80'58"N & $74^0$14'26.2"E) located in Karwar taluka. Kali river arises from the place called Diggi Joida Taluka. It flows to south west into Kadra Reservoir, and is joined by the Thana Halla just below the dam at Kadra. From Kadra the river flows west through marshland to join the Arabian sea in Karwar.

The Aghanashini or Tadri River ($14^0$52'25.6"N& $74^0$36'67.5"E) originates in the Sirsi taluk of Uttara Kannada district in the central Western Ghats of Karnataka State. The river meets the tides of the Arabian Sea and forms a large estuarine expanse in the coastal taluk of Kumta. The estuary has its outlet into the sea in between the villages of Aghanashini in the South and Tadri in the North.

Sample Collection & Analysis

Bivalves (*Meretrix meretrix*) and Sediment samples were collected monthly from both the estuaries i.e. Kali and Aghanashini estuaries for thirteen months (September 2021 to October 2022). The samples were collected during low tide. Sediment and *M.meretrix* samples collected in clean polythene bags, and were immediately transported to lab in ice box. *M.meretrix* samples were carefully washed with ultra pure water. The samples were refrigerated at -20^0 C until the analysis.

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Figure 1.*Meretrix meretrix*

Heavy Metal Analysis

The collected sediment samples were oven dried at 60^{0}C for 48 hours, and *M.meretrix* samples were dissected and the tissue was oven dried at 60^{0}C for 48 hours, using hot air oven. The dried samples were powdered and used for digestion.

Digestion of samples

One to five grams of dried sample were added to 25 ml concentrated hydrochloric acid and was digested over hot metal plate for about 30 minutes till all material is digested.Cooled samples were carefully transferred into the flask containing water, mixed well to homogenise. Filtered the sample using whatman no 42 filter paper. Finally added concentrated nitric acid at 2%v/v to the filterate and mixed well, this solution is used for analysis. Heavy metals (Cd, Cr, Ni, Pb, Zn and As) in sediment and *M.meretrix* samples were analysed on Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) using ICP-OES OPTIMA 8000 (Pekin Elmer).

Calculation

The Calculation of the quantity in mg/kg of the element in the sample by multiplying this value by Dilution factor.

$$\text{Concentration, ppm} = \frac{\text{C x Dilution Factor}}{1000}$$

Where, C = concentration of metal in sample (ppb)

$$\text{Dilution Factor (D)} = \frac{\text{Final volume after digestion(ml)}}{\text{Weight of sample(g)}}$$

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Results

The concentration of heavy metals like Cd, Cr, Ni, Pb, Zn and As in edible bivalve *Meretrix meretrix* and sediment of two estuaries Kali and Aghanashini was carried out from September 2021 to October 2022.Observed results showed variation in concentration of metals between the estuaries.

Heavy Metals

Cadmium (Cd)

The concentration of Cadmium in *M.meretrix* of Kali estuary ranged between 0.97 ppm to 2.53 ppm. The maximum concentration of Cd of 2.53 ppm was observed in September 2021 in Kali estuary, followed by 1.91 ppm in October 2021 and 1.59 ppm in October 2022. Whereas, the least concentration of 0.97 ppm in January 2022 was observed in *M.meretrix* of Kali estuary (Fig.2). Cadmium is not varying much from the permissible limit of 2.00 ppm.
The concentration of Cadmium in *M.meretrix* of Aghanashini estuary ranged between 0.78 ppm to 1.58 ppm. The maximum concentration of 1.58 ppm was observed in October 2021 followed by 1.19 in October 2022 and 1.07 ppm in May 2022. Whereas the least concentration of 0.78 ppm was observed in the month of March,2022 (Fig.2).

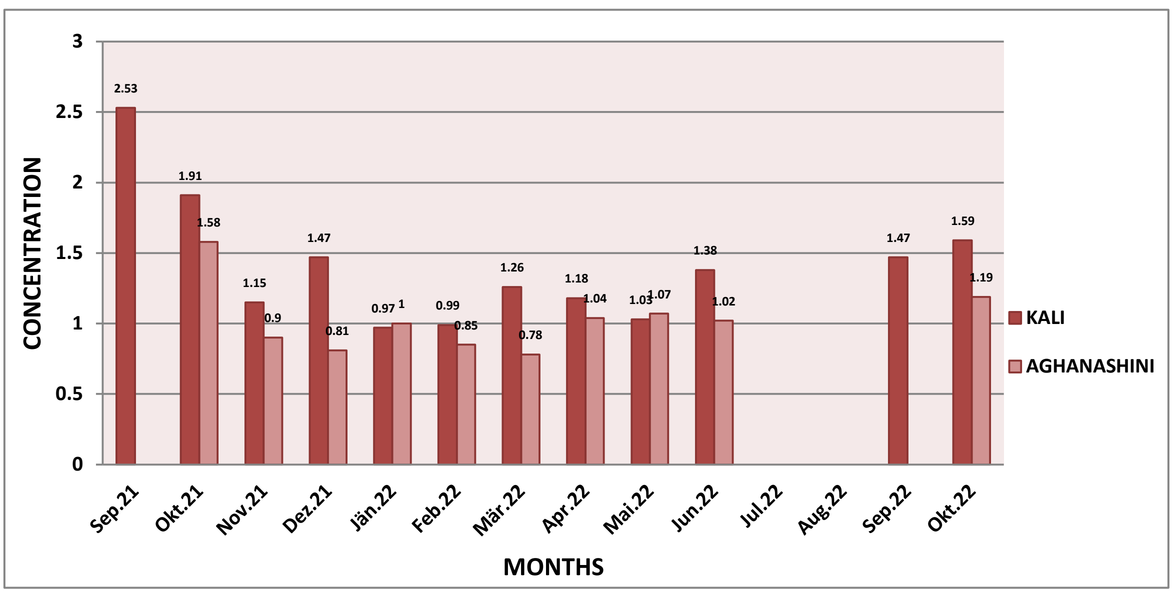

Figure.2. Monthly Cadmium(ppm)concentration in *M.meretrix* of Kali & Aghanashini estuary during study period

The concentration of Cadmium in Sediment of Kali estuary ranged between 0 ppm to 0.30 ppm. The maximum concentration of Cd in Sediment 0.30 ppm was observed in March 2022 followed by 0.28 ppm in April 2022 and 0.27 in May 2022. Whereas, the least concentration of Cd was 0.0 ppm in December 2021, June 2022, July 2022, August 2022 and September 2022 (Fig.3).
The concentration of Cadmium in Sediment of Aghanshini estuary ranged between 0 ppm to 0.31 ppm. The maximum concentration of Cd was observed 0.31 ppm in January 2022 and

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March 2022 followed by 0.30 ppm in February 2022 and 0.29 in April 2022. Whereas, the concentration of Cd 0.0 ppm in August 2022, October 2022 and 0.01 ppm was observed in September 2022 (Fig.3).

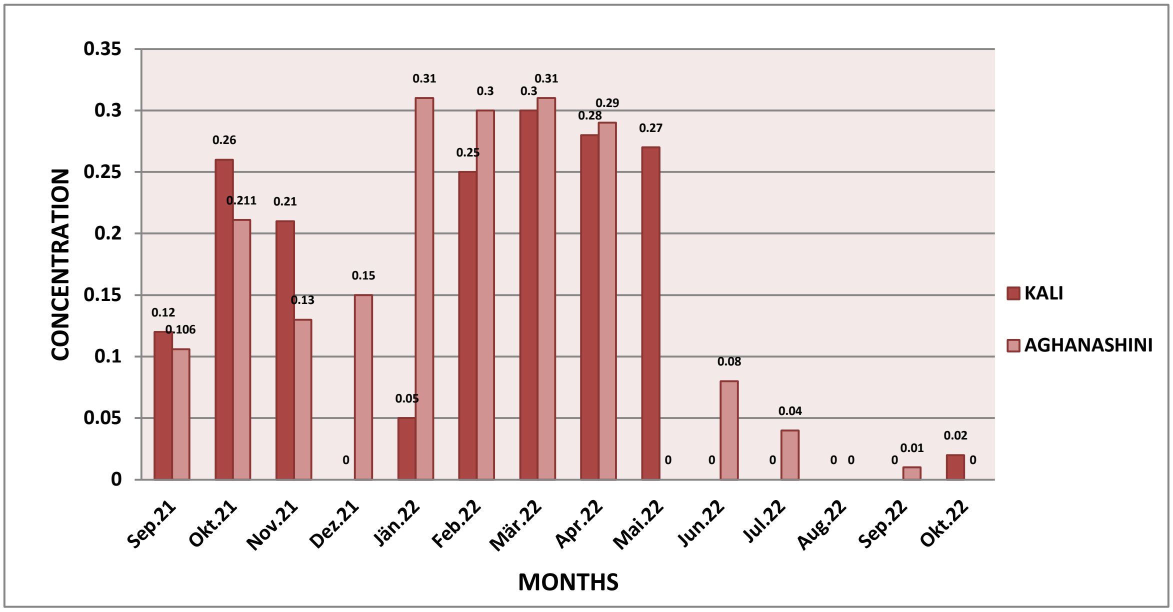

Figure.3. Monthly variation of Cadmium(ppm) concentration in Sediment of Kali & Aghanashini estuary during study period

Chromium (Cr)

The concentration of Chromium in *M.meretrix* of Kali estuary ranged between 4.36 ppm to 79.34 ppm. The highest concentration of Cr 79.34 ppm was observed in September 2021 followed by 64.21ppm in October 2022 and 14.37 ppm in November 2021. Whereas, the lowest concentration of 4.36 ppm was observed in March 2022 in *M.meretrix* of Kali estuary (Fig.4). The permissible limit of Chromium in sea foods is 12.00 ppm, observed values were much higher than the limits.

The concentration of Chromium in *M.meretrix* of Aghanashini estuary ranged between 5.30 ppm to 103.10 ppm. The highest concentration of 103.10 ppm observed in October 2021 followed by 15.18 ppm in June 2022 and 11.02 ppm in December 2021. Whereas, the lowest concentration of 5.30 ppm was observed in January 2022 in studied bivalvesof Aghanashini estuary (Fig.4).

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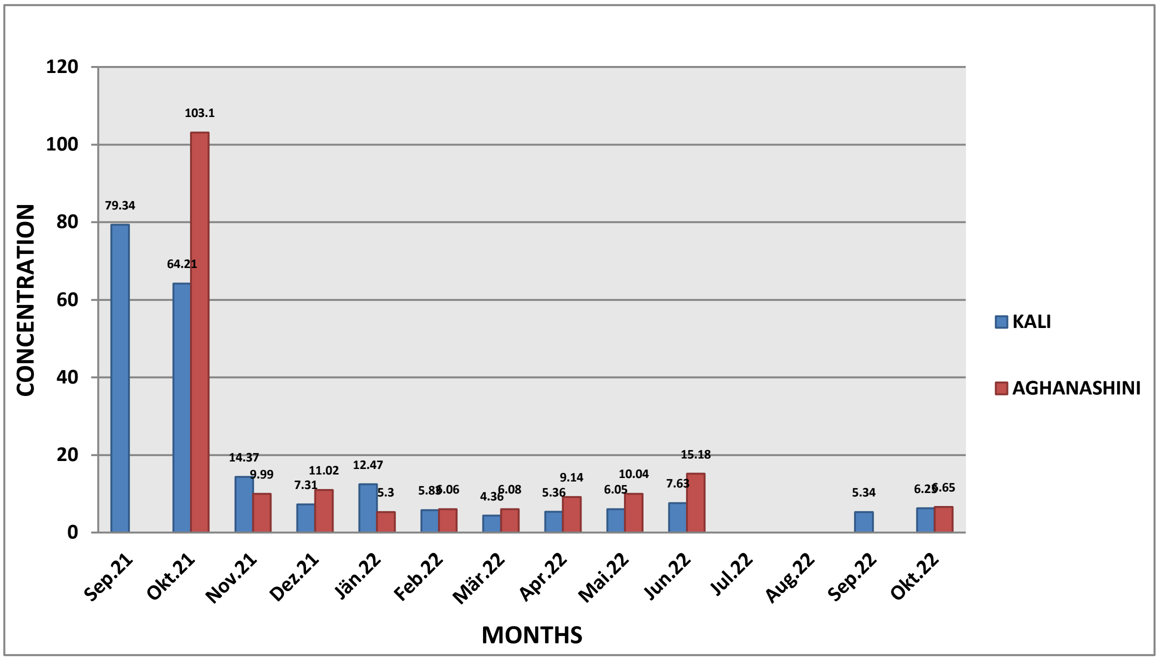

Figure.4. Monthly variation of Chromium(ppm) concentration in *M.meretrix* of Kali & Aghanashini estuary during study period.

The concentration of Chromium in Sediment of Kali estuary ranged between 17.70 ppm to 94.70 ppm. The highest concentration of 94.70 ppm observed in September 2021 followed by 91.33 in May 2022 and 84.20 ppm in October 2021. Whereas, the lowest concentration of 17.70 ppm was observed in June 2022 in the sediment of Kali estuary (Fig.5).

The concentration of Chromium in Sediment of Aghanashini estuary ranged between 93.38 ppm to 172.41 ppm. The highest concentration of 172.41 ppm was observed in February 2022 followed by 148.26 ppm in December 2021 and 147.70 ppm in January 2022. Whereas, the lowest concentration of 93.38 ppm was observed in May 2022 in the sediment of Aghanashini estuary (Fig.5).

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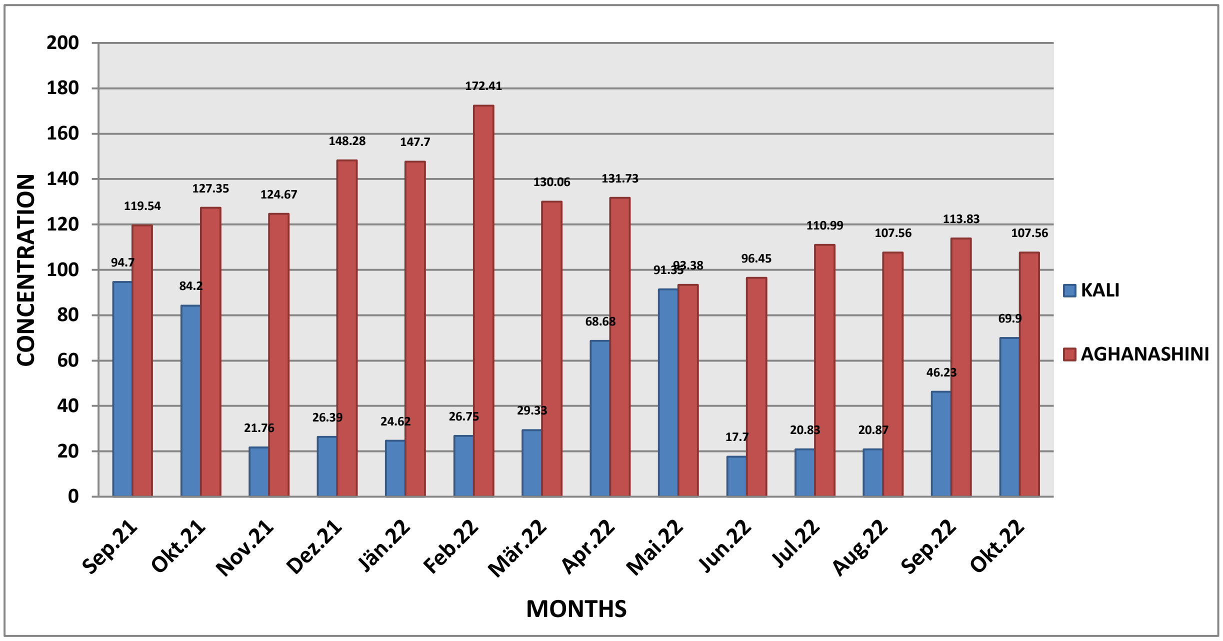

Figure.5. Monthly variation of Chromium(ppm) concentration in Sediment of Kali & Aghanashini estuary during study period

Nickel (Ni)

The concentration of Nickel in *M.meretrix* of Kali estuary ranged between 1.75 ppm to 20.84 ppm. The maximum concentration of 20.84 ppm is noticed in October 2021 followed by 20.35 ppm in September 2021 and 16.32 ppm in November 2021.Whereas, the least concentration of 1.75 ppm was observed in May 2022 in studiedbivalves of of Kali estuary (Fig.6).

The concentration of Nickel in *M.meretrix* of Aghanashini estuary ranged between 5.41 ppm to 12.30 ppm. The maximum concentration of 12.30 ppm found in October 2021 followed by 11.49 ppm in June 2022 and 10.46 ppm in October 2022.Whereas, the least concentration of 5.41 ppm was observed in November 2021 in the *M.meretrix* of Aghanashini estuary (Fig.6).

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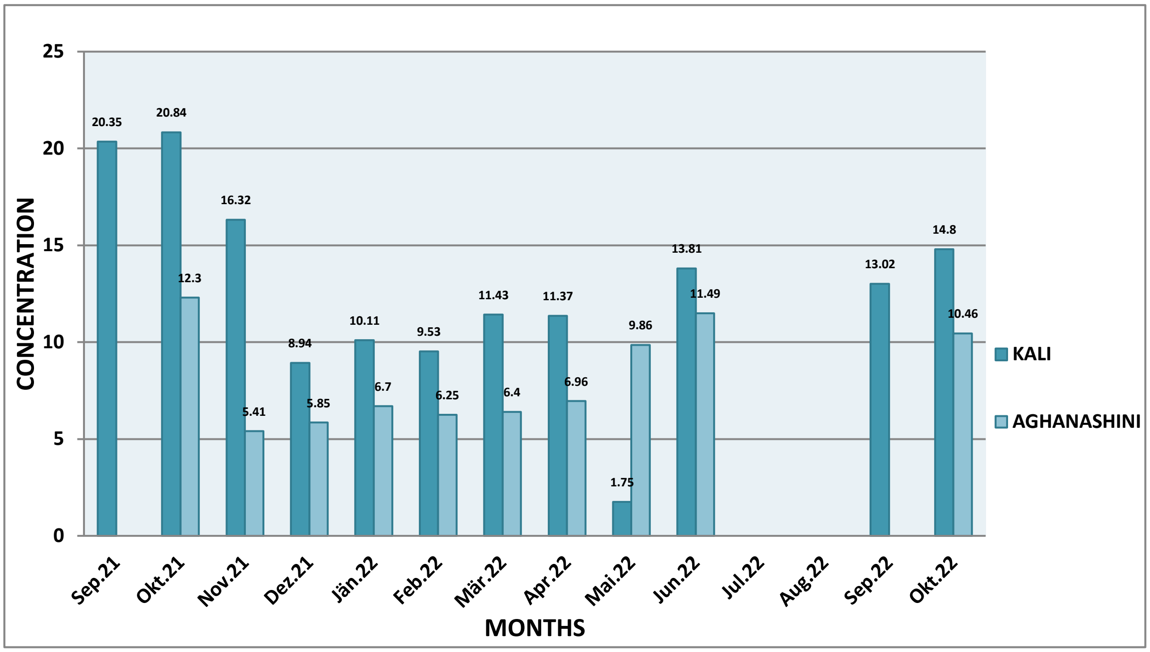

Figure.6. Monthly variation of Nickel(ppm) concentration in *M.meretrix* of Kali & Aghanashini estuary during study period

The concentration of Nickel in Sediment of Kali estuary ranged between 5.34 ppm to 26.93 ppm. The maximum concentration of 26.93 ppm observed in October 2021 followed by 23.70 ppm in May 2022 and 18.44ppm in November 2021.Whereas, the least concentration of 5.34 ppm was observed in June 2022 in the Sediment of Kali estuary (Fig.7). The observed values are much higher than permissible limits (0.5 to 0.6 ppm) with reference to Nickel.

The concentration of Nickel in Sediment of Aghanashini estuary ranged between 18.44 ppm to 40.20 ppm. The maximum concentration of 40.20 ppm observed in October 2021 followed by 33.93 ppm in January 2022 and 33.71 ppm in April 2022.Whereas, the least concentration of 18.44 ppm was observed in November 2021 in the Sediment of Aghanashini estuary (Fig.7).

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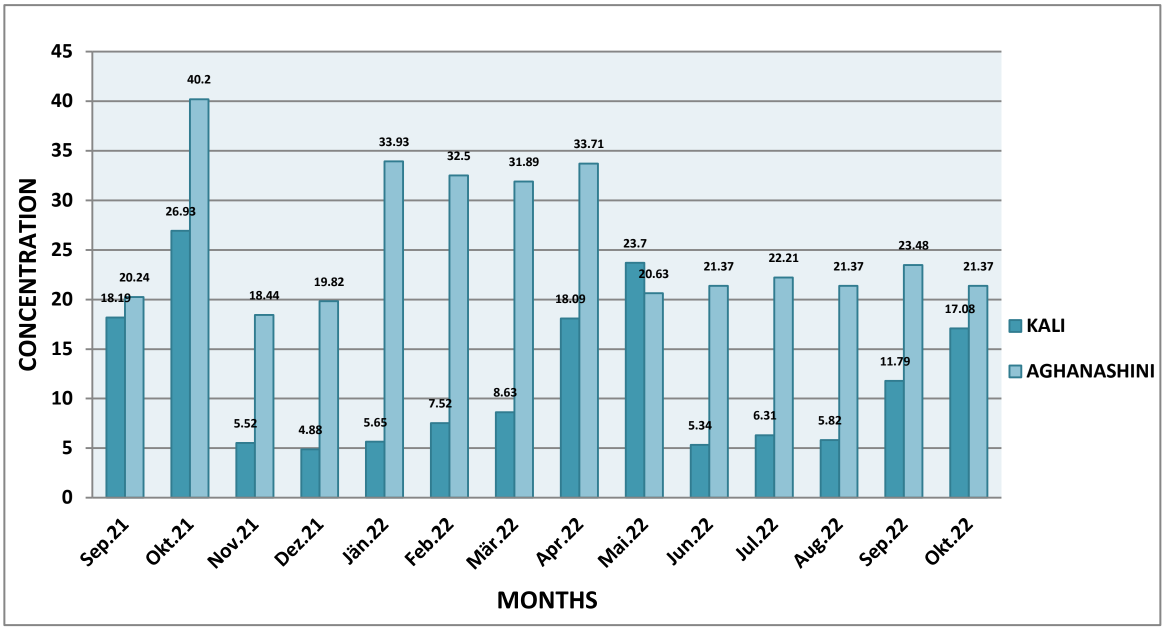

Figure.7. Monthly variation of Nickel(ppm) concentration in Sediment of Kali & Aghanashini estuary during study period

Zinc (Zn)

The concentration of Zinc in *M.meretrix* of Kali estuary ranged between 65.82 ppm to 110.90 ppm. The maximum concentration of 110.90 ppm observed in September 2021 followed by 107.98 ppm in June 2022 and 102.48 ppm in November 2021.Whereas, the least concentration of 65.82 ppm was observed in May 2022 in bivalves of Kali estuary (Fig.8). Reported values of Zinc are much higher in range than permissible limits (40.00ppm)

The concentration of Zinc in *M.meretrix* of Aghanashini estuary ranged between 48.71 ppm to 83.20 ppm. The maximum concentration of 83.20 ppm was found in October 2022 followed by 82.11 ppm in June 2022 and 80.01 ppm in October 2021.Whereas, the least concentration of 48.71 ppm was observed in November 2021 in the *M.meretrix* of Aghanashini estuary (Fig.8).

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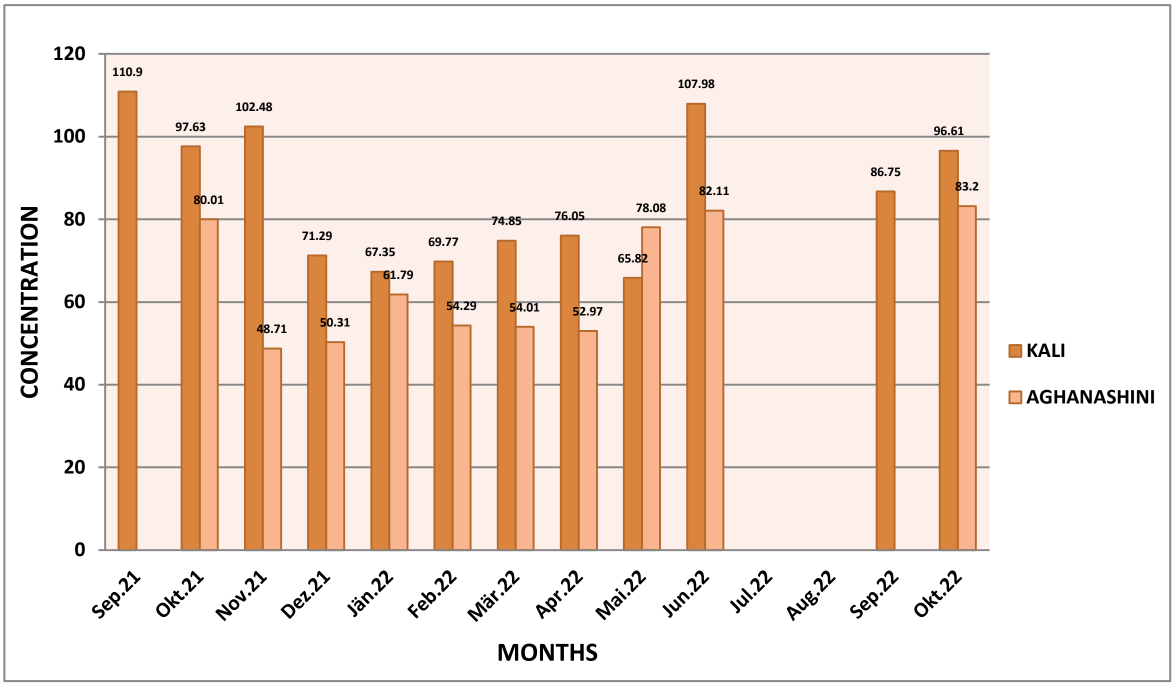

Figure.8. Monthly variation of Zinc(ppm) concentration in *M.meretrix* of Kali & Aghanashini estuary during study period

The concentration of Zinc in Sediment of Kali estuary ranged between 5.58 ppm to 26.03 ppm. The maximum concentration of Zn was observed 26.03 ppm in October 2021 followed by 21.55 ppm in May 2022 and 17.00 ppm in April 2022.Whereas, the leastconcentration of Zn 5.58 ppm was observed in June 2022 in the Sedimentof Kali estuary (Fig.9).

The concentration of Zinc in Sediment of Aghanashini estuary ranged between 1.03 ppm to 46.35 ppm. The maximum concentration of 46.35 ppm was reported in October 2021 followed by 29.26 ppm in April 2022 and 28.83 ppm in March 2022.Whereas, the least concentration of 1.03 ppm was observed in July 2022 in the Sediment of Aghanashini estuary (Fig.9)

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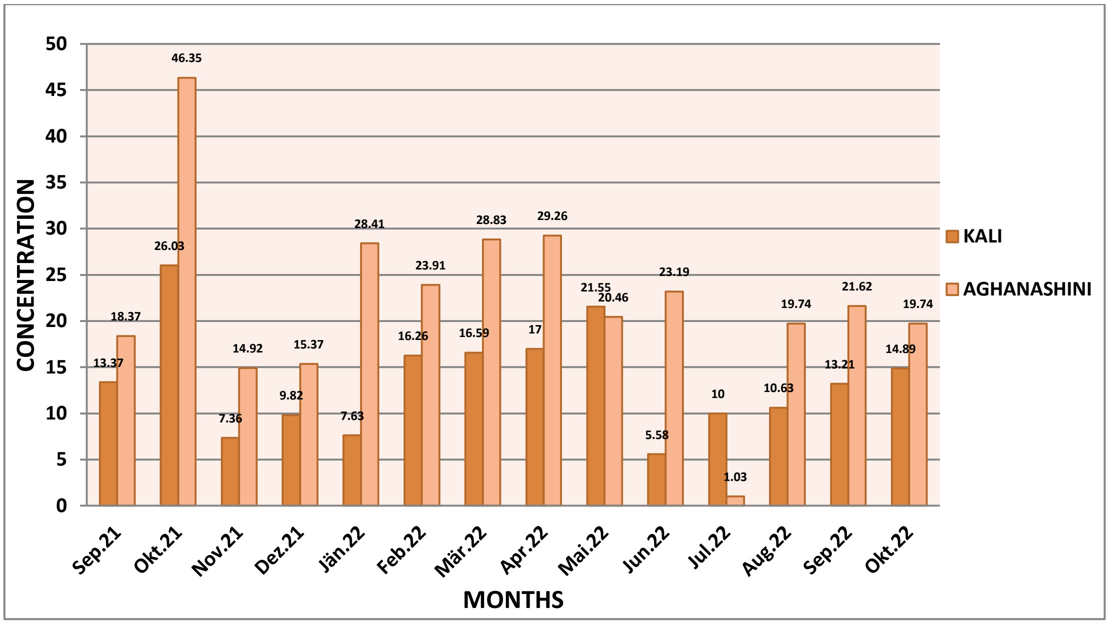

Figure.9. Monthly variation of Zinc(ppm) concentration in Sediment of Kali & Aghanashini estuary during study period

Arsenic (As)

The concentration of Arsenic in *M.meretrix* of Kali estuary ranged between 1.03 ppm to 6.10 ppm. The maximum concentration of 6.10 ppm was observed in February 2022 followed by 5.67 ppm in September 2022 and 4.89 ppm in October 2022.Whereas, the least concentration of 1.03 ppm was observed in November 2021 in the *M.meretrix* of Kali estuary (Fig.10). Arsenic was observed very much below the permissible limits 86.00 ppm.

The concentration of Arsenic in *M.meretrix* of Aghanashini estuary ranged between 0.96 ppm to 7.61 ppm. The maximum concentration of As was observed 7.61 ppm in December 2021 followed by 7.15 ppm in May 2022 and 5.76 ppm in June 2022.Whereas, the least concentration of 0.96 ppm was observed in October 2021 in studied bivalves of Aghanashini estuary (Fig.10).

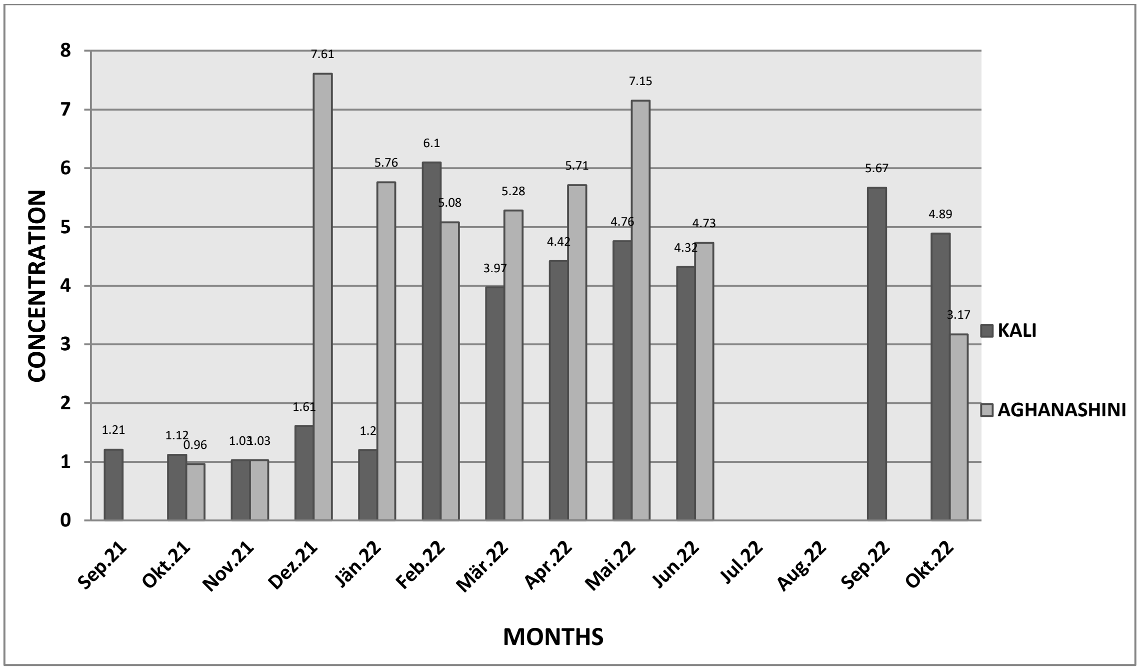

Figure.10. Monthly variation of Arsenic(ppm) concentration in *M.meretrix* of Kali & Aghanashini estuary during study period

The concentration of Arsenic in Sediment of Kali estuary ranged between 1.11 ppm to 6.85 ppm. The maximum concentration of 6.85 ppm was found in September 2021 followed by 6.37 ppm in October 2022 and 5.02 ppm in October 2021.Whereas, the least concentration of 1.11 ppm was observed in March 2022 in the Sediment of Kali estuary (Fig.11).

The concentration of Arsenic in Sediment of Aghanashini estuary ranged between 3.86 ppm to 10.80 ppm. The maximum concentration of 10.8 ppm noticed in February 2022 followed by 9.68 ppm in October 2021 and 9.01 ppm in March 2022.Whereas, the least concentration of 3.86 ppm was observed in September 2021 in the Sediment of Aghanashini estuary (Fig.11).

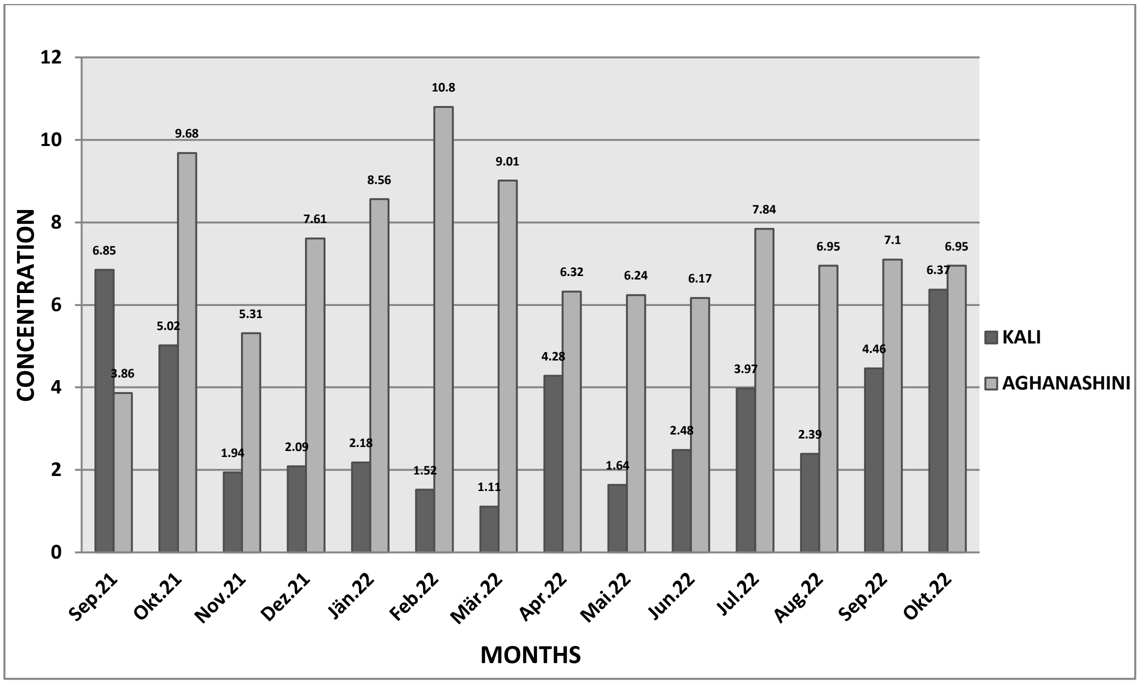

Figure.11. Monthly variation of Zinc(ppm) concentration in Sediment of Kali & Aghanashini estuary during study period

Conclusion

From the time immemorial fish and shell fishes are main sources of protein for majority of coastal population of Uttara Kannada. Heavy metals are becoming one of most serious environmental problems due to their adverse effect on human health. Aquatic organisms can accumulate heavy metals in body tissues and these metals undergo biotransformation in the body and induce mutagenic changes. Consumption of such heavy metal contaminated fishes and shell fishes has lead to health hazards. *Meretrix meretrix* is one of commercially important edible bivalve of this region. In order to find out accumulation of certain selected heavy metals a study was carried out. In the present investigation highest concentration of Chromium 103.10 ppm at Aghanashini and 79.34 ppm at Kali was observed, which are much higher than permissible limits (12 ppm) as per Indian standards. Permissible limit of Zinc is 40 ppm, whereas higher concentration of 110.90 ppm at Kali and 83.20 ppm of Zinc at Aghanashini was observed. Nickel 20.84 ppm at Kali and 12.30 ppm at Aghanashini observed which is higher than permissible limit (0.5 to 0.6 ppm). Whereas,2.53 ppm of Cadmium was observed in Kali estuary which was slightly higher than permissible limit (2.0 ppm). Lower concentration of 7.61 ppm of Arsenic was observed at Aghanashini which was in low concentration than permissible limit (86.0 ppm). The higher bioaccumulation of Cadmium and Zinc was observed in *M.meretrix* of both the estuaries, since these two metals were observed in low concentrations in sediment than that of other heavy metals. From above findings it is concluded that*Meretrix meretrix*species of these two estuaries are not safe for consumption with reference to Chromium, Zinc and Nickel.

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