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Seasonal variation of heavy metal concentration in *Labeo rohita* and *Edaphodon kawai* fishes of River Yamuna, Allahabad, Utter Pradesh

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Abstract: *Seasonal variations in concentration of toxic heavy metals such as lead, copper, and arsenic was monitored during the year 2010 and 2011. The fish samples collected in summer, monsoon and winter seasons were analyzed using atomic absorption spectrophotometer. The results obtained are presented and compared with the permissible limit as declared by WHO.*
Keywords: *WHO, heavy metals, permissible limit.*

I. Introduction

Aquatic foods have essential amino acids, fatty acids, protein, carbohydrates, vitamins and minerals. Among sea foods, fish are commonly consumed and, hence, are a connecting link for the transfer of toxic heavy metals in human beings. Heavy metals have the tendency to accumulate in various organs of marine organisms, especially fish, which in turn may enter into the human metabolism through consumption causing serious health hazards. Fishes are major part of the human diet and it is, therefore, not surprising that numerous studies have been carried out on metal pollution in different species of edible fish. Predominantly, fish toxicological and environmental studies have prompted interest in the determination of toxic element contamination in the same.

Heavy metal is one of major hazardous components discharged from industries and agriculture. It cannot be degraded or destroyed easily. They are accumulated in water, sediment and living organisms. Heavy metals are taken up and subsequently accumulated by organisms through food web and food chain. Human beings are normally at the top of food chain and accumulate all sorts of heavy metals via food and water. As trace elements, some heavy metals are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning.

Heavy metals contaminated with input water can be accumulated and flowed through the food chain and food web in the River Yamuna. *Labeo rohita* and *Edaphodon kawai* are omnivorous fishes but the major feeds are various types of plant in the pond. The amount of heavy metals accumulated in Labeo rohita and Edaphodon kawai will be very useful information for health concerns of most peoples. Ingestion of contaminated fish could result in metal accumulation in human and lead to adverse health effect. The distribution of heavy metals in water, sediment and fish can be very useful for water management purpose.

The fish has occupied a significant place in the human dietary system as they are one of the good sources of protein. Worldwide, people obtain about 25% of their animal protein from fish and shellfish **(Bahnasawy et al., 2009).** Worldwide, people obtain about 75% (105.6 million tons) of estimated world fish production was used for direct human consumption **(FAO, 2006)**. It has been predicted that fish consumption in developing countries will increase by 57 percent, from 62.7 million tons in 1997 to 98.6 million in 2020 **(Retnam et al.,2010)** .

The real importance of fish in human diet is not only in its content of high-quality protein, but also to the two kinds of Omega-3 polyunsaturated fatty acids: Eicosapentenoic acid (EPA) and docosahexenoic acid (DHA). Omega-3 (n-3) fatty acids are very important for normal growth where the ported y reduce cholesterol levels and the incidence of heart disease, stroke, and preterm delivery. Fish also contain vitamins and minerals which play essential role in human health **(Burger et al., 2005)**.

Since fish represent a part of human diet, the intake of polluted fish can be the main route of exposure to heavy metals. It proves that polluted fish could be a dangerous dietary source of certain toxic heavy metals **(Bogut, 1997).**

Heavy metals cannot be degraded further. They tend to accumulate in the body. They can be stored in soft and hard tissues of human beings such as liver, muscles and bone. The heavy metals are now considered the most dangerous category of pollutants in the sea or other bodies **(Castro-Gonzeza et al., 2008).**

The origin of Minamata disease in the vicinity of the Japanese fishing harbor of Minamata in 1952 and Ita-Ita Disease in Fugawa, Japan in 1955 **(Hassaan et al., 2007)** are examples of environmental pollution due to contaminated fish.

II. Material and Methods

Sample collection

The sampling process was performed with the help of expert fish catcher of Allahabad Yamuna River. The specimens were placed immediately in poly-ethylene bags, put into isolated container of polystyrene icebox and, then, brought to the Toxicology laboratory at the Department of Forensic Science, Sam Higginbottom Institute of Agriculture, Technology & Sciences, Allahabad.

Types and origin of Fish

The fish species : *Labio rohita, Edaphodon kawai* was bought from local fisherman who caught them from the river Yamuna at different studied sites. These fish species were common in river Yamuna and most eatable by the local peoples.

Fish handling and preservation

After taking the measurements and identification, fish were washed with deionized water, sealed in polyethylene bags and kept in a freezer/ Icebox until chemical analysis.

Reagents and Chemicals

All the chemicals and reagents used were of analytical or equivalent grade and obtained from Merck (Germany). The glassware used Borosil and Polylab manufactured company. De-ionized water was used to prepare all aqueous solutions. All plastic and glassware used were rinsed and soaked in 10% (v/v) HNO_3 overnight. They were rinsed with de-ionized water and dried prior using. All acids such as Nitric (HNO_3), Sulfuric ($H2SO_4$), Hydrochloric (HCl) and Perchloric acid ($HClO_4$) and oxidants Hydrogen peroxide (H_2O_2) were of standard pure quality.

Experimental Methods

Atomic Absorption Spectrometer

The analytical technique used to determine heavy metal levels in all samples was Spectra AA 220G Atomic Absorption Spectroscopy (Varian GTA110). It is a standard laboratory analytical tool for metal analysis and is based on the absorption of electromagnetic radiation by atoms. The absorption wavelengths and detections limits for the heavy metals were 217.0 nm and 0.001ppm respectively.

Sample Preparation

Digestion of Fish samples

The present study followed wet digestion process with different concentrations and volume of acids. Before analysis, the fish were thawed and dissected. The visceral tissues of each fish were taken out and homogenized. About 4 grams of the homogenized visceral tissues of each specimen were taken and placed in porcelain basin and removed its moistures by heating over water bath, for 15 min. After completion of process, kept all visceral tissues in conical flask and added digestion mixture (conc. H_2SO_4, Conc. HNO_3), red fumes appear, kept the sample on sand bath for digestion, when all the fumes were disappeared and liquid became clear, then remove it from water bath and kept it to cool, After cooling, the samples were filtered through Whatman filter paper no. 42. The digested portion was diluted to a final volume of 50 ml using de-ionized water. Blank reagents without fish samples were also digested using the same method **(Manutsewee et al., 2007)**.

The ratio of chemical/ digestion mixture was differed with the respect of weight of fish.

III. Result & discussion

Heavy metal concentration in fish

1.1 Concentration of copper in fish

The concentration of Copper in Fish samples of both species at four different Sites of Yamuna River during Year 2010 and 2011 in season's summer, monsoon, and winter seasons was detected and the results are discussed below.

The detected Copper in Fish samples of both species in the summer season for all samples is given. The average values of Copper for *Labeo rohita* vary between 3.530-3.569 mg/kg at Site 1, 2.167-2.594 mg/kg at Site 2, 2.120-2.842 mg/kg at Site 3, and 3.169-3.699 mg/kg at Site 4 in Year 2010 and 2011 Whereas for *Edaphodon kawai* concentration varied between 1.2.117-2.862 mg/kg at Site 1, 2.576-2.722 mg/kg at Site 2, 2.778-2.856

mg/kg at Site 3, and 2.5-3.264 mg/kg at Site 4 in Year 2010 and 2011, which are graphically represented in Figure 1(a).

The highest average value of Cu concentration in *Labeo rohita* was 3.699 mg/kg in Year 2010 at Site 4 whereas in *Edaphodon kawai* was 3.264 mg/kg in Year 2010 at Site 4 which showed a constant increase in Copper concentration which was very toxic to human as well as other living beings.

The detected Copper in Fish samples of both species in the Monsoon season for all samples in both years are given.

The average values of Copper for *Labeo rohita* varied between 2.037-2.642 mg/kg at Site 1, 1.919-2.295 mg/kg at Site 2, 1.521-2.312 mg/kg at Site 3, and 1.737-1.919 mg/kg at Site 4 in Year 2010 and 2011 Whereas for *Edaphodon kawai* concentration varied between 1.311-1.754 mg/kg at Site 1, 0.873-1.787 mg/kg at Site 2, 1.311-1.529 mg/kg at Site 3, and 1.493-2.213 mg/kg at Site 4 in Year 2010 and 2011 which are graphically represented in Figure 1(b).

The highest average value of Cu concentration in *Labeo rohita* 2.642 mg/kg in Year 2010 at Site 1 whereas in *Edaphodon kawai* was 2.313 mg/kg in Year 2010 at Site 4 which showed a constant increase in Copper concentration which was very toxic to human consumption as well as other living beings.

The detected Copper in Fish samples of both species in the winter season for all samples is given. The average values of Copper for *Labeo rohita* varied between 2.707-3.116 mg/kg at Site 1, 2.789-3.149 mg/kg at Site 2, 2.593-2.717 mg/kg at Site 3,and 2.285-2.813 mg/kg at Site 4 in Year 2010 and 2011 Whereas for *Edaphodon kawai* concentration varied between 1.815-2.778 mg/kg. at Site 1, 1.5-2.757 mg/kg at Site 2,1.85-2.09 mg/kg at Site 3, and 2.19-3.714 mg/kg at Site 4 in Year 2010 and 2011 which is graphically represented in Figure 1(c).

The highest average value of Cu concentration in *Labeo rohita* was 3.149 mg/kg in Year 2010 at Site 2 whereas in *Edaphodon kawai* was 3.714 mg/kg in Year 2011 at Site 4 which showed a constant increase in Copper concentration which is very toxic to human as well as other living beings.

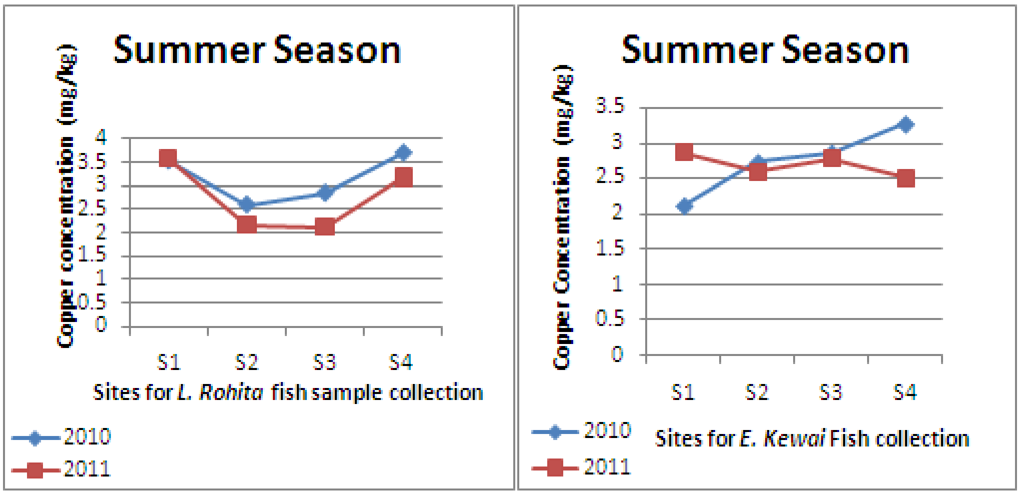

Fig 1 (a): Copper concentration in *Labeo rohita* Fish species in Summer Season during 2010 and 2011 at four different Sites.

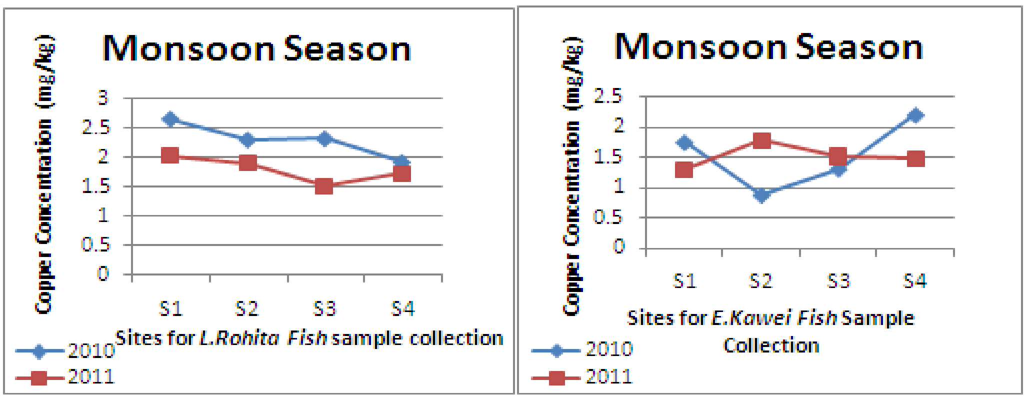

Fig 1(b): Copper concentration *in Labeo rohita* Fish species in Monsoon Season during 2010 and 2011 at four different Sites.

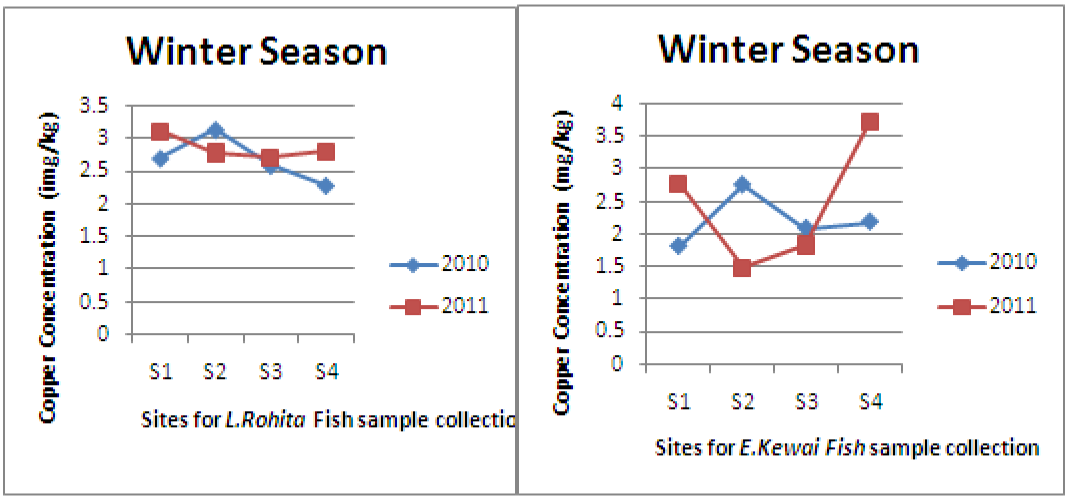

Fig 1(c): Copper concentration in *Edaphodon kawai* Fish species in Winter Season during 2010 and 2011 at four different Sites.

The WHO guidelines for prescribed maximum permissible limit of Copper in Fish are 3 mg/kg. The average concentration of Copper throughout all the three seasons in Fish was 2.642 mg/kg (at Site 1, 2010), 3.699 mg/kg (at Site 4, 2010) for Labeo rohita and from 2.313 mg/kg (at Site 4,2010) and 3.714 mg/kg (at Site 4,2011) for *Edaphodon kawai*.

The Copper detected in Year 2010 was below the permissible limit in *Labeo rohita* Fish at Site 1 and *Edaphodon kawai* at Site 4, whereas crosses the limit at Site 4 for Labeo rohita in Year 2010 and for Edaphodon kawai Fish in Year 2011.The higher levels of Copper in Fish resulted in toxic effects on human being after digestion. As higher range of Copper suggested adverse effects on consumption by human being.

Besides the higher concentration of Copper were detected at Site 4 in both species of Fishes which suggested that the Fish collected Site 4 Gau Ghat was more polluted than the other Ghats studied when compared.

The concentration of Copper obtained in Fish samples of both species were statistically studied using Analysis of Variance- Four Way Classification during 2010 and 2011 and study seasons i.e. Summer, Monsoon and Winter the results and found statistically significant ($p<0.05$) due to season, Fish species and due to sample whereas the data were non significant due to Sites.

1.2 Lead Concentration

The concentration of Lead in Fish samples of both species at all four different Sites of Yamuna River during Year 2010 and 2011 in three seasons Summer, Monsoon, and Winter were detected and the results are discussed below.

The detected Lead in Fish samples of both species in the Summer season for all samples is given. The average values of Lead for *Labeo rohita* vary from 0.814 to 1.527 mg/l at Site 1, from 1.112 to 1.861 mg/l at Site 2, from 0.934 to 2.165 mg/l at Site 3, from 2.227 to 2.301 mg/l at Site 4 in Year 2010 and Whereas in *Edaphodon kawai* concentration varied from1.246 to 1.971 mg/l at Site 1, from1.525 to 2.162 mg/l at Site 2, from1.887 to 2.778 mg/l at Site 3, from 1.292 to 2.059 mg/l at Site 4 in Year 2010 and 2011, which are graphically represented in Figure 2(a).The highest average value of Pb concentration in *Labeo rohita* was 2.301 mg/l in Year 2010 at Site 4 whereas in *Edaphodon kawai* was 2.778 mg/l in Year 2011 at Site 3 which showed that there was a constant increase in Lead concentration which was very toxic to human consumption as well as other living beings in food chain.

The detected Lead in Fish samples of both species in the Monsoon season for all samples are given in Table no 4.21 and 4.22. The average values of Lead for *Labeo rohita* vary from 0.429 to 0.915 mg/l at Site 1, from0.498 to 1.880 mg/l at Site 2, from1.150 to 1.355 mg/l at Site 3, from 1.182 to 1.621 mg/l at Site 4 in Year 2010 and 2011 Whereas for *Edaphodon kawai* concentration varied from 0.505 to 1.216 mg/kg at Site 1, from 0.730 to 1.595 mg/kg at Site 2, from 0.925 to 1.025 mg/kg at Site 3, from 0.702 to 1.535 mg/kg at Site 4 in Year 2010 and 2011, which are graphically represented in Figure 2(b). The highest average value of Pb concentration in Labeo rohita was 1.880 mg/l in Year 2011 at Site 2 whereas in Edaphodon kawai was 1.595 mg/kg in Year 2011 at Site 2, which showed a constant increase in Lead concentration which is very toxic to human as well as other living beings.

The detected Lead in Fish samples of both species in the Winter season for all samples is given.

The average values of Lead for *Labeo rohita* varied from 0.922 to 2.238 mg/kg at Site 1, from 0.438 to 2.789 mg/kg at Site 2, from 1.0123 to 1.139 mg/kg at Site 3, from 1.353 to 2.211 mg/kg at Site 4 in Year 2010 and 2011 Whereas for *Edaphodon kawai* concentration varied from 0.805 to 1.273 mg/kg at Site 1, from 0.521 to 1.641 mg/kg at Site 2, from1.3 to 1.415 mg/kg at Site 3, from 1.129 to 1.927 mg/kg at Site 4 in Year 2010 and 2011 which is represented graphically in Figure 2(c).

The highest value of Pb concentration in *Labeo rohita* was 2.789 mg/kg in Year 2011 at Site 2, whereas in *Edaphodon kawai* was 1.927 mg/kg in Year 2011 at Site 4 which showed a constant increase in Lead concentration which is very toxic to human as well as other living beings.

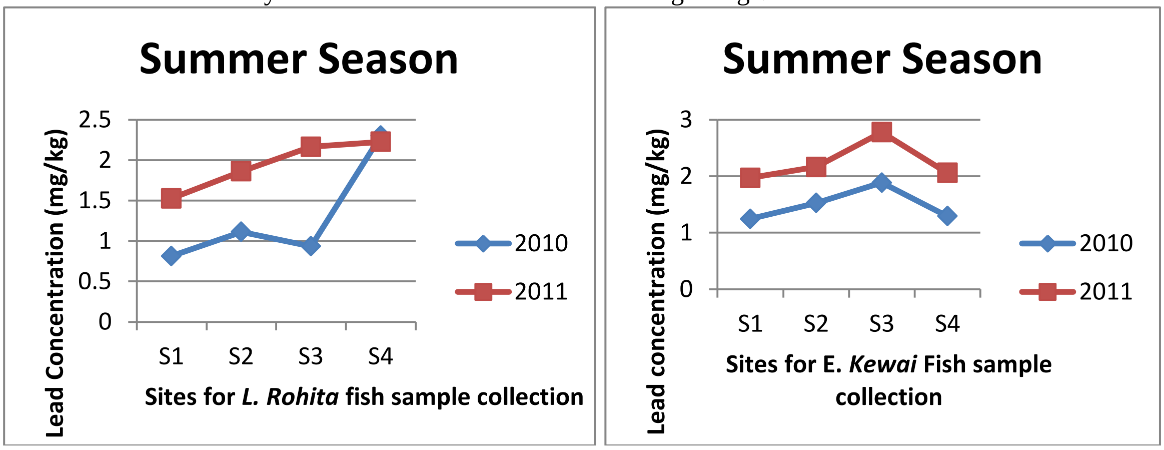

Fig 2(a): Lead concentration in *Edaphodon kawai* Fish species in Summer Season during 2010 and 2011 at four different Sites.

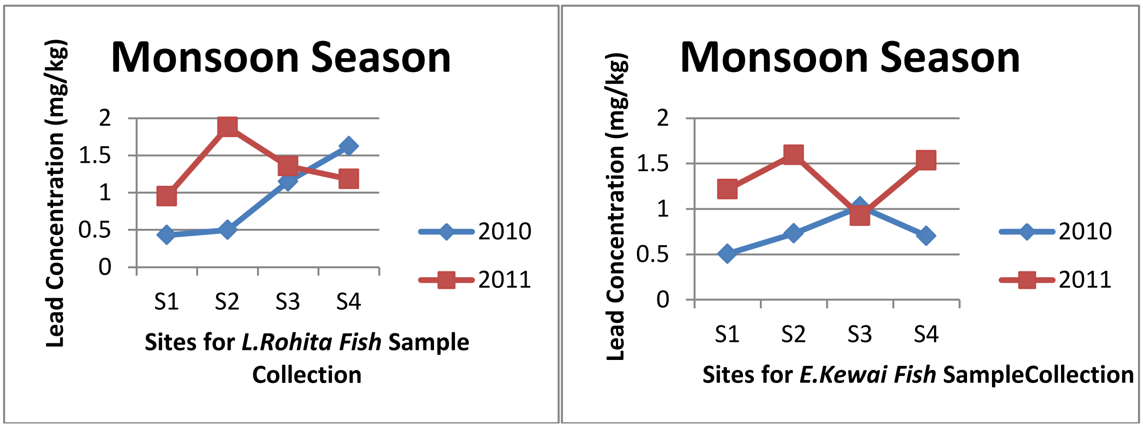

Fig 2(b): Lead concentration in *Edaphodon kawai* Fish species in Monsoon Season during 2010 and 2011 at four different Sites.

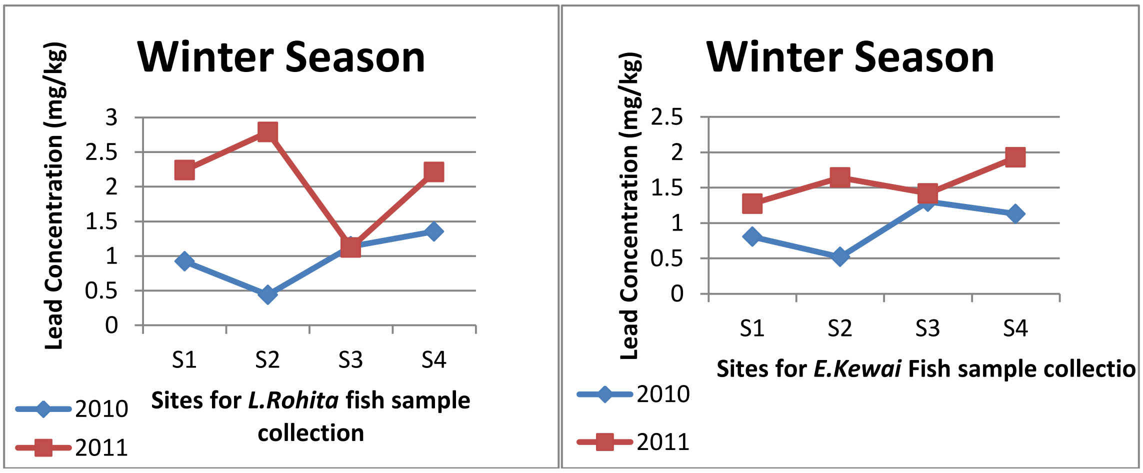

Fig 2(c): Lead concentration in *Edaphodon kawai* Fish species in Winter Season during 2010 and 2011 at four different Sites.

The W.H.O. guidelines for maximum permissible limit of Lead in Fish are 2 mg/kg. The average concentration of Lead throughout all the three seasons in Fish ranged from 1.880 mg/kg to 2.789 at Site 2 in Year 2011 for *Labeo rohita* and from 1.595 mg/kg (at Site 4) to 2.778 mg/kg (at Site 3) in Year 2011for *Edaphodon kawai*.

The Lead detected was above the permissible limit in *Labeo rohita* Fish at Site 2 in Year 2011 for *Labeo rohita* and for *Edaphodon kawai* at Site 3 in Year 2011.The higher levels of Lead in Fish showed probable in toxic effects on human being after ingestion. As higher range of Lead suggested adverse effects on consumption.

Besides the higher concentration of Lead were detected at Site 2 in *Labeo rohita* and *Edaphodon kawai* at Site 3 is more polluted than the other Ghats studied

The concentration of Lead obtained in Fish samples of both species were studied statistically using Analysis of Variance- Four Way Classification during 2010 and 2011 and study seasons i.e. Summer, Monsoon and Winter the results were found statistically significant ($p<0.05$) due to season, Fish species and due to Sites whereas the data found were non significant due to Sample.

1.3 Arsenic Concentration

The concentration of Arsenic in the Fish samples of both species at all four different Sites of Yamuna River during Year 2010 and 2011 in Summer, Monsoon, and Winter seasons were detected and the results are discussed below. The detectable Arsenic in Fish samples of both species in the Summer season for all samples is given. The average values of Arsenic for Labeo rohita vary from 0.0119 to 0.0178 mg/kg at Site 1, from 0.0158 to 0.0302 mg/kg at Site 2, from 0.0257 to 0.0543 mg/kg at Site 3, from 0.0268 to 0.0366 mg/kg at Site 4 in Year 2010 and 2011 whereas for *Edaphodon kawai* concentration varies from 0.0226 to 0.0393 mg/kg at Site 1, from 0.017 to 0.0239 mg/kg at Site 2, from 0.0201 to 0.0261mg/kg at Site 3, from 0.0151 to 0.022 mg/kg at Site 4 in Year 2010 and 2011, which is graphically represented in Figure 3(a). The highest average value of As concentration in Labeo rohita was 0.0543 mg/kg in Year 2010 at Site 3 whereas in Edaphodon kawai was 0.0393 mg/kg in Year 2010 at Site 1 which shows a constant increase in Arsenic concentration which was very toxic to human consumption as well as other living beings.

The detected Arsenic in Fish samples of both species in the Monsoon season for all samples is given. The average values of Arsenic for *Labeo rohita* vary from 0.0059 to 0.0162 mg/kg at Site 1, from 0.0111 to 0.012 mg/kg at Site 2, from 0.0113 to 0.0134 mg/kg at Site 3, from 0.0092 to 0.0095 mg/kg at Site 4 in Year 2010 and 2011 whereas for *Edaphodon kawai* concentration varied from 0.0116 to 0.0157 mg/kg at Site 1, from 0.013 to 0.016 mg/kg at Site 2, from 0.011 to 0.0126 mg/kg at Site 3, from 0.0092 to 0.0112 mg/kg. at Site 4 in Year 2010 and 2011 which is graphically represented in Figure 3(b).The highest average value of As concentration in *Labeo rohita* was 0.0162 mg/kg in Year 2011 at Site 1 whereas in *Edaphodon kawai* was 0.016 mg/kg in Year 2011 at Site 2 which shows a constant increase in Arsenic concentration which was very toxic to human for consumption as well as other living beings.

The detected Arsenic in Fish samples of both species in the Winter season for all samples is given. The average values of Arsenic for *Labeo rohita* varied from 0.0171 to 0.0227 mg/kg at Site 1, from 0.0208 to 0.0229 mg/kg at Site 2, from 0.015 to 0.074 mg/kg at Site 3, from 0.015 to 0.026 mg/kg at Site 4 in Year 2010 and 2011 whereas for *Edaphodon kawai* concentration varied from 0.011 to 0.017 mg/kg at Site 1, from 0.017 to 0.024 mg/kg at Site 2, from0.013 to 0.018 mg/kg at Site 3, from 0.015 to 0.018 mg/kg at Site 4 in Year 2010 and 2011 which is graphically represented in Figure 3(c).

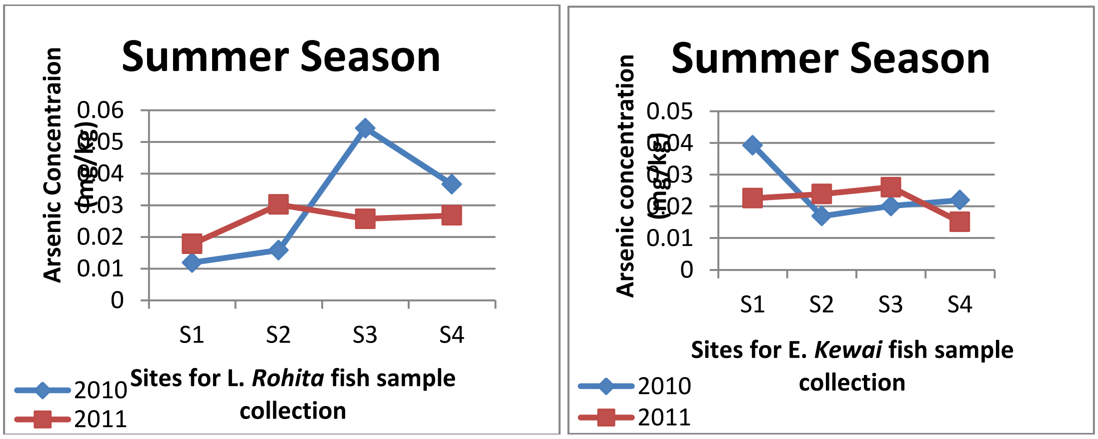

Fig 3(a): Arsenic concentration in *Labeo rohita* Fish species in Summer Season during 2010 and 2011 at four different Sites.

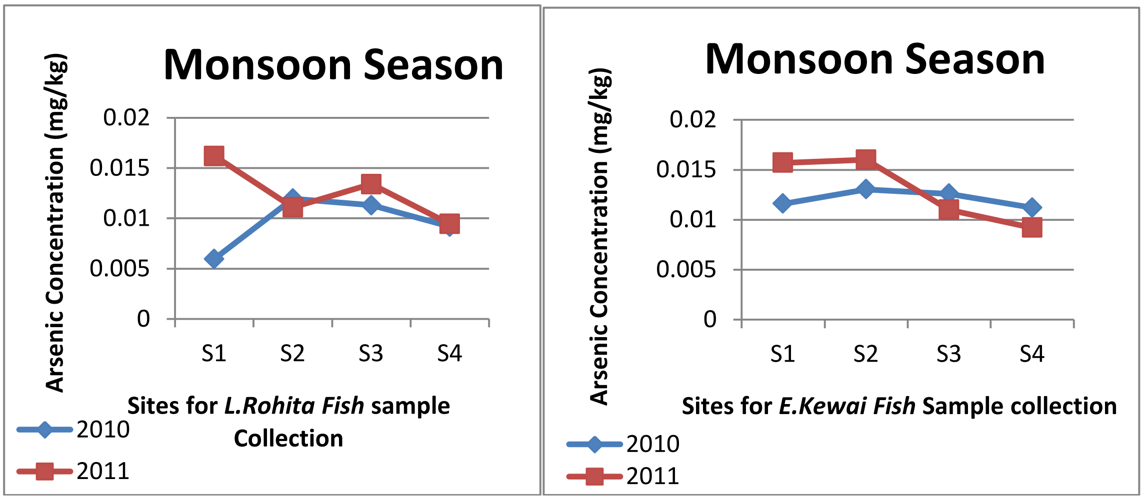

Fig 3(b): Arsenic concentration in *Edaphodon kawai* Fish species in Monsoon Season during 2010 and 2011 at four different Sites

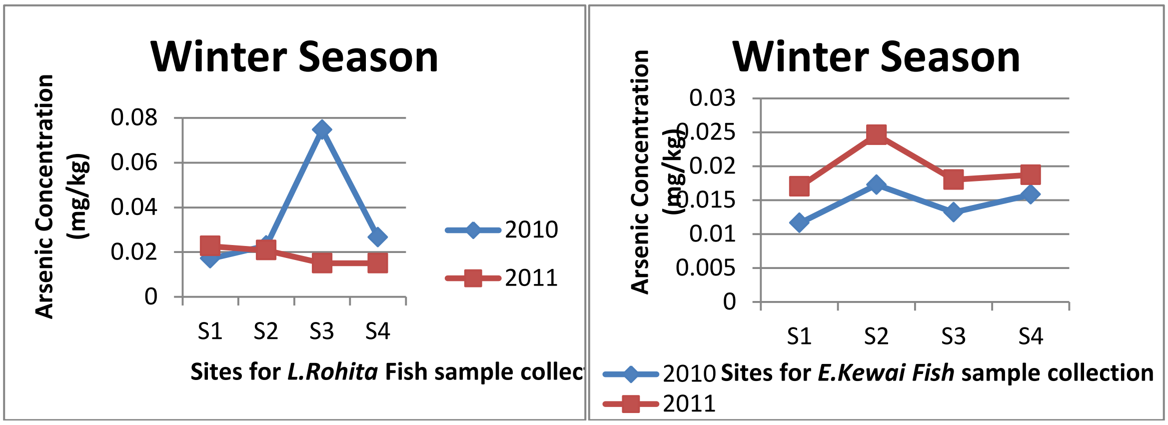

Fig 3(c): Arsenic concentration *in Edaphodon kawai* Fish species in Winter Season during 2010 and 2011 at four different Sites.

The highest average value of As concentration in *Labeo rohita* was 0.074 mg/kg in Year 2010 at Site 3 whereas in *Edaphodon kawai* was 0.024 mg/kg in Year 2011 at Site 2 which shows a constant increase in Arsenic concentration which is very toxic to human as well as other living beings.

The W.H.O. guidelines for maximum permissible limit of Arsenic in Fish is 0.026 mg/kg. The average concentration of Arsenic throughout all the three seasons in Fish ranged from 0.0162 mg/kg (at Site 1, 2011) to 0.074 mg/kg (at Site 3, 2010) for *Labeo rohita* and from 0.016 mg/kg (at Site 2,2011) to 0.0393 mg/kg (at Site 1,2010) for *Edaphodon kawai*.

The Arsenic detected was above the permissible limit in *Labeo rohita* Fish at Site 3 in Year 2010 for Labeo rohita and for *Edaphodon kawai* at Site 1 in Year 2010. The higher levels of Arsenic in Fish was probable toxic effects on human being after ingestion. As higher range of Arsenic suggested adverse effects on consumption.

Besides the higher concentration of Arsenic were detected at Site 3 in *Labeo rohita* and *Edaphodon kawai* at Site 1 is more polluted than the other Ghats studied.

The concentration of Arsenic obtained in Fish samples of both species were statistically studied using Analysis of Variance- Four Way Classification during 2010 and 2011 and study seasons i.e. Summer, Monsoon and Winter the results were found statistically significant ($p<0.05$) due to season and Fish species whereas the data were non significant due to Sites and due to sample.

IV. Conclusion

The present work has been done considering the rising pollution of heavy metals in water bodies. Pollution among water bodies is a major global problem. which contaminates water, sediment and aquatic life such as fish.

The *Labeo rohita* and *Edaphodon kawai* fish samples being most common eatables fishes were collected from the four different Ghats of Yamuna River. Gau Ghat, New Yamuna Bridge Ghat, Balua Ghat, Arail Ghat.

The study was carried out in the all three seasons of summer, monsoon and winter in order to check seasonal variation of heavy metal pollution. Total 20 samples of fish (10 of each species) were analyzed. The three heavy metals lead, copper and arsenic which are considered highly toxic were detected in the samples in the year 2010 and 2011.

Two species of fish '*Labeo rohita* and *Edaphodon kawai*' were examined for Copper, Lead and Arsenic concentration. In Summer, the copper was found more in *Labeo rohita* and *Edaphodon kawai* as 3.699 mg/kg and 3.264 mg/kg in Year 2010 at Site 4 whereas in Monsoon *Labeo rohita* was having 2.642 mg/kg at Site 1 and in *Edaphodon kawai* it was 2.313 mg/kg at Site 4 in Year 2010. In Winter, the copper was found highest in *Labeo rohita* (3.149 mg/kg, Year 2010 at Site 2) and in *Edaphodon kawai* (3.714 mg/kg, Year 2011 at Site 4).

In Summer, the highest average value of Pb in *Labeo rohita* was 2.301 mg/l in Year 2010 at Site 4 and in *Edaphodon kawai* it was 2.778 mg/l in Year 2011 at Site 3. In Monsoon, the lead was found highest in *Labeo rohita* as 1.880 mg/l and in *Edaphodon kawai* it was 1.595 mg/kg, in Year 2011 at Site 2 for both species. In winters the lead was found highest in *Labeo rohita* at Site 2 as 2.789 mg/kg whereas in *Edaphodon kawai* was 1.927 mg/kg at Site 4 in Year 2011.

From the heavy metal concentrations mentioned above we can see that somewhere the concentration is crossing the limits as permissible by the World Health Organization. It suggests a high risk to the health of human being on the consumption of contaminated water and fish **(WHO, 2001).**

Therefore it is recommended that the practice of trace element detection should be continued in order to update whether the heavy metal concentration is above or below the permissible limits and if it is above the limit then precautions must be taken to avoid possible consumption of contaminated eatables. It is also recommended that awareness should be spread among the people regarding the hazards on consumption of polluted water and related eatables. It is also essential that farmers should be educated to reduce such contamination and should be encouraged to use the controlled amount of pesticides, to avoid the leaching of waste water and cultivating in a field far away from industrial area as well as areas prone to contamination **(Abdel-Baki et al. 2011)**.

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