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Bioaccumulation pattern of heavy metals in river Basantar, Samba (J&K), India

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ABSTRACT

In the present study concentration of heavy metals viz. lead, copper, iron and zinc were determined in water, sediments and muscles of *Labeo rohita* by using Atomic absorption spectrophotometer (AAS). The results depicted seasonal and spatial fluctuations in concentration of heavy metals both in water as well as sediments with summer maxima and monsoon minima. The heavy metal concentration in water, sediments and muscles of *Labeo rohita* was recorded in the following order: Pb > Zn > Fe > Cu; Fe > Zn > Pb > Cu and Fe > Pb > Zn > Cu respectively. Also, on the basis of BAF, the order of accumulation of heavy metals in *Labeo rohita* was Fe > Cu > Pb > Zn from water and Pb > Cu > Zn > Fe from sediments. Moreover, concentration of some of the heavy metal was much higher than the permissible limit as recommended by World Health Organization, which clearly suggests that this water body needs immediate attention.

Key words: *AAS, Bioaccumulation, Basantar, Heavy metals, Industries, Sediments.*

Introduction

The earth is very special among other planets because of the presence of water which is a prime natural resource and precious asset responsible for the existence of life (Dapam *et al*., 2016). Of the total water present on Earth only 0.3% is fresh and its 22.7% is unavailable which remains confined in atmospheric moisture, icecaps and glaciers and the remaining is available and utilizable in the form of freshwater ecosystem. River, ponds and lakes are the most sensitive freshwater ecosystems that hold a strategic importance in every aspect of life viz. domestic purposes, irrigation, power generation, industry, recreation, tourism, aquaculture and agriculture activity. Due to developmental activities, the surface water which is an important source of water for humans is under severe environmental stress. Water quality measurements provides significant information about aquatic ecosystem functions and conditions for supporting life and suitability for human use (Lianthuamluaia *et al.*, 2013). Any damage to water quality not only disrupts the aquatic ecosystem but also makes life miserable in it too.

Among various causes of pollution, urbanisation and industrialisation are the two important culprits that not only lead nation towards progress but also towards demolition. For trouble-free accessibility of water numbers of industries are established on its bank which is chaotically discharging the waste directly into them without considering environmental protective measures (Pandey, 2006). Discharge of wide variety of pollutants such as alkalies, dyes, acids, hydrocarbons and heavy metals etc from industries directly or indirectly affects the ecological balance of the environment and ultimately affect human beings (Patil, 2006; Singare *et al.*, 2014; Saini *et al.*, 2016). As per Central Pollution Control Board, 90% of the water supplied to the town and cities in India is polluted, out of which only 1.6% gets treated

(2007- 2008).

The worsening of aquatic ecosystem by heavy metals is looming large, hence this issue is getting momentum globally (Iqbal *et al.,* 2017). Heavy metal pollution is therefore described as tickling environmental bomb as their entry into aquatic ecosystem decline life supporting quality of water, harming flora and fauna therein (Bohlmark, 2003; Wani *et al.,* 2017). Heavy metals are known to be naturally occurring but anthropogenic activites introduces them abundantly into the environment (Khan *et al.,* 2008). Natural sources of heavy metals include volcanic eruptions, weathering of rocks, sea-salt spray, biogenic sources and forest fires and are found in the form of hydroxides, sulphides, sulphates, silicates and various other compounds. While industrial wastes, automobile exhaust, smelting, mining, agriculture runoff, burning of fossil fuel are some of the most significant anthropogenic sources of heavy metals.

These are toxic and pose major threat to the aquatic ecosystem due to their non-biodegradable, persistent nature and very high tendency to accumulate in living organisms and adsorbed on sediment particles (Ahmed *et al.,* 2015a,b; Ali *et al.,* 2016; Dapam *et al.,* 2016). Concentration of heavy metal is usually monitored by measuring their levels in water, sediments and biota as they dilute in water, settle in sediments and enter in aquatic organisms (Ozturk *et al.,* 2009). Moreover these metals get transferred from water and sediments into aquatic organisms and start bio-magnifying from low trophic level to higher one (Jia *et al.,* 2017). Level of metals however remain generally low in water and acquires considerable accumulation in sediments and biota (Namminga and Wilhm, 1976).

The aquatic biota over the time when exposed to heavy metals retains and accumulates them in their body. Fish representing the oldest class of vertebrates, acquire top position in aquatic food chain are most commonly affected when absorbs heavy metals through food or sediments, gills, drinking water or adsorption through skin (Abdullah *et al.,* 2007; Iqbal *et al.,* 2017; Pal and Maiti, 2018). Various factors like habitat, feeding behaviour, growth rate of different species determine the distribution and accumulation of heavy metals in fish (Jia *et al.,*2017). The aim of the present study is to assess the concentration of heavy metals such as lead, iron, zinc and copper in water, sediments and fish muscles (*Labeo rohita*) as metals have far reaching implications directly to biota and indirectly to humans. Fish is an important component of human diet and thus act as connecting link for the transfer of heavy metals from environment to humans (Sen *et al.,* 2011). In freshwater ecosystem, sediments and fish have been widely used for the assessment of metal pollution (Islam *et al.,* 2015; Ali *et al.,*2016).

Material and Methods

Study area

Basantar is a tributary of river Ravi, originating from Shivalik hills at an altitude of 1300 km above sea level and is an important water body of J&K. It flows through Samba district and ultimately meets river Ravi in Pakistan. It is one of the main sources of drinking water for the inhabitants of Samba district but due to extensive urbanization and industrialization along the river side, it is getting polluted.

A modern industrial complex named as SIDCO (State Industrial Development Corporation) is established on its bank. The direct discharge of industrial effluents from the industrial complex into the river is deteriorating its water quality. In order to assess the heavy metal load of river Basantar, a study was carried out for a period of one year, i.e. 2018-2019. Three study stations were established along the profile of this river based on various anthropogenic load viz. Station I, located near Chichi Mata Temple where religious waste from the temple is dumped, Station II near SIDCO industrial complex and is approximately 1.5 km away from station I and receives direct discharge of waste from the industrial complex and station III lies 2 km downstream from station II and can be designated as the revival zone (Fig. 1).

Methodology

Water sample

From selected stations water sample was collected in 1L polyethylene bottles and brought to the laboratory for the assessment of heavy metals such as Pb, Zn, Fe & Ni. To prevent water from any degradation and to stop microbial growth, pH was maintained as 2.0 by adding 2-3 ml of concentrated HNO_3 into sample (APHA, 2012). All the samples thus collected were kept in refrigerator (-4!) prior to analysis through AAS (Model no. Shimadzu AA 7000).

Fig. 1. Study area (a) Station I (b) Station II and (c) Station III

Sediment samples

Sediment samples were taken from three different stations and collected into polythene bags. The samples were air dried, pulverized using mortar and pestle and sieved through 5mm mesh. 1g of the homogenous sediment of each location was weighed and mixed with 8 ml of concentrated HNO_3. This mixture was heated on hot plate with a magnetic stirrer until a clear solution was obtained. The digested sample was left to cool, filtered using whatmann filter paper no. 41 into volumetric flask and diluted up to 25 ml. The resultant solution was analysed for heavy metals viz. Pb, Zn, Fe and Cu through Atomic Absorption Spectrophotometer. Digestion and detection was done in triplicate and results were expressed in parts per million (ppm).

Fish sample

Fishes were caught using cast net with the help of fisherman at selected stations and brought to the laboratory in ice box for analysis of metals viz. Pb, Zn, Fe & Ni from its muscles. Individual fish was anesthetized and its length and weight was noted before dissection. The dissection was done by using sterilized scissor and forceps. The muscles were removed and then put into separate petri plates and kept in oven at 90^{0}C for 48 hours until constant weight was reached. Dried muscles were ground to a fine powder using mortar pestle and then weighed. The sample was then stored in Teflon vessel and kept at -4^{o}C temperature prior to analysis. Before analysis samples were acid digested by following proper methodology with certain modifications (Ashraf *et al.*, 2012; Bat *et al.*, 2012). To 1 gm of each powder sample, 8 ml of concentrated HNO_3 was added and mixture was heated on hot plate with magnetic stirrer until a clear solution is obtained. Then the solution was filtered using whatmann filter paper no. 41 into volumetric flask and diluted up to 25 ml. The samples thus prepared were analyzed using Atomic absorption spectrophotometer (model: Shimadzu AA 7000). In order to avoid error, digestion and detection was done three times and results were expressed in ppm.

Results and Discussion

Heavy metals in water

The level of heavy metals in the water of river Basantar showed both seasonal as well as spatial variations during the study period of one year 2018-2019.

Lead

In river Basantar, concentration of Pb varied from lowest i.e; below detection level -1.4 ± 1.21 ppm during monsoon to the highest 3.43 ± 0.12 ppm during summer season. Spatial distribution of Pb at different stations revealed minimum concentration at station I (0.78 ± 1.24 ppm) and maximum concentration at station II (1.81 ± 1.02 ppm) (Table 1 & Fig. 2a). However, its concentration remained above the optimum limits of WHO (Ramchander *et al.,* 2015).

Table 1. Seasonal variations in concentration (ppm) of Lead in water at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	1.66	2.54	2.45	2.21 ± 0.48
Summer	3.31	3.56	3.43	3.43 ± 0.12
Monsoon	–2.71	–0.31	–1.18	–1.4 ± 1.21
Winter	0.88	1.51	1.00	1.1287 ± 0.33
Mean ± SD	0.7 ± 1.24	1.81 ± 1.02	1.38 ± 1.22	1.345 ± 0.512

Zinc

Mean values of Zn revealed summer maxima 2.59 ± 0.624 ppm and monsoon minima 0.176 ± 0.193 ppm. While the station wise assessment recorded the mean values to fluctuate from minimum of 0.59 ± 1.07 ppm at station I to maximum of 1.32 ± 1.49 ppm at station II (Table 2 & Fig. 2b). Concentration of Zn was found within the permissible limit of 3ppm (WHO, 2011).

Copper

Temporal mean variations in Cu concentration in Basantar river revealed higher concentration of 0.6344 ± 0.034 ppm during summer season while its complete absence was recorded during monsoon season. Along the profile at selected stations, the mean values fluctuated from minimum of 0.182 ± 0.28 ppm (station I) to maximum of 0.20 ± 0.30 ppm (station II) (Table 3 & Fig. 2c).However, its value was recorded within the permissible limit of as recommended by WHO (Ramchander *et al.,* 2015).

Iron

During the one year study, the level of Fe in water samples depicted certain variations. Its mean values were recorded highest (0.5854 ± 0.120 ppm) during summer season and lowest (0.0594 ± 0.080 ppm) during monsoon season. Spatial variation in concentration of iron along the profile of river Basantar revealed its mean highest value at station II (0.41 ± 0.30 ppm) and mean lowest value at station I (0.22 ± 0.29 ppm) (Table 4 & Fig. 2d). Moreover, when compared with the standard limits of WHO (2011) concentration of Fe remained above the permissible value of 0.2 ppm.

Table 2. Seasonal variations in concentration (ppm) of Zinc in water at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	0.33	1.60	0.53	0.8186 ± 0.679
Summer	2.11	3.30	2.38	2.59 ± 0.624
Monsoon	-0.38	0.00	-0.15	0.176 ± 0.193
Winter	0.30	0.37	0.33	0.334 ± 0.03
Mean ± SD	0.59 ± 1.07	1.32 ± 1.49	0.77 ± 1.11	0.97 ± 0.38

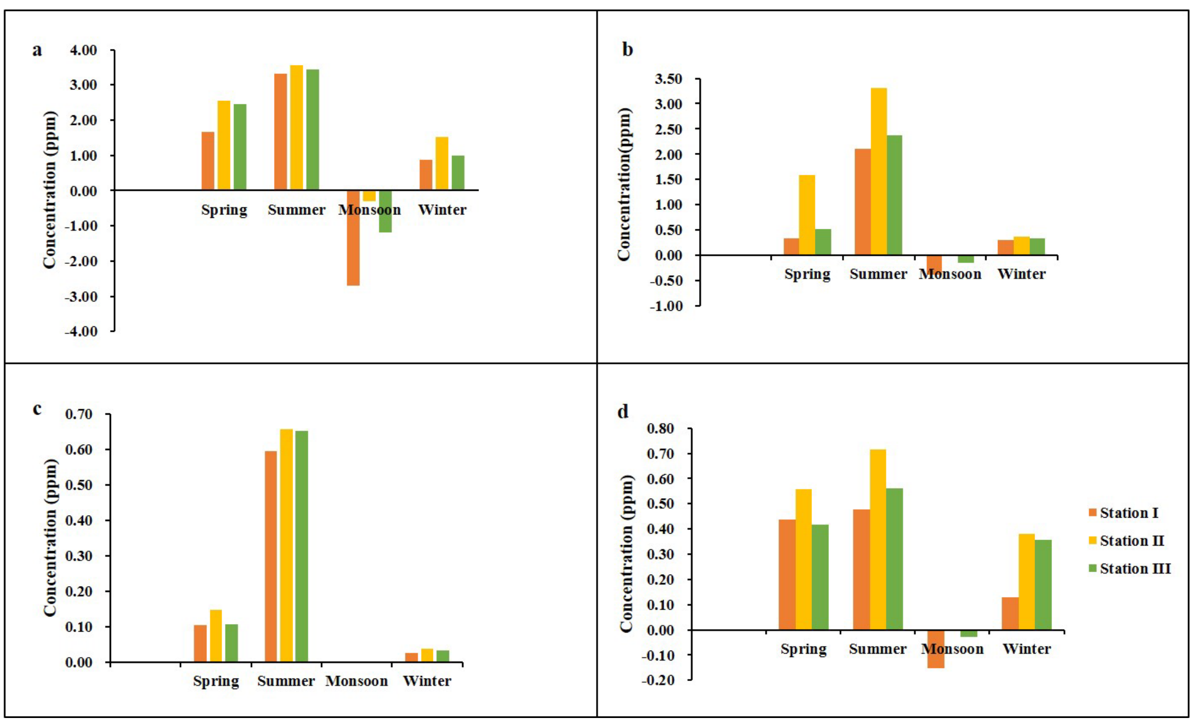

Fig. 2. Seasonal variations in concentration (ppm) of various heavy metals in water at selected stations of river Basantar (a) Lead (b) Zinc (c) Copper (d) Iron

Table 3. Seasonal variations in concentration (ppm) of Copper in water at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	0.11	0.15	0.11	0.0776 ± 0.023
Summer	0.59	0.66	0.65	0.6344 ± 0.034
Monsoon	0.00	0.00	0.00	0.00
Winter	0.03	0.04	0.03	0.0022 ± 0.005
Mean ± SD	0.18 ±0.28	0.2 ± 0.30	0.19 ± 0.31	0.196 ± 0.009

Table 4. Seasonal variations in concentration (ppm) of Iron in water at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	0.44	0.56	0.42	0.470 ± 0.076
Summer	0.48	0.72	0.56	0.5854 ± 0.120
Monsoon	-0.15	0.00	-0.03	0.0594 ± 0.080
Winter	0.13	0.38	0.36	0.2894 ± 0.137
Mean ± SD	0.22 ± 0.29	0.41 ± 0.30	0.32 ± 0.25	0.35 ± 0.095

Heavy metals in sediments

Lead

Temporal analysis of heavy metals in sediments of river Basantar revealed high concentration of Pb than water and its annual values fluctuated from minimum of Below Detection Limit (BDL) - 2.7 ± 0.05 ppm during monsoon season to a maximum of 4.07 ± 0.017 ppm during summer season. While the spatial analysis of Pb revealed its mean value to fluctuate from minimum of 2.32 ± 2.06 ppm at station I to maximum of 2.52 ± 2.19 ppm at station II (Table 5 & Fig. 3a). However, its concentration remained above the permissible limit viz. 0.01 mg/l (WHO, 2011).

Zinc

Seasonal variations in mean concentration of Zn in river sediments also revealed summer maxima of 3.5328 ± 0.3311 ppm and monsoon minima of 1.4521 ± 0.4435 ppm. Station wise distribution of Zn at different stations revealed maximum concentration of Zn at station II (3.035± 0.8936 ppm) and minimum at station I (2.3073 ± 1.1004 ppm) (Table 6 & Fig. 3b). Level of Zn in sediments was found within the permissible limit of 5ppm (WHO, 2011). Moreover, the concentration of Zn was found higher in sediments than water.

Copper

Its concentration varied from lowest i.e; BDL -0.476 ± 0.0852 (monsoon season) to the highest 4.0680 ±

Table 5. Seasonal variations in concentration (ppm) of Lead in sediments at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	2.5455	3.3091	3.0545	2.97 ±0.3888
Summer	4.0631	4.0925	4.0631	4.07 ± 0.0170
Monsoon	–2.7127	–2.7599	–2.6655	–2.7 ± 0.05
Winter	-0.0163	-0.0443	-0.0373	–0.04 ± 0.01
Mean ± SD	2.32± 2.06	2.52± 2.19	2.43± 2.13	4.3±0.1016

Table 6. Seasonal variations in concentration (ppm) of Zinc in sediments at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	3.1698	3.3998	3.2000	3.2565± 0.1250
Summer	3.2358	3.8898	3.4727	3.5328± 0.3311
Monsoon	0.9520	1.7975	1.6068	1.4521±0.4435
Winter	1.8716	3.0550	1.9494	2.292±0.6619
Mean ± SD	2.30 ± 1.10	3.03 ± 0.89	2.55± 0.91	2.63± 0.37

2.9227 ppm (summer season). Spatial variation in concentration of Cu along the profile of river Basantar revealed its mean highest values at station II (1.76 ± 3.14 ppm) and mean lowest values at station I (0.21 ± 0.48 ppm) (Table 7 & Fig. 3c). However, during most of the seasons concentration of Cu remained within the acceptable limit 2.02(WHO, 2011) except summers when its value reached upto 5.0215 ppm at station III and 6.3950 ppm at station II.

Iron

In sediments of river Baantar, seasonal Fe concentration revealed summer maxima of 56.567 ± 1.0350 ppm and monsoon minima of 27.711 ± 0.0409 ppm. While the station wise analysis revealed its mean highst concentration at station II (41.38 ± 14.15 ppm) and mean lowest concentration at station I (36.467 ± 13.12 ppm) (Table 8 & Fig. 3d). It was found that the concentration of Fe in sediments was much more than the permissible limits 0.3 ppm (WHO, 2011). The possible reason for highest concentration in sediments may be its abundance in earth crust (Radulescu *et al.,* 2014).

It was observed that both water as well as sediments showed elevated values of heavy metals viz. Pb, Cu, Fe and Zn during the summer season of study period (2018-2019) which may be due to decrease in water level because of more evaporation. During monsoon months river Basantar seems to remain heavily flooded which leads to drop in the concentration of metals due to dilution. Moreover, excessive extraction of river water for more demand during summer months and addition of polluted water (Industrial waste) and sewage also accounts for increase in heavy metal concentration in the presently studied water body (Collvin, 1985; Gupta *et al.,* 2009). At station III the presence of modern industrial complex SIDCO comprising of several industrial units, like metal work industries that deals in old batteries and lead indigos, paint industries, chemical industries, pharmaceutical industries, fertilizer industries, chemical steel rolling mill, wire industries, electrical spare part industries along with automobile spare-part laboratory etc. and their direct discharge rich in heavy metals is responsible for enhancing their level in this stretch of river. While station III & I are quite away from the industrial discharge point & thus are not under direct influence which thereby speaks of their low concentration in both water as well as sediments. A comparative investigation of heavy metal absorption in both water and sediments clearly reveals their high value in sediments than in water which may be due to the fact that sediments act as sinks for heavy metals.

Heavy metals in fish muscles

In river Basantar, *Labeo rohita* was found only at stations I and III and remained completely absent from station II. Concentration of heavy metal viz; Pb, Cu, Zn and Fe when detected in the muscles of *Labeo rohita* revealed certain variations (Table 9). Along the longitudinal profile of river Basantar, concentration of Pb in the muscle of *Labeo rohita* was recorded as 1.50 ppm, Cu as 0.25 ppm, Zn as 1.28 ppm and Fe as 3.92 ppm at station I while at station III Pb was found to be 2.71 ppm, Cu – 1.08 ppm, Zn – 1.52 ppm

Table 7. Seasonal variations in concentration (ppm) of Copper in sediments at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	0.3311	0.9300	0.3913	0.5507 ± 0.3298
Summer	0.7877	6.3950	5.0215	4.0680 ± 2.9227
Monsoon	-0.3786	-0.5385	-0.5137	“0.476 ± 0.0861
Winter	0.1005	0.2708	0.1897	0.187 ± 0.0852
Mean ± SD	0.21±0.48	1.76±3.14	1.27±2.52	1.082 ± 0.79

Table 8. Seasonal variations in concentration (ppm) of Iron in sediments at selected stations of river Basantar

	Station I	Station II	Station III	Mean ± SD
Spring	34.7522	48.7132	39.9459	41.1431± 7.0563
Summer	55.5300	57.6000	56.5650	56.5674± 1.0350
Monsoon	27.6850	27.7583	27.6901	27.711±0.0409
Winter	27.9025	31.4536	29.4586	29.6049±1.7801
Mean ± SD	36.46±13.12	41.38±14.15	38.41±13.25	38.75±2.476

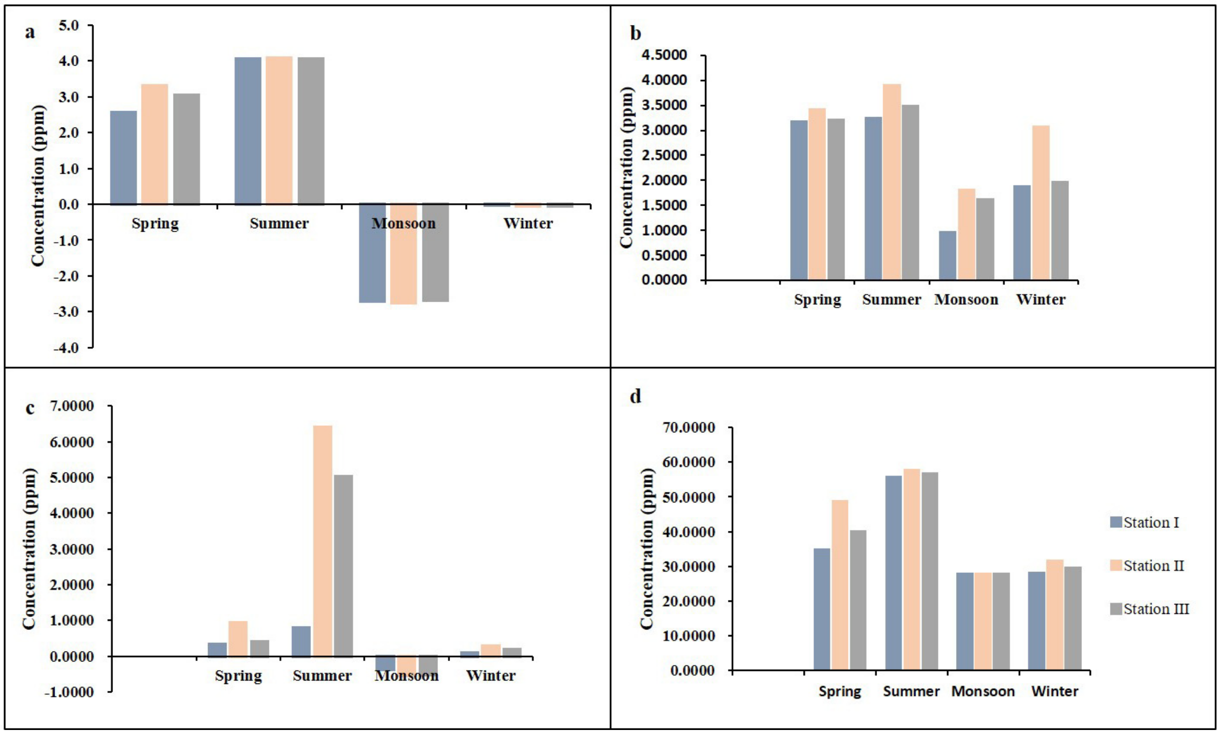

Fig. 3. Seasonal variations in concentration of Various heavy metals in sediments at river Basantar (a)Lead (b) Zinc (c) Copper (d) Iron

and Fe – 4.87 ppm. The mean values of Pb, Cu, Zn and Fe were found to be 1.40 ± 0.85 ppm, 0.44 ± 0.58 ppm, 0.93 ± 0.17 ppm and 2.93 ± 0.66 ppm respectively (Table 9). The above data indicated that Fe was maximally and Cu was minimally accumulated in the muscles of *Labeo rohita.* Finally mean concentration of heavy metals found in edible part of fish when compared to the permissible values provided by WHO (1989) indicated that the concentration of Pb & Zn was higher than the acceptable limits whereas mean values of Cu & Fe were found within the optimum values. The metal concentration in the muscles of *Labeo rohita* were in the decreasing order of Fe > Pb > Zn > Cu. The rate of accumulation of heavy metals in fish depends on various factors such as size, season, feeding habit, ability for metal digestion, reproductive cycle and environment (Usman *et al.,* 2017; Ogueri *et al.,* 2018).

Bio-Accumulation Factor (BAF)

It is the ratio of the contaminant in an organism to the concentration in the environment at steady state, where the organism can take in the contaminant through ingestion with its food as well as through content (Friday *et al.,* 2013). BAF when calculated for different heavy metals from water was found to be 1.04 ppm (Pb), 2.29 ppm (Cu), 0.95 ppm (Zn) and 8.35 ppm (Fe) while BAF from sediments was 0.58 ppm (Pb), 0.42 ppm (Cu), 0.36 ppm (Zn) and 0.08 ppm (Fe). On the basis of BAF, the order of accumulation of heavy metals in *Labeo rohita* was Fe > Cu > Pb > Zn from water and Pb > Cu > Zn > Fe from sediments (Tables 10-11). The present results clearly confirmed that BAF of heavy metals in the muscles

Table 9. Heavy metal concentration (ppm) in muscles of *Labeorohita* at selected stations of river Basantar

	Station I	Station II	Station III	MEAN ± SD
Lead	1.50955	–	2.7122	1.4072 ± 0.85
Copper	0.2599	–	1.089	0.4496 ± 0.58
Zinc	1.28625	–	1.52902	0.9384 ± 0.17
Iron	3.9282	–	4.8704	2.9328 ± 0.66

Table 10. Bioaccumulation Factor (BAF) of Heavy metals in muscles of *Labeo rohita* at selected stations of river Basantar

Heavy metals	Water	Fish Muscles	BAF
Lead (Pb)	1.3453	1.4072	1.04
Copper (Cu)	0.196	0.44965	2.29
Zinc (Zn)	0.9796	0.9384	0.95
Iron (Fe)	0.351	2.9328	8.35

Table 11. Bioaccumulation Factor (BAF) of Heavy metals in muscles of *Labeo rohita* at selected stations of river Basantar

Heavy Metals	Sediments	Fish Muscles	BAF
Lead (Pb)	2.44	1.4072	0.58
Copper (Cu)	1.0822	0.44965	0.42
Zinc (Zn)	2.6335	0.9384	0.36
Iron (Fe)	38.75	2.9328	0.08

from sediments was lower than from water and the plausible reason for this may be due to its feeding habits (omnivorous/column feeder) which change from fingerling stage onwards and also depends on other factors like size, season, reproductive cycle and environment (Sawsan *et al.*, 2016). Since fish is known to be column feeder, so its contamination of heavy metals is maximum from water and minimum from sediments.

Conclusion

The study of heavy metal (Pb, Zn, Cu and Fe) contamination on Basantar river indicated that in both water and sediments concentration of Pb & Fe was found beyond the permissible limits, whereas Cu and Zn was found within the permissible limits as recommended by WHO. While in *Labeo rohita* level of Pb and Zn was observed higher than the permissible limits and Cu and Fe were found within the acceptable limits of WHO. However, restriction of *Labeo rohita* at station III and I and its complete absence at station II during the whole year clearly indicates that at station II the conditions are not favourable for the survival of biota as it received direct industrial discharge. The order of concentration of heavy metals in water, sediment and muscles of *Labeo rohita* was: Pb> Zn> Fe > Cu; Fe > Zn > Pb > Cu and Fe > Pb > Zn > Cu respectively. In water body concentration of metals become gradually accumulated on the sediments and in due course gets transferred to fish[33]. As fish contribute as important component of human diet, these metals find direct entry into the human body which may lead to disorders like irregularity in blood composition, neurotoxicity and badly affected vital organs like kidney, liver etc. if ingested over long period of time. The present study thus suggests that strict methods of management should be adopted to check the increased industrial load rich in heavy metals and entry of raw waste in the river.

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Conflict of Interest

The authors declare no conflict of interest.

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