IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS)
e-ISSN:2278-3008, p-ISSN:2319-7676. Volume 12, Issue 4 Ver. VII (Jul – Aug 2017), PP 14-24
www.iosrjournals.org

Seasonal variation of heavy metals in selected stations of Periyar river at Ernakulam district, Kerala, India

Asha Raj Kariyil Rajappan[1,2], Mundanchery Lonan Joseph[1]*.
[1] *Department of Zoology, St. Albert's College, Ernakulam, Kerala, India.*
[2]*Department of Biotechnology, SCMS, Ernakulam, Kerala, India.*
Corresponding Author: Mundanchery Lonan Joseph

***Abstract*:** *Pollution status of heavy metals like nickel, zinc, arsenic and cadmium in water, sediment and the corresponding bioaccumulation in biomass of Anabas testudineus from different stations of periyar river at ernakulam district during three seasons of an year was analysed. Result showed that the concentration of heavy metals was higher in the water, sediment, biomass from station I and II than control station indicating the pollution status of the river system. The metal bioaccumulations in tissues may be related to the influx of metals from the industries on the banks of the River and their increased bioavailability to the fish there. Out of the four selected elements arsenic was not reported (always below detection level) from any of the samples. Heavy metals followed the order Zn > Ni > Cd in all the samples. Concentration was highest in the sediment samples following in the water sample and the least in the biomass with significant positive correlation between them. Seasonal variation followed a trend as premonsoon > postmonsoon > monsoon in majority of cases with exceptions. Liver > gills > muscle was the commonly found trend in bioaccumulation and varied with respect to metal, season and site.*

Keywords: *heavy metal, periyar, Anabas testudineus*

Date of Submission: 23-06-2017 Date of acceptance: 17-08-2017

I. Introduction

Periyar, the longest river of Kerala state. It is the carter of booming city of Kochi, one of the most urbanised and industrialised region of Kerala, it receives both urban and industrial waste in an alarming rate. A variety of xenobiotics and heavy metals have been reported from different regions of Periyar (Stringer et al, 2003) and Eloor industrial area located at the banks are considered as one among the toxic hotspot of global concern. Since heavy metals are non-biodegradable and being bioaccumulated through food chain, the toxicity studies explaining the bioaccumulation trend and the factors affecting its rate in aquatic organisms are relevant as far as the human beings are concerned. The tendency of each of the selected heavy metals to get absorbed and accumulated also varies depending on the organ, season, species and age of fish and bioavailability of heavy metals in the environment. Since the gills of fishes are in direct contact with the polluted environment it can be considered as one among the common route of uptake and accumulation. The heavy metal accumulation tendency of organs dependent on its metabolic activity. Because of high metabolic rate liver is actively engaged in heavy metal accumulation. Muscle as the ultimate sink of bioaccumulation and the most important tissue as far as the food value of the organism is concerned and the heavy metals may undergo high rate of dilution on reaching muscle tissue. The influence of season and the variation in bioavailability of heavy metals on the bioaccumulation rate of heavy metals in the organs are the focus of this investigation.

II. Materials And Methods

The methodology adopted to attain the objective of seasonal variation of heavy metal pollution in water, sediment and biomass from Periyar as follows.

2.1. Study area

A stagnant water body located in an unpolluted area of Cherthala, Alappuzha district of Ketala, India was selected as a reference site (Control station). Based on specific geographical features, water flow regimes and anthropogenic activities, two sampling locations (Station I and Station II) were selected in Periyar River at Ernakulam district of Kerala, India. One of the sampling area flowing through the Eloor industrial Estate (Station I). The other one, Station II is located at Irumbanam. Three separate samples were collected from the two stations.

2.1.1. Station I – Eloor

Station I is a portion of Periyar River passing through the Eloor- Kalamassery, Ernakulam, Kerala, India. The sampling station is 1.5 Km upstream to Eloor ferry (Plate 1). The sampling station is located downstream of industrial belt well known for large- and small- scale industries. The major industries include FACT, TCC, IRE, BZL, etc and are on the banks of the Periyar River (Sobha and Anish, 2003).

2.1.2. Station II- Irumbanam

Station II is located at Irumbanam, Trippunitura, Ernakulam, Kerala, India (Plate 2). It is considered as a site located at chithrapuzha, a tributary of Periyar River. Factory out lets of BPCL, FACT, IOCL etc were near to this site.

2.2. Study period

The study period was divided into 3 seasons: Premonsoon (February-May), Monsoon (south west monsoon June-September) and Post monsoon (October-January). Water, sediment and fish samples were collected at 3 seasons during the last week of the last month of each season.

2.3. Experimental materials

Since the seasonal variation ofnickel, zinc, arsenic and cadmium in the river system and the biomass is the focus of this study, water, sediment and *Anabas testudineus*were selected as the experimental materials. Systematic position and the image of experimental animal, *A. testudineus*(Plate 3)selected for the study is as follows;

Kingdom	:	Animalia
Phylum	:	Chordata
Class	:	Actinopterygii
Order	:	Perciformes
Family	:	Anabantidae
Genus	:	*Anabas*
Species	:	*A. testudineus*

Heavy metal analysis of the water and sediments from the study area during the study period will give the idea about the seasonal fluctuation of heavy metal pollution load in the river and that in the selected organs viz., liver, gill and muscle from the fish will give the information about its bioaccumulation rate.

2.4. Experimental design

Three samples of water and sediments and twelve fish coming under similar size range were collected from each station (Control, Station I and Station II) during the study period as described. The collected materials were prepared variously.

2.5. Sampling and storage

Surface water samples were collected in a 2-litre conventional polyethylene container. Three samples were collected from the same location. A stainless steel plastic-lined Van Veen grab was used to collect sediment samples. The top 5 cm layer was carefully skimmed from the grabs using a polyethylene scoop, homogenized and stored in polyethylene containers. Fish sample (*Anabas testudineus*) were collected using Cast net with the help of local fishermen. All the sample materials were taken to the laboratory without delay.

2.6. Sample processing

All glassware and plasticware used in the experiments were previously washed, soaked in dilute nitric acid and then rinsed with double distilled water. Reagents and standard solutions were prepared with double distilled water. The preparation of various samples for heavy metal analysis was done following the method suggested by(APHA 1995).

2.6.1. Preparation of water sample for heavy metal analysis

Five cm^3 of concentrated hydrochloric acid were added to 250 cm^3 of water sample and evaporated to 25 cm^3. The concentrate was then diluted to 50 cm^3 using de-ionized water. The processed water sample were then filtered through the Whatmann No.1 filter paper then labeled and stored for analysis.

2.6.2. Preparation of sediment sample for heavy metal analysis

One gram dried, sieved sediment samples were placed in a clean 20 ml glass vial and one ml de-ionized water, two ml 70 % HNO_3 and one ml 65% $HClO_4$ were added. The open vials were placed in 80^0C

temperature for 12 hours. The digested samples were diluted to 50 ml using de-ionized water. The processed sediment sample were then filtered through the Whatmann No.1 filter paper then labeled and stored for heavy metal analysis.

2.6.3. Preparation of biomass sample for heavy metal analysis

Six fish (*Anabas testudineus*) from the collection were dissected to remove liver, gills and muscle. One gram tissue sample (wet mass) was weighed and placed into a clean glass vial and one ml de-ionized water, two ml 70 % HNO_3 and one ml 65% $HClO_4$ were added. The open vials were placed in 80^0C temperature for 12 hours. The digested samples were diluted to 50 ml using de-ionized water. The processed biomass sample were then filtered through the Whatmann No.1 filter paper then labeled and stored for heavy metal analysis.

2.7. Heavy metal analysis

The processed water, sediment and biomass sample were sent to STIC (Sophisticated Test and Instrumentation Centre, Kochi, Ernakulam) for the analysis of heavy metalconcentration in it using ICP-AES system.

2.8. Statistical analysis

The statistical analysis was carried out using the SPSS software 20.0 Package. One-way analysis of variance (ANOVA) was carried out to compare the concentration of each heavy metal in water, sediment and biomass (liver, gills and muscle) in three stations (control, Station I and Station II) during three seasons (premonsoon, monsoon and postmonsoon). If significant differences were revealed by the ANOVA test, Turkey's test was used to further elucidate which season and station were significantly different. Correlation analysis was also carried out to know the concentration of each heavy metal in water, sediment, liver, gills and muscle in each station.

III. Results

In the present study the concentration of heavy metal was analysed in water, sediment and biomass from two stations of Periyarriver. The collection and analysis was done during three seasons of the year (premonsoon, monsoon and postmonsoon). Data of analysis of heavy metal is presented in the following way.

3.1. Seasonal variation of nickel

During every seasons in Station II and premonoon in station I, nickel concentration was significantly increased ($P<0.05$) than control waters (Table 1). Significant decrease ($P<0.05$) in nickel concentration in Station I water from Station II was noticed during monsoon and postmonsoon seasons however no significant difference during premonsoon season. Sediment from Station I and Station II showed significant elevation ($P<0.05$) than control nickel concentration during every seasons. However the concentration in sediment from control station was below detection limit during monsoon season. The Station I sediment nickel concentration was significantly elevated than Station II during every season. Nickel bioaccumulation in liver was observed only during premonsoon and it was below detection limit during other seasons (monsoon and postmonsoon). During premonsoon nickel bioaccumulation in liver of fish from control, Station I and Station II did not show any significant variation. Significant increase ($P<0.05$) in the nickel bioaccumulation in gills of fish from Station I and Station II compared to control was observed during every seasons. Compared to Station I, the gills of fish from Station II showed a significant increase in bioaccumulation of nickel during monsoon and postmonsoon. However the increase in Station II was not much significant during premonsoon season. Elevated bioaccumulation rate of nickel in muscle of fish from Station II compared to Station I was significant ($P<0.05$) during every season. The concentration was below detectable limit in the case of muscle of fish from Station I and control stations during postmonsoon and monsoon seasons respectively. Nickel concentration in water and gills at the same time liver and gill from three stations (control, Station I and Station II) showed significant positive correlation at 1 % confidence level (Table 2).

3.2. Seasonal variation of zinc

During every seasons zinc concentration in water, sediment and corresponding bioaccumulation in organs in fish from stations in periyar was significantly increased ($P<0.05$) than control station (Table 1). Among two stations water, sedimentand biomass from Station I showed higher concentration of zinc than Station II.Zinc concentration showed a varying sample-wise hierarchy but in majority of cases sediment showed maximum and muscle showed least concentration**.**The seasonal hierarchy also showed a varying trend. But there found a dominating tendency to show increased concentration during non-monsoon months than monsoon seasons. There occurs a significant positive correlation at 5 % confidence level in Zinc concentration of water and liver, sediment and liver, sediment and gills. The correlation was significant at 1% confidence level between water and muscle, sediment and muscle, liver and gills, liver and muscle, gills and muscle from three stations (Table 3).

3.3. Seasonal variation of Cadmium

Cadmium concentration in water from Station I and Station II was significantly elevated than control during all the seasons (Table 1). Even though the station-wise and sample-wise seasonal variation showed a varying trend, the post monsoon season recorded the highest and monsoon the least. The maximum concentration was recorded in sediments in each station and season and the minimum in muscle in most of the cases. Cadmium concentration in water and liver, water and muscle, gills and muscle from three stations showed significant positive correlation at 1 % confidence level. Water and Gills, sediment and gills were significantly correlated positively at 5 % confidence level (Table 4).

IV. Discussion

The results of the pollution analysis revealed that, out of the four heavy metals (Nickel, Zinc, Arsenic and Cadmium) selected, Arsenic was always below detection level in all the samples (water, sediment, liver, gills and muscle). The remaining metals; nickel, zinc, cadmium was found in varying concentration in the samples. During the study there noticed a decreasing trend as Zinc > Nickel > Cadmium as far as heavy metal concentration in different samples are concerned. IRE (Indian Rear Earth) processes the mineral monazite, manufacturing compounds of rare earth elements and may discharge effluents containing metals such as zinc, may be the source of this metal in periyar and FACT manufactures various fertilizer products and discharges waste streams contaminated with a range of heavy metals including cadmium, chromium, copper, mercury, nickel, lead and zinc (Stringer et al. 2003). Farombi et al. (2007) observed that Zinc was accumulated highest in the fish and cadmium the lowest.

Pioneers of pollution studies in periyar (Paul & Pillai 1976) identified the presence of heavy metals like Zn and Cd among other metals like Hg and Cu in the riverine environment. High concentrations of dissolved Zinc, Cadmium, Iron and Mercury were recorded at industrial belt located towards the northern side of the backwater (Kaladharan et al. 2011); (Anju et al. 2011); (Ciji & Bijoy Nandan 2014). Shibu et al. (1990) also quantified the concentration of Zinc and Cadmium in Periyar River. The concentrations of Fe, Cu, Pb, Zn, Cd, Ni, Co, Cr, Mn, Mg, Hg and Al in the sediments of Cochin backwaters and adjoining Periyar River was reported by (Mohan et al. 2012). Similarly (Paul &Pillai 1976) reported <1 µg/L of Ni during post monsoon in Periyar River. However (Anju et al. 2011) could not find detectable amount of Ni in periyar during any seasons and they reported that the nickel concentration in Cochin backwaters was <1-36 µg/L. Seasonal variation in the concentrations of nickel was negligible in Cochin estuary (Ouseph 1992). The perusal of literature never came across with reports on presence of measurable amount of Arsenic in Periyar.

The samples collected from the control station, which lies in a non-polluted environment recorded some concentration of heavy metals zinc and cadmium. The observed concentration was near to or slightly higher than the permissible limit set for metals. Investigators like (Odobasic 2012) mentioned that unpolluted sea or fresh water contains very low concentrations of heavy metals like Cu, Cd, Zn, Pb, etc, mostly dissolved and absorbed on organic and inorganic colloid substances like, simple hydrated metal ions ($Cd(H_2O)_6^{2+}$), Stabile inorganic complex ($ZnCO_3$), etc.

In the present study results it was found that the metal concentrations in the selected samples exhibit a seasonal variation in each station. In most of the cases (Ni in sediments from station II, gills from station I, Zn in water from station I, sediment and muscle of fish from control, Zn in liver of fish from control and station II, Cd in water of fish from station I, liver of fish from control) the variation followed a hierarchy of Premonsoon > Postmonsoon > Monsoon. However the trend became Premonsoon > Monsoon > Postmonsoon in the case of Zn and Cd in sediment from station II and Cd in muscle of fish from station II. Somewhat varied order of decrease i.e., Premonsoon > postmonsoon = monsoon was noticed in the case of Ni water from station I and II, liver of fish from station I, Cd in muscle of fish from control. Such a result may be the direct influence of south west monsoon during monsoon season and north east monsoon during postmonsoon season and absence of water inflow and reduced water column to dilute the heavy metal concentration during premonsoon season. The observation of seasonal highest during premonsoon was noticed and supported by Kumar et al. (2011) regarding the trend of heavy metals in Periyar River with respect to the concentration of lead. Anju et al (2011) reported that the concentration of heavy metals in the Periyar River was very high in pre monsoon period. Ali & Abdel-Satar (2005) noticed increase of metal concentrations in the water during hot seasons (spring and summer) due to their lease of heavy metals from the sediment to the overlying water under the effect of both high temperature and a fermentation process resulting from the decomposition of organic matter (Elewa et al. 2001). Goher

(2002) reported that the values of Cu and Zn showed an obvious decrease in the water during cold period (winter and autumn) due to precipitation of heavy metals from water column to the sediments under slightly high pH values, the adsorption of heavy metals onto organic matter and their settlement downward. The increase in concentration of dissolved cadmium during pre-monsoon and postmonsoon due to the formation of chloride complexes, occurring during the mixing of fresh water with seawater and to the desorption of exchangeable metals due to the increasing concentration of major cations (Paucot. &Wollast 1997); (Elbaz-Poulichet et al. 1987); (Windom. et al. 1991); (Chiffoleau et al. 1994); (Dai & Martin 1995).

Increase of metal's levels in tissues of some invertebrate and fish species were observed during summer months that were related to the increased metabolism due to high temperature (Khaled 2004); (Ali & Abdel-Satar 2005). Trace metal concentrations (Fe, Co, Ni, Cu, Zn, Cd, and Pb) in the muscle, gill and liver of the fishes *Mugil cephalus, Etroplus suratensis, Sillago sihama* and *Arius arius* collected from the Cochin backwaters during monsoon, post-monsoon and pre-monsoon periods were studied by (George et al. 2012) and reported that the elevated accumulation of metals in the fishes was well above the natural background levels during all the seasons and could be attributed to the favourable absorption and bioavailability of metals arising from the environmental compartments that are chronically exposed to industrial effluents under the prevailing physicochemical conditions.

A varied trend in seasonal variation as Monsoon > Premonsoon > Postmonsoon was noticed in the case of Ni in sediment from station I, Ni and Zn in muscle from station I. Similarly a decreasing trend as Monsoon > Postmonsoon > Premonsoon was observed in the case of Zn in sediment from station I and muscle from station II, Cd in water from station II and sediment and gills from station I. However the seasonal variation of Monsoon > Premonsoon = Postmonsoon was noticed in the case of Ni in muscle of fish from station II, Cd in liver of fish from station I and II. The deliberate release of effluents into the river from factories by exploiting the increased water flow during monsoon months i.e., the anthropogenic release greater than natural dilution may be the reason behind the strange observation. The observation was supported by the opinion of Shibu et al. (1990) that metal speciation and fate in the estuary are influenced by environmental factors such as influx of riverine inputs of metals, introduction of industrial effluents and sewage, modification due to anthropogenic activities and hydrographic changes related to complexity of water use.

There found a different decreasing trend as Postmonsoon > Premonsoon > Monsoon in the case of seasonal variation of Zn in water from station II and gills of fish from control, Cd in water, sediment and gills of fish from control, Cd in gills and muscle of fish from station II. However Postmonsoon > Monsoon > premonsoon was the order of Ni in gills of fish from control, Zn in water from control, Zn in liver and gills of fish from station I, Zn in gills of fish from station II. During postmonsoon season there is the availability of north east monsoon and even though it has only a secondary influence, the flow rate will be more than the premonsoon months. The deliberate industrial discharges during monsoon months may be attributed to this observation.

Metal absorption in fish is carried out via two uptake routes: digestive tract (diet exposure) and gill surface (water exposure). Metals are further transferred via blood to other target organs, such as the liver, kidney (Turkmen et al. 2009), gills, muscle, etc. During the present investigation the bioacucmlation tendancy of Zn in control, station I and II was Liver > Gills > Muscle. The high accumulation of Zn in the liver and gills is supported by the observation of (Sehgal&Saxena 1986) in *Clarias gariepinus* in *Channa punctatus* (Murugan et al. 2008) in gills of *C. punctatus* (Vineeta 2007). Javed&Usmani (2011) reported high accumulation of zinc in liver and low in gills and muscles of *C. punctatus* and *L. rohita*. At the same time Cd in station I and II followed the hierarchy Liver > Muscle > Gills. George et al. (2012) published the concentration of cadmium (Cd) in tissues was in the order, liver > muscles >gills > kidney in *Mugil cephalus*, *Etroplus suratensis, Sillago sihama,* and *Arius arius* collected from the Cochin backwaters.

The heavy metals accumulate mainly in metabolically active tissues such as the liver, here metals are bound to metallothioneins, low molecular weight proteins with high cysteine content (Oymak, Akın & Doğan 2009). At the same time gills are the first organs which come in contact with environmental pollutants. So they are highly vulnerable to toxic chemicals because primarily, their large surface area facilitates greater toxicant interaction and absorption and secondarily, their detoxification system is not much efficient as liver. It is well known that fish muscle is not an active tissue in accumulating heavy metals (Uysal et al. 2008). The metal concentration in muscle tissue is important because it is the chief edible part of the fish. From the observation (Vinodhini & Narayanan 2008) suggested that flesh is one of the ultimate parts for heavy metal accumulation. The heavy metals were uniformly spread over the body muscles. Hence, the observed values were relatively lower than the other potential organs. During the study (George et al. 2012) concluded that regardless of the season, metal bioaccumulation was higher in liver than in gill or muscle.

However the bioaccumulation trend was Gills > Liver > muscle in the case of Cd in control. Vinodhini& Narayanan (2008) supported this trend of bioaccumulation in *C. carpio.* Gills are directly exposed to the external environment and they play a major role as a route for the entry of heavy metals. The accumulation of heavy metals in liver as an organ of storage may be the cause for this observation. Cadmium has high affinity towards storage organs like liver due to the presence of metallothionine (Anju et al. 2011). Vincent & Ambrose (1994) observed Cd accumulation in *Cyprinus carpio* was maximum in gill. Andersen et al. (1998) reported low muscle concentrations of Cd in fish (roach, perch, and bream).This might be attributed to the high growth factor of muscle tissue as growth may dilute the toxicant concentration (Lohner et al. 2001). However Ni in control and station I followed the bioaccumulation tendency as Gills > muscle > Liver.

The bioaccumulation trend as Muscle > Gills > Liver. The high metal concentrations in these tissues are most likely related to the high influx of metals as a result of pollution from the industries located on the banks of the river and the consequent increased bioavailability of metals to the fish there. Site- wise difference may be another cause. There were some reports (Mance 1987) that heavy metal concentrations in the water, sediment and fish were variable from one site to another and also among fish species e.g. eels accumulated more metals in muscle and grey mullet in the liver. According to (Doherty et al. 2010) heavy metals were accumulated in the flesh of the fishes to varying extent. Bioaccumulation rate varies with species and period (Kaladharan et al. 2011).

The correlation analysis revealed that the concentration of metals like Zinc and Cadmium in water, sediment, liver, gills and muscle was positively correlated significantly. However the significant positive correlation in water, liver and gills in the case of Nickel. These are the reflection of the varying concentration, reaction between water and sediment and influence of other water quality parameters like salinity, hardness and the rate of bio accumulating tendency of different heavy metals or the variations in heavy metal concentration depending on the fluctuation in the surrounding environment under the influence of drainage water discharged (Bahnasawy et al. 2011); (Abdel-Baky et al. 1998) and the related dissimilarity in concentration in water and organs was supported by (Wong et al. 2001). These are in accordance with the present observation of positive correlation between the heavy metal concentration in water, sediment, liver, gills and muscle. However Wong et al. (2001) also reported that despite high metal levels in the water and sediments, concentrations of Cd in fish flesh did not exceed permissible levels, showing the absence of any relationship between environmental concentration and bioaccumulation. The observation of Kock & Hofer (1998) need a special mention in this context because they reported that even low concentrations of heavy metal in the water may result in high concentrations in fish flesh, a clear evidence of bio magnification.

As a whole, the seasonal variation of Pb, Zn and Cd in water and sediments was prevailing than that of Ni. Ouseph (1992) analysed the concentrations of dissolved and particulate copper, zinc, cadmium, lead, nickel, and iron in cochin backwaters based on three consecutive surveys conducted during July (monsoon), November (post-monsoon) 1985 and April (pre-monsoon) 1986 and recorded a supporting observation. The concentrations of dissolved and particulate zinc and cadmium showed high seasonal variation. Seasonal variation in the concentrations of nickel was negligible. In all the cases, heavy metal concentration was higher in sediments than in water and Biomass (liver, gills, muscle). The reason for the higher concentration in sediment may be because they are rapidly removed from waters into the underlying sediments. So, sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Aderinola et al. 2012). Ibrahim & Omar (2013) found that Ni was lower than the permissible limit in all sites under investigation and they justified the observation due to its low solubility and was corroborated by the findings of (Pandey & Gopal 2003). During the present study also there observed very low levels of Ni (mostly below detection level and rarely just above the detection level).

Among the elements selected Zn was the most abundant heavy metal, an essential element taking part in various metabolic processes and enzymatic reactions they may be naturally be occurring in abundance in the environment (Ibrahim 2007); (Mekkawy et al. 2008). According to Ravera (2001) if an environment receives metal pollutants, the organisms living in it could take up the pollutants from the water or/and food and concentrate it in their bodies. Shakweer (1998) concluded that the concentration of trace metals in various organs of fish reflects the degree of water pollution in the aquatic environments in which such fish are living. In the river, fish are often at the top of the food chain and have the tendency to concentrate heavy metals from water (Mansour & Sidky 2002). Therefore, bioaccumulation of metals in fish can be considered as an index of metal pollution in the aquatic bodies (Karadede-Akin & Unlu 2007); (Tawari-Fufeyin & Ekaye 2007). The trend of bioaccumulation was different with respect to each metal, organ, season and station possibly due to differences in metal concentrations of water and sediments from which fish were sampled, ecological needs, metabolism and feeding patterns of fish, and also the season in which studies were carried out (Ibrahim & Omar 2013). Metals like Lead and Cadmium are taken up passively from the water and deposited in the organisms and hence the organisms contain more quantity of these metals than water (Markert et al. 1997). This might increase the bioaccumulation level in fish and increase the actual dose of metal to which the local population is exposed (Chakraborty et al. 2003); (Chandrasekhar et al. 2003). The present study result did not show higher concentration in organs than in water except accumulation of zinc in liver of fish from Station II during postmonsoon season.

The accumulation rate was not corresponding of their concentration in water. In contrast to the present findings Ibrahim & Omar (2013) noticed that the metal concentrations in fish organs exhibited seasonal variations in which all of the detected metals attained their highest levels during summer, while the lowest values were found during winter. These seasonal variations were more or less similar to the fluctuation in the surrounding environment from the increase or decrease of drainage water discharged (Bahnasawy et al. 2011) ; (Abdel-Baky et al. 1998). The dissimilarity in concentration in water and organs was supported by Wong et al. (2001), they reported that despite high metal levels in the seawater and sediments, concentrations of Pb, Cd and Hg in fish flesh did not exceed permissible levels. Kock & Hofer (1998) reported that even low concentrations of heavy metal in the water may result in high concentrations in fish flesh.

From the observation in *Clarias gariepinus* (Ibrahim 2007)the different metals have different rate of absorption in tissues. Cadmium accumulates easily but Nickel doesn't. The variation lies in the differences in metal concentration, which was observed between different areas and the amount, depend on the concentration in the surrounding environment, feeding habit and adaptability of the species to the chemicals and mechanisms developed by the species to biotransformation (Nziku 2013). Generally, the uptake and bio accumulation of heavy metals in the target organs are also influenced by the biochemical functions of the tissue or organ and physiological processes that go on in them, some of which occur in an intricately complex network of interrelationships (Avenant-Oldewage & Marx 2000).

There was also observed that the concentration of metals in water, sediment and the biomass show varying but significant positive correlations depending on many environmental and physiological characters. At the same time the clearance rate of heavy metals, Pb, Ni, and Zn was very slow from liver but was high from gills and muscle, as an indication of organ- wise variation of heavy metal clearance rate. Bioaccumulation rate of metals is different for each heavy metal (Ibrahim 2007). Accumulation of heavy metals like led and cadmium is a passive process (Markert et al. 1997) and they accumulate easily (Anju et al. 2011). Zn as essential element, organisms takes it up as a physiological need. But the case of Ni is different because it does not accumulate in organs easily (Ibrahim 2007). Irrespective of tissue the clearance rate of cadmium was slow as a reflection of its increased half-life (more than 1 year according to Haux & Larsson 1982). So it is clear that the presence of heavy metals in water is a clear indication of its presence in the fishery resources and the bio accumulated metals can be removed in fish by transferring and keeping them in pollutant free water for days not less than one month before consumption. But this is not an effective method for removing metals like Cadmium and the treatment should be prolonged for removing a potent pollutant like cadmium.

V. Conclusion

The result analysis reached at a conclusion that the selected heavy metals (Ni, Zn, Cd) concentration was higher in the water, sediment, biomass from station I and II than control station indicating the pollution status of the river system. The metal bioaccumulations in tissues may be related to the influx of metals from the industries on the banks of the River and their increased bioavailability to the fish there. Out of the four selected elements Arsenic was not reported (always below detection level) from any of the samples and the remaining followed the order Zn > Ni > Cd in all the samples. Concentration was highest in the sediment samples following in the water sample and the least in the biomass with significant positive correlation between them. Seasonal variation followed a trend as premonsoon > postmonsoon > monsoon in majority of cases. Liver > gills > muscle was the commonly found trend in bioaccumulation. If we can check further release of industrial effluents into the river there lays the possibility of complete recovery of the system in long run.

Acknowledgment

The work was carried out with the financial assistance from UGC, New Delhi.

References

[1] T.E. Abdel-Baky,et al. Environmental impact assessment of pollution in Lake Manzala, I-Distribution of some heavy metals in water and sediment. J. of Egyp. Ger. Soc. for Zoo., 26 (B), 1998, 25–38.

[2] O.J. Aderinola,et al. Heavy Metals in Surface Water, Sediments, Fish and Perwinkles of Lagos Lagoon American-Eurasian. Journal Of Agricultural & Environmental Sciences, 5(5), 2012, 609–617.

[3] M. Ali and A. Abdel-Satar, Studies of some heavy metals in water, sediment, fish and fish diets in some fish farms in El-Fayoum province. Egyptian Journal of Aquatic Research, 31(2), 2005, 261–273.

[4] American Public Health Association (APHA), Standard Methods for Estimation of Water and Wastewater, 19th ed., American Water Works Association, Water environment Federation, Washington, 1995.

[5] F. Andersen, et al. Interaction between two dietary levels of iron and two forms of ascorbic acid and the effect on growth, anti oxidant status and some non-specific immune parameters in Atlantic salmon (Salmo salar) smolts. Aquaculture,161, 1998, 437–451.

[6] A.K. Anju, S. Dipu and V. Sobha. Seasonal Variation of Heavy Metals in Cochin Estuary and Adjoining Periyar and Muvattupuzha Rivers, Kerala, India. Global Journal of Environmental Research, 5(1), 2011, 15–20.

[7] A. Avenant-Oldewage andH.M. Marx, Bioaccumulation of chromium, co er and iron in the organs and tissues of Clarias gariepinus in the Olifants River, Kruger National Park. Water SA, 26(4), 2000, 569–582.

[8] J.F. Chiffoleau, et al. Trace metal distribution, partition, and fluxes in the Seine estuary (France) in low discharge regime. Marine Chemistry, 47, 1994, 145 – 158.

[9] P.P. Ciji and S. Bijoy Nandan, Toxicity of co er and zinc to Puntius parrah (Day, 1865). Marine Environmental Research Volume, 93, 2014, 38–46.

[10] M. Bahnasawy, A. Khidr and N. Dheina. Assessment of heavy metal concentrations in water, plankton, and fish of Lake Manzala,. Egyp. Turk. J. of Zoo., 35(2), 2011,271–280.

[11] R. Chakraborty,et al., Accumulation of heavy metals in some freshwater fishes from eastern India and its possible impact on human health. Poll. Res., 22(3), 2003, 353–358.

[12] K. Chandrasekhar, et al., Fractionation studies and bioaccumulation of sediment bound heavy metals in KolleruLake by edible fish. Environment International, 29, 2003, 1001–1008.

[13] M.H. Dai and J.M. Martin,First data on the trace metal and behaviour in two major arctic river/estuarine systems (Ob and Yenissei) and the adjacent Kara sea (Russia). Earth and Planetary Science Letters, 131, 1995, 127 –141.

[14] V.F.Doherty, O.O. Ogunkuade and U.C. Kanife, Biomarkers of Oxidative Stress and Heavy Metal Levels as Indicators of Environmental Pollution in Some Selected Fishes in Lagos , Nigeria. Ame. Euras. J. of Agri. and Env. Sc., 7(3), 2010, 359–365.

[15] F. Elbaz-Poulichet, et al. Dissolved cadmium behaviour in some selected French and Chinese estuaries. Consequences on Cd su ly to ocean. Marine Chemistry, 22, 1987, 125 – 136.

[16] A.A. Elewa,M.B. Shehata,A.M. Abdel Satar, M.H.H. Ali and M.E. Goher.Effect of the drainage water on Lake Qarun ecosystem, Egypt. 9th international Conference on the Conservation and management of Lakes. Shigha Prefectural Government – Japan. 2001.

[17] E.O. Farombi, O.A.Adelowo and Y.R. Ajimoko. Biomarkers of oxidative stress and heavy metal levels as indicators of environmental pollution in African cat fish (Clarias gariepinus) from Nigeria Ogun River. International Journal of Environmental Research and Public Health, 4(2), 2007, 158–165.

[18] M. Javed andN. Usmani, Accumulation of heavy metals in fishes : A human health concern. International Journal of Environmental Sciences, 2(2), 2011, 659–670.

[19] R. George, et al. Biomonitoring of Trace Metal Pollution Using Fishes From the Cochin Backwaters. Env. Foren., 13(3), 2012, 272–283.

[20] M.E.M. Goher, Chemical studies on the precipitation and dissolution of some chemical elements in Lake Qarun. Chemistry Department, Fac. of Sci., Al-Azhar Univ. Cairo, Egypt. 2002. 359.

[21] C. Haux and A. Larsson,Influence of inorganic lead on the biochemical blood composition in the rainbow trout, Salmo gairdneri. Ecotoxicology and Environmental Safety, 6, 1982, 28–34.

[22] A.T. Ibrahim,Distribution patterns of some heavy metals and pollution induced changes in some organs of three Nile fish species from Assuit, Egypt. MSc thesis. Assiut Univ. Assuit: Egypt. 2007.

[23] A.T.A. Ibrahim and H.M.Omar,Seasonal variation of heavy metals accumulation in muscles of the African Catfish Clarias gariepinus and in River Nile water and sediments at Assiut Governorate, Egypt. Journal of Biology and Earth Sciences, 3(2), 2013, B236–B248.

[24] P. Kaladharan, et al. Assimilative capacity of Cochin inshore waters with reference to contaminants received from the backwaters and the upstream areas. Ind. J. of Fish., 58, 2011, 75–83.

[25] H. Karadede-Akin and E. Unlu,Heavy Metal Concentrations in Water, Sediment, Fish and Some Benthic Organisms from Tigris River, Turkey. Environmental Monitoring Assessment, 131(1-3), 2007, 323– 337.

[26] A. Khaled, Trace metals in fish of economic interest from the west of Alexandria, Egypt. Chem. Ecol., 25, 2004, 1–11.

[27] G. Kock andR. Hofer, Origin of Cadmium and Lead in ClearSoftWaterLakes of High-altitude and High-latitude, and Their Bioavailability and Toxicity to Fish. EXS j., 86, 1998, 225–257.

[28] A.A. Kumar, S. Dipu and V. Sobha, Seasonal Variation of Heavy Metals in Cochin Estuary and Adjoining Periyar and Muvattupuzha Rivers, Kerala, India. Glo. J. of Env. Res. 5 (1), 2011, 15-20.

[29] T.W. Lohner, et al. Assessment of tolerant populations (Lepomis sp.) inhabiting selenium-laden coal ash effluents. Ecotoxicology and Environmental Safety, 50, 2001, 203 – 216.

[30] S. Mansour and M, Sidky,Ecotoxicological Studies. 3. Heavy Metals Contaminating Water and Fish from Fayoum Governorate. Egyptian journal of Food Chemistry, 78(1), 2002, 15–22.

[31] G. Mance,Pollution threat of heavy metals in Aquatic environments. Elsvier A lied Science Publishers LTD, London and New York. 1987.

[32] B. Markert, et al. A contribution to the study of the heavy-metal and nutritional element status of some lakes in the southern Andes of Patagonia (Argentina). The Science of the Total Environment, 206(1), 1997, 1–5.

[33] I.A.A. Mekkawy, U.M. Mahmoud and A.T.A. Ibrahim, Heavy metal distribution and their corresponding damage effect in some organs of Bagrus bajad (Forsskal, 1775) from three localities at Assiut,. journal of Egyptian German Society for Zoology, 54 (A), 119–137.

[34] M. Mohan, et al. Fractionation of selected metals in the sediments of Cochin estuary and Periyar River, Southwest coast of India. The Environmentalist-Springer, 32(4), 2012, 383–393.

[35] Murugan, et al., Bioaccu- mulation patterns of zinc in fresh water fish Channa punctatus (Bloch.) after chro- nic exposure. Turkish journal of Fisheries and Aquatic Sciences, 8, 2008, 55– 59.

[36] A. Nziku,Heavy Metal Pollution in the Receiving Environment of the University of Dar Es Salaam Waste Stabilization Ponds.

Journal of Biology and Life Science, 4(1), 2013, 2157–2176.
[37] A. Odobasic,Determination and Speciation of Trace Heavy Metals in Natural Water by DPASV, Water Quality Monitoring and Assessment, Dr. Voudouris (Ed.). 2012.
[38] P.P. Ouseph, Dissolved and particular trace metals in Cochin estuary. Marine Pollution Bulletin, 24, 1992, 181.
[39] S. Oymak,H. Akın,N. Dogan,Heavy metal in tissues of Tor grypus from Atatürk Dam Lake, Euphrates River-Turkey. Biologia, 64(1), 2009, 151–155.
[40] A.C. Pandey and K. Gopal, River pollution and its impact on Fisheries Resources: An Overview. In River pollution in India and its Management. 2003, 209.
[41] A.C. Paul and K.C. Pillai,Studies on pollution aspects of Periyar river. Project Report. 1976.
[42] H. Paucot and R. Wollast,Transport and transformation of trace metals in the Scheldt estuary. Marine Chemistry, 58, 1997. 229 – 244.
[43] O. Ravera,Monitoring of the aquatic environment by species accumulator of pollutants: a review. Journal of Limnology, 60(1), 2001, 63–78.
[44] R. Sehgal and A. Saxena.Toxicity of zinc to a viviparous fish, Lebistes reticulatus (Peters). Bull Environ Contam Toxicol., 36, 1986, 888–894.
[45] L.M. Shakweer,Concentration levels of some trace metals in Oreochromis niloticus at highly and less polluted areas of Mariut Lake. journal of Egyptian German Society for Zoology, 25(A), 1998, 125–144.
[46] M.P. Shibu, A.N. Balchand and N.P.K. Nambisan. Trace metal speciation in a tropical estuary: significance of environmental factors. Sci. of the Total Env., 97/98, 1990, 267–287.
[47] V Sobha and M. Anish, Imprints of environmental pollution on laterite/clay and groundwater of Eloor-Kalamassery industrial belt, kerala state, India. Env. Geol. 44, 2003, 914-918.
[48] R. Stringer,I. Labunska and K. Brigden, Pollution from Hindustan Insecticide Ltd. And other factories in Kerala, India: a follow-up study. Greenpeace research laboratories, University of Exeter UK. Technical note 05/03, 2003.
[49] P. Tawari-Fufeyin and S. Ekaye Fish Species Diversity as Indicator of Pollution in Ikpoba River, Benin City, Nigeria. Reviews in Fish Biology and Fisheries, 17, 2007, 21–30.
[50] M.A. Turkmen,et al., Determination of metals in fish species from Aegean and mediterranean seas. Food chem., 2009, 233–237.
[51] K. Uysal, Y. Emre and E. Kose, The determination of heavy metal accumulation ratios in muscle, skin and gills of some migratory fish species by inductively coupled plasma-optical emission spectrometry (ICP-OES) in Beymelek Lagoon (Antalya?Turkey). Microchemistry Journal, 90, 2008, 67–70.
[52] S. Vineeta,Bioaccu- mulation of Zn, Cu and Cd in Channa punctatus. Journal of Environmental Biology, 2(28), 2007, 395– 397.
[53] S. Vincent and T. Ambrose,Uptake of heavy metals, cadmium and chromium in tissues of Indian major carp. Catla catla (Ham). Indian Journal of Environmental Health, 36, 1994, 200–204.
[54] R. Vinodhini, and M.Narayanan, Bioaccumulation of heavy metals in organs of fresh water fish Cyprinus carpio (Common carp). Int. J. of Env. Sci. & Tech., 5(2), 2008, 179–182.
[55] H. Windom, et al. Trace metal nutrient relationships in estuaries. Marine Chemistry, 32, 1991, 177 – 194.
[56] C. Wong, et al. Specific expression of cytochrome P4501A1 gene in gill, intestine and liver of tilapia exposed to coastal sediments. Aqua. Toxicol., 54, 2001, 69–80.

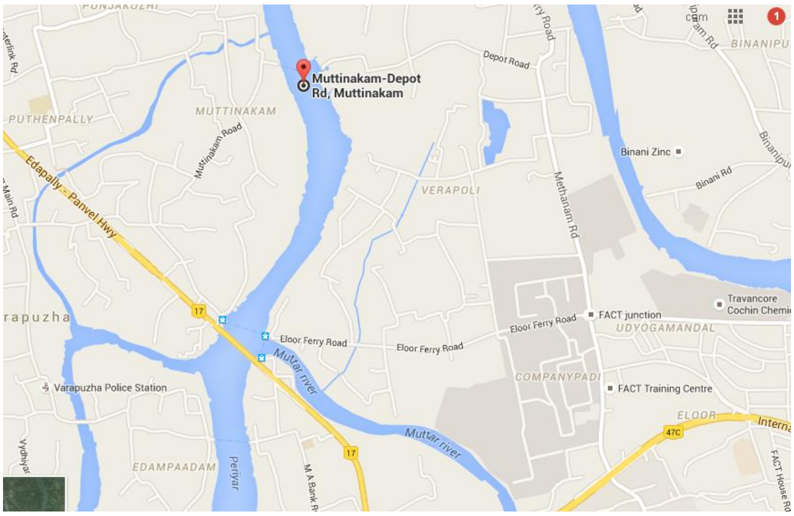

Plate 1: Station I

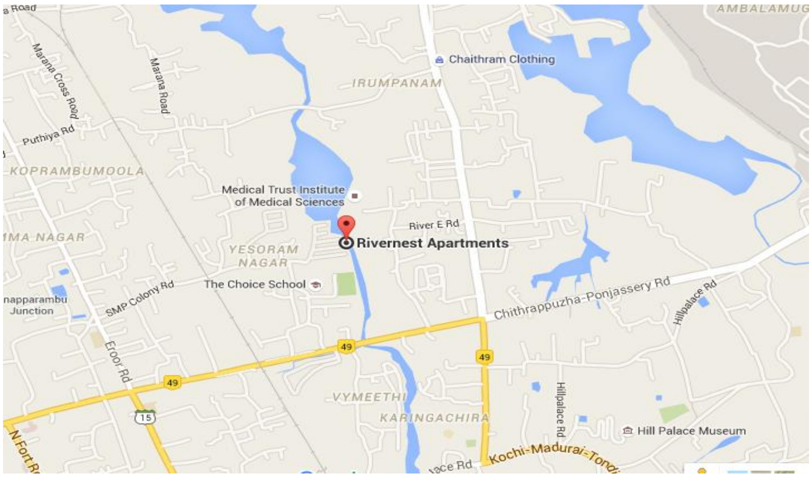

Plate 2: Station II

Plate 3: *Anabas testudineus*

Table 1: Season-wise variation of selected heavy metals in water, sediment and biomass collected from different stations

	Control			Station I			Station II		
Nickel	**Pre-monsoon**	**Monsoon**	**Post-monsoon**	**Pre-monsoon**	**Monsoon**	**Post-monsoon**	**Pre-monsoon**	**Monsoon**	**Post-monsoon**
Water	$_{a}0.01\pm0.002^{A}$	$_{a}0.01\pm0.002^{A}$	$_{a}0.01\pm0.002^{A}$	$_{b}0.03\pm0.002^{B}$	$_{a}0.01\pm0.002^{A}$	$_{a}0.01\pm0.002^{A}$	$_{b}0.03\pm0.002^{B}$	$_{b}0.02\pm0.001^{A}$	$_{b}0.02\pm0.001^{A}$
Sediment	$_{a}0.01\pm0.009$	BDL	$_{a}0.01\pm0.001$	$_{c}1.3\pm0.12^{A}$	1.58 ± 0.1^{B}	$_{c}1.26\pm0.1^{A}$	$_{b}0.4\pm0.03^{A}$	0.18 ± 0.1^{A}	$_{b}0.34\pm0.12^{A}$
Liver	BDL	BDL	BDL	0.01 ± 0.001	BDL	BDL	0.01 ± 0.001^{A}	0.01 ± 0.001^{A}	0.01 ± 0.001^{A}
Gills	$_{a}0.01\pm0.001^{A}$	$_{a}0.011\pm0.001^{A}$	$_{a}0.014\pm0.00^{B}$	$_{b}0.02\pm0.001^{B}$	$_{b}0.016\pm0.001^{A}$	$_{b}0.019\pm0.00^{B}$	$_{b}0.02\pm0.001^{A}$	$_{c}0.02\pm0.001^{A}$	$_{b}0.02\pm0.001^{A}$
Muscle	$_{a}0.01\pm0.001$	BDL	0.01 ± 0.001	$_{a}0.01\pm0.002$	0.011 ± 0.001	BDL	$_{b}0.02\pm0.001^{A}$	0.024 ± 0.002^{B}	0.02 ± 0.001^{A}
Zinc									
Water	$_{a}0.46\pm0.2^{A}$	$_{a}0.49\pm0.21^{A}$	$_{a}1.46\pm0.12^{B}$	$_{c}4.87\pm0.2^{C}$	$_{c}1.3\pm0.1^{A}$	$_{b}2.35\pm0.2^{B}$	$_{b}1.21\pm0.12^{A}$	$_{b}0.92\pm0.11^{A}$	$_{b}1.95\pm0.15^{B}$
Sediment	$_{a}1.82\pm0.2^{B}$	$_{a}1.23\pm0.12^{A}$	$_{a}1.32\pm0.12^{A}$	$_{c}5.21\pm0.4^{A}$	$_{c}24.51\pm2^{B}$	$_{c}7.3\pm0.7^{A}$	$_{b}3.34\pm0.3^{B}$	$_{b}3.23\pm0.3^{B}$	$_{b}2.48\pm0.2^{A}$
Liver	$_{a}0.92\pm0.08^{B}$	$_{a}0.52\pm0.05^{A}$	$_{a}0.65\pm0.05^{A}$	$_{b}1.17\pm0.11^{A}$	$_{c}1.32\pm0.1^{A}$	$_{b}2.26\pm0.2^{B}$	$_{ab}1\pm0.1^{A}$	$_{b}0.81\pm0.07^{A}$	$_{a}0.89\pm0.07^{A}$
Gills	$_{a}0.66\pm0.05^{A}$	$_{a}0.54\pm0.05^{AB}$	$_{a}0.76\pm0.06^{B}$	$_{b}0.82\pm0.07^{A}$	$_{b}1.01\pm0.1^{A}$	$_{b}1.31\pm0.1^{B}$	$_{ab}0.67\pm0.06^{A}$	$_{b}0.87\pm0.07^{B}$	$_{a}0.9\pm0.08^{B}$
Muscle	$_{a}0.37\pm0.03^{A}$	$_{a}0.31\pm0.03^{A}$	$_{a}0.35\pm0.03^{A}$	$_{b}0.65\pm0.06^{AB}$	$_{c}0.7\pm0.06^{B}$	$_{b}0.52\pm0.05^{A}$	$_{a}0.42\pm0.03^{A}$	$_{b}0.54\pm0.04^{A}$	$_{b}0.47\pm0.03^{A}$
Cadmium									
Water	$_{a}0.01\pm0.002^{A}$	$_{a}0.008\pm0.001^{A}$	$_{a}0.009\pm0.000^{A}$	$_{a}0.013\pm0.002^{A}$	$_{a}0.01\pm0.002^{A}$	$_{ab}0.011\pm0.00^{A}$	$_{a}0.011\pm0.00^{A}$	$_{b}0.017\pm0.001^{B}$	$_{b}0.014\pm0.02^{AB}$
Sediment	$_{a}0.011\pm0.00^{A}$	$_{a}0.01\pm0.002^{A}$	$_{a}0.012\pm0.001^{A}$	$_{b}0.08\pm0.02^{A}$	$_{c}0.29\pm0.02^{C}$	$_{c}0.14\pm0.01^{B}$	$_{b}0.078\pm0.01^{B}$	$_{b}0.052\pm0.01^{A}$	$_{b}0.045\pm0.04^{A}$
Liver	$_{a}0.007\pm0.003$	BDL	$_{a}0.006\pm0.0002$	$_{ab}0.01\pm0.001^{A}$	0.011 ± 0.001^{A}	$_{b}0.01\pm0.001^{A}$	$_{b}0.013\pm0.00^{A}$	0.039 ± 0.003^{B}	$_{b}0.011\pm0.001^{A}$
Gills	$_{a}0.005\pm0.00^{A}$	$_{a}0.004\pm0.001^{A}$	$_{a}0.007\pm0.002^{A}$	$_{b}0.009\pm0.001^{A}$	$_{b}0.011\pm0.00^{A}$	$_{a}0.01\pm0.001^{A}$	$_{ab}0.008\pm0.002^{A}$	$_{a}0.006\pm0.001^{A}$	$_{b}0.015\pm0.001^{B}$
Muscle	$_{a}0.005\pm0.001$	BDL	BDL	$_{ab}0.007\pm0.001^{A}$	0.006 ± 0.001^{A}	0.005 ± 0.001^{A}	$_{b}0.008\pm0.001^{A}$	0.008 ± 0.001^{A}	0.014 ± 0.001^{B}

Table 2: Relationship of nickel concentration in samples from three stations Correlations

	Water	Sediment	Liver	Gills	Muscle
Water	1	.043	.237	.715**	.100
Sediment		1	.170	.346	-.258
Liver			1	1.000**	.050
Gills				1	.348
Muscle					1

**. Correlation is significant at the 0.01 level (2-tailed).

Table 3: Relationship of zinc concentration in samples from three stations Correlations

	Water	Sediment	Liver	Gills	Muscle
Water	1	.073	.394*	.359	.607**
Sediment		1	.428*	.483*	.760**
Liver			1	.879**	.545**
Gills				1	.625**
Muscle					1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

Table 4: Relationship of cadmium concentration in samples from three stations Correlations

	Water	Sediment	Liver	Gills	Muscle
Water	1	-.004	.785**	.382*	.565**
Sediment		1	-.049	.454*	-.281
Liver			1	-.194	.157
Gills				1	.690**
Muscle					1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS) is UGC approved Journal with Sl. No. 5012, Journal no. 49063.

Asha Raj Kariyil Rajappan. “Seasonal variation of heavy metals in selected stations of Periyar river at Ernakulam district, Kerala, India.” IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS), vol. 12, no. 4, 2017, pp. 14–24.