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Heavy metals concentration in water, sediments and accumulation patterns in fish muscle tissues of (*O. mossambicus* and *M. cephalus*) collected from Kedilam River, Tamil Nadu, India

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Abstract
The present investigation was carried out to determine the metals (Zn, Cr, Cd, Pb and Ni) in water, sediments and fish tissue of *Mugilcephalus* and *Oreochromis mossambicus* collected from Kedilam River, Tamil Nadu during the period from 2013-2014. Samples were collected three different places of the river (Up, mid and Downstream) and fixed with chemicals. Muscle tissues were dried and make a powdered form and finally, metals were detected by the use of atomic absorption spectrophotometer (AAS). The results showed that significant values reported in metals like zinc and nickel in water at $P<0.05$ level, whereas in sediment except chromium others Zn, Cd, Pb and Ni were shown significant value at $p<0.05$ level. Among the two fish species metals accumulated significantly in *O. mossambicus* as compared to *M. cephalus*. Present work shows that the heavy metals distributed in different level of organization. Immediate action need to mitigate the aquatic problems.

Keywords: heavy metals, bio concentration, bioaccumulation, bio concentration factor, asssessment

Introduction
During this 21st century globally industrialization and digitalization has been dominated. Especially countries like India become one of the fastest growing after china in worldwide. We need development but at the same time it's not threats to our ecosystem also. To protect our ecosystem first save wet lands, mostly rivers. Rivers in India are highly polluted because of illegal discharge of industrial, agricultural and municipal waste. River damaged due to illegal sand mining in riverside area also reduce the water flow which directly impacts on ecology of aquatic organisms (CPCB 2011) [11].
Discharge of heavy metals impacts on feeding behavior of fishes which makes vulnerable and heavily exposed to pollution because they cannot escape from the detrimental effects of pollutants (Authman *et al*. 2015) [7]. Due to contamination of heavy metals in water and sediment with persistence for longer period cause serious threats to food chain, mostly fishes which can accumulate and biomagnifying the heavy metals (Bhuyan and Anandhan 2013; Bhuyan *et al*. 2014) [8, 9].
Fishes are considered to be most significant biomonitors in aquatic systems for the estimation of metal pollution level (Rashed 2001; Authman 2008) [13, 6], they offer several specific advantages in describing the natural characteristics of aquatic systems and in assessing changes to habitats.

Materials and Methods
Study area
Kedilam River some time ago pronounced as Gadilam is located in parts of Cuddalore and Villupurum Districts of Tamil Nadu, India. It lies between 79°0'E to 79°47'E longitudes and 11°30'N to 11°55'Eatitudes. The total length of the river is about 112 km and the catchment area is about 900 km² (Prasanna *et al*. 2011) [12].

Sampling Stations
The three chosen sampling stations are

S1: Point source nearer to the industrial and agricultural regions at Thiruvandipuram.
S2: Right bank of the river dominated by domestic and municipal wastes at Thirupadripuliyur.
S3: River entering in to the sea area at Cuddalore town region

Sample collection and physico-chemical parameter analysis of water

Each one liter of water samples were collected using precleaned washed (5% HNO_3) polypropylene containers. All samples were collected at a depth of 5 cm from the surface water level, temperature; pH and Electrical Conductivity were measured at the sampling sites. For further analysis of different parameters samples (stored in precleaned plastic bottles in ice box) were transferred immediately to the laboratory followed by (APHA 1989) [1] and (Trivedy and Goel 1986) [20].

Sample collection of sediments and metals analysis in water

Sediment samples were collected from each selected site 5meter near to river bed by grabbing below 5cm and were brought to the laboratory in clean polythene bags for further analysis. The method was adopted from (Chester and Huges 1967) [10] followed by (APHA 1989) [1] and (Katip *et al*. 2012). Determination metals in water were carried out by protocol followed by (Brooks *et al*. 1967) [10]. Metals (Zn, Cr, Cd, Pb and Ni) in water and sediment were analyzed by using atomic absorption spectrophotometer (EC AAS4141) suggested by (APHA 1989) [1].

Collection and metals analysis of fish sample

Fish samples were collected from each selected site in the morning (8-10 a.m) by taking the help of local fishermen. Live fishes of *Oreochromis mossambicus* and *Mugil cephalus* were collected and edible muscle tissues were dissected out, fixed in 10% formalin on the spot and brought back to the laboratory by ice box.

In the laboratory the muscle tissues were placed in an oven by Petridish at 120 ˚C for two days until it gained a constant weight. Then the dried tissues were made into powered form and kept in to a plastic bottle. Dried tissue powder of 0.5g was taken and added with concentrated nitric acid and perchloric acid (3:1) as suggested by (Topping 1973) [19]. The digested material was then made up to 25 ml with distilled water and analysed for different metals by the use of Atomic Absorption Spectrophotometer (EC AAS4141) as suggested by (APHA 1989) [1].

The bioconcentration factor (BCF), which is the ratio between the accumulated concentration of a given pollutant in any organ and its dissolved concentration in water, sediment (Authman *et al*. 2007) [5] was calculated using the following equation:

BCF = Pollutant concentration in fish organ /Pollutant concentration in water or sediment

Statistical analysis

Each reported result was the average value of the three analyses. The results were offered as means ±SEM. The statistical differences of mean metal levels among tissues and species were analyzed using multiple comparison tests (SPSS package program). One-way ANOVA was utilized to compare the data by species and by tissue. Results were considered significant at $p < 0.05$.

Results

The concentration of metals are- may be deleted) in water and sediments are as Zn>Ni>Cr>Cd>Pb and Zn>Cr>Ni>Cd>Pb each respectively (Table 1). In muscle tissue the metals are accumulated in order of Zn>Ni>Cr>Cd>Pb and Zn>Ni>Cd>Cr>Pb of *O. mossambicus* and *M. cephalus* each respectively. Statistically (ANOVA) significant variation observed in metals like Zn, Ni in water and Zn, Cd and Ni in sediment at p<0.05 level (Table 2, Table3). Similar types of trend were also observed in both the fishes in this assessment.

Concentration of cadmium in water was ranging from 2.15-19.53 µg/l over two years of study in Kedilam River (Table 1). In water cadmium and nickel was above the permissible limit where aszn, cr and pb under safe limit according to (WHO 2003) [23] and (BIS 1992). Where as in sediment Cr and Cd are above the threshold level prescribed by (Mcdonald *et al*. 2000).

Table 1: Annual average means (±SD), range and international standard of heavy metals concentration in water (µg/l) and sediment (µg/g) samples.

Metals	Water (µg/l)		Standard for water (BIS 1992;WHO 2003)(mg/l)	Sediments (µg/g)		Threshold concentration for sediments (McDonald *et al* 2000)((µg/g)
	Annual Average mean	Range		Annual Average mean	Range	Not available
Zn	42.00	28.57-55.54	15	45.31	33.18-62.34	Not available
Cr	23.70	17.98-44.78	0.05	27.30	12.47-52.18	0.99
Cd	7.25	2.15-14.14	0.01	10.45	6.28-19.68	0.99
Pb	1.07	0.55-1.86	0.01	1.25	0.28-2.14	22.7
NI	27.46	15.44-39.21	0.02	24.31	11.27-42.13	35.8

Table 3: ANOVA calculations for water and sediment samples collected from Kedilam River.

Metals	Water	sediments
	F value	F value
Zn	12.07**	179.07**
Cr	4.079*	1.898*
Cd	4.506*	8.370**
Pb	3.168*	8.106**
Ni	231.62**	14.899**

**Significant P<0.05, * not significant P<0.05 level.

Table 4: ANOVA calculations for metals accumulation in muscle tissues of *O. mossambicus* and *M. cephalus*

Metals	*O. mossambicus*	*M. cephalus*
	F value	F value
Zn	0.285*	244.08*
Cr	7.966**	0.901*
Cd	7.985**	1.095*
Pb	6.734**	1.605*
Ni	19.062**	9.386**

**Significant P<0.05, * not significant P<0.05 level.

The concentration of Cr in *M. cephalus* and *O. mossambicus* was ranging from 0.08-3.85 µg/g d.wt and 0.02-2.25 µg/g d.wt respectively over the two years of study period (Table 4). Concentration of Ni was ranging from 1.25-15.74µg/g and 5.36-19.25 µg/g in *M. cephalus* and *O. mossambicus* during the two years of study period.

Table 4: Annual average means (±SD), range and standard of heavy metals accumulation (µg/g.d.wt) in muscle tissues of *O. mossambicus* and *M. cephlaus*.

Metals	*O.mossambicus*		*M.cephalus*		Standard (FAO 1983)
	Annual average mean (µg/g.d.wt)	Range	Annual average mean (µg/g.d.wt)	Range	
Zn	15.64±5.35	7.55-24.45	13.92±8.50	6.23-27.45	50
Cr	0.94±0.70	0.02-2.25	1.79±1.24	0.08-3.85	2.00
Cd	0.73±0.65	0-1.69	2.72±2.32	0.25-5.91	NA
Pb	0.038±0.05	0-0.03	0.16±0.16	0.007-0.45	4.00
Ni	11.08±5.62	5.36-19.25	8.74±5.63	1.25-15.74	10.00

A study on the transfer of Zn, Cr, Cd, Pb and Ni through the food chain of the river Kedilam proved the existence of bioaccumulation in fish. The Bio- concentration factor of the heavy metals in muscle tissues of fish from the river water are presented in Table 5. The BCF value in water was highest (0.40) and lowest (0.035) for lead in *O. mossambicus*. Where as in sediment BCF value was highest (1.129) in *O. mossambicus* for nickel and was lowest (0.065) in *M. cephalus* for chromium. The trends of BCF for heavy metals in four species of fish were in the ranking order of Ni>Zn>Cr>Pb>Cd.

Table 5: Bioconcentration factors (BCF) for heavy metals in muscle tissues of O.mossambicus and *M. cephalus* collected from Kedilam River.

BCF	*M. cephalus*	*O.mossambicus*	BCF	*M. cephalus*	*O.mossambicus*
Zn muscle/Zn water	0.312	0.372	Zn muscle/Zn sediment	0.289	0.92
Cr muscle/Cr water	0.075	0.039	Cr muscle/Cr sediment	0.065	0.86
Cd muscle/Cd water	0.375	0.100	Cd muscle/Cd sediment	0.260	0.69
Pb muscle/Pb water	0.149	0.035	Pb muscle/Pb sediment	0.128	0.85
Ni muscle/Ni water	0.318	0.40	Ni muscle/Ni sediment	0.359	1.129

Discussion

Concentration of cadmium in water was ranging from 2.15-19.53 µg/l over two years of study in Kedilam River. The present result is above the permissible limit of 3 µg/l (WHO 2003) [23]. Similar results were observed by (Ahmed *et al*. 2010) [2]. Concentration of lead in water was ranging from 0.55-2.11µg/l over two years of study in Kedilam River. The present result was below the BIS (10 µg/l) standard values. Similar results were observed by (Robin *et al*. 2012; Utete *et al*. 2013; Ciji and Bijoy 2014) [15, 21]. Nickel in water was ranging from 12.39-39.21µg/l during the study period. Present results were above the permissible limit Similar results were reportedby (Ahmed *et al*. 2010; Rejomon *et al*. 2010) [2]. Concentration of nickel is above the permissible limit of 20 µg/l (WHO 2003) [23].

The concentration of chromium above the permissible limit of 2.0 µg/g prescribed by (FAO 1983). Hexavalent chromium (Cr6+) is considered to be toxic (i.e. carcinogenic) because of its powerful oxidative potential and ability to cross cell membranes (WHO 1990; Authman *et al*. 2015) [22, 7]. Poor treatment of these effluents can lead to the presence of Cr (VI) in the surrounding water bodies, where it is commonly found at potentially harmful levels to fish (Sfakianakis *et al*. 2015) [16].

The concentration of nickel are above the permissible limit (10 µg/g) prescribed by (FAO 1983). Similar type of results were observed by fish *Labeo umbratus*, (Taweel *et al*. 2012) [18] in *O. niloticus* and (Javed 2012) in *Cirrhinus mrigala*.

Presence of 'Cr in water, sediment and tissue in this study is due to industrial release especially sugar mill effluent and paint industry which are near by the river. Similar results were observed by Javed and Usmani (2013) and Fatima and Usmani (2013).

Chromium is more deposited in *M. cephalus* and nickel is highly accumulated in *O. mossambicus*. Metal uptake by fish also depends upon the zone of the water body inhabited by fish. Indicated that animals which have close relationship with sediment, show relatively high concentrations of metals. This viewpoint was supported by (Ali and Fisher 2005; Ali and Abdel-Satar 2005) [3, 4] who recorded higher concentration of heavy metals in *Mugilcephalus* (bottom feeder) than *Oreochromis mossambicus* (filter feeder) and by (Soegianto and Irawan 2008) [17] who recorded higher concentration of metals in *Arius leptonotacanthus* than *Mugilvaigiesis* and *Johnius belengeri*. Among the two fish species total load of metals such as Cr and Ni was highly accumulated in *M. cephalus*, whereas, Zn, Cd and Pb in *O. mossambicus.* Present study reveals that metals accumulation depend on species to species. Species dependent, feeding habit and aquatic habitat is the major cause for this variation.

Bioaccumulation factor was high in fish muscle tissue/sediment as compared to fish muscle/water. Similar type of results observed by Ibrahim and Omar (2013). Bioaccumulation factor shows the transfer of metals especially nickel and chromium is warning signal for fish consumption towards food safety.

Conclusion

In this study results indicate the presence of metals in water, sediments and fish tissue is a warning signal for the riverine ecosystem. In addition Bioconcentration factor of metals transfer from water to muscle and sediment to muscle tissue has strong evident that metals transfer higher in sediment to muscle tissue then water to muscle tissue. It demands the state pollution control board to continuous monitoring of water quality and take necessary steps towards the mitigate problems for sustainable socio-economic status of people around the river.

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