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Assessment of spatio-temporal variation of heavy metals in Tunga reservoir at Gajanur, Karnataka

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Abstract
Surface water samples from Tunga reservoir at Gajanur were analyzed quantitatively for the estimation of five heavy metals such as Iron, Manganese, Lead, Copper and Zinc using atomic absorption spectrophotometer (AA 240 FS, Varian) under specific wave lengths. The values of metals analysed found in the increasing order as follows: Cu (0.9%), Mn (9%), Fe (9%), Pb (12%) and Zn (69%). Metals studied are found throughout the study period confirming that heavy metals are naturally occurring in water. The probable sources of heavy metals in Tunga Reservoir are lithogenic, anthropogenic and agricultural runoff. Hence, very low concentrations of heavy metals were recorded which lies within the acceptable limits of BIS and WHO. The data obtained has been statistically analysed for mean, standard deviation and standard error by using SPSS 16.0 package in Microsoft office excel 2007. Inter relationships among the heavy metals has been worked out by adopting Karl Pearson's correlation coefficient using SPSS 10.0 software. The results revealed that, as such no ecological risk to humans from the waters of the reservoir.

Keywords: Tunga reservoir, Gajanur, heavy metals

Introduction
Reservoirs are built across the rivers for flood control, drinking water supply, irrigation and power generation where, they serve as a sink for the accumulation of water along with inorganic elements, organic nutrients and heavy metals. Irrespective of the size of the reservoirs, tropical climate of very high temperature coupled with adequate rainfall throughout the year results in increased rate of leaching in the upstream area causing transportation and deposition of heavy metals (Fonsea *et al.*, 2011) [4]. Positively charged metallic elements figured in group 1 to 3 of periodic table with a density greater than 5 are referred as heavy metals. Source of heavy metals in aquatic environment include geological formations, industrial, agricultural, pharmaceutical, domestic effluents and environmental pollution. They naturally occur through bio-geochemical cycles (Garrett, 2000) [18]. In the transformed scenario of the environmental conditions due to excessive use of agro fertilisers for long time, the heavy metals are being accumulated in soils and reach the aquatic system by a process of leaching which cause threat to human life (Nicholson *et al.*, 2003) [15]. Heavy metal contamination in aquatic ecosystems is increasing due to the impact of urbanisation and industrialisation (Sekabira *et al.*, 2010, Bai *et al.*, 2011, Martin *et al.*, 2015) [22, 3, 9]. Water becomes toxic when contaminated with higher concentration of heavy metals and cause acute impact on the aquatic organisms (Ginguere *et al.*, 2004) [6]. The presence and biologically non-degradable nature of heavy metals in water is responsible for toxicity and can cause pollution (Gale *et al.*, 2004) [5]. Being toxic heavy metals affect the plant growth in lotic ecosystems therefore, it is very much required to protect the soil without allowing it to contaminate by heavy metals which facilitate the non entry of such heavy metals in to the food chain thereby bio accumulation and bio magnification of heavy metals can be avoided. The evaluation of heavy metals in fresh water is used as a tool to assess the impact of industrial and anthropogenic activities which intern affect the lotic ecosystems (Zheng *et al.* 2008, Saleem *et al*, 2015) [31, 20]. Rivers play a very important role in the transportation of sewage, effluents and also surface runoff from agricultural and mining area.

Although a report is available on the assessment of water quality of Gajanur reservoir by the enumeration of physico chemical properties and bacteriological population (Prathibha and Murulidhar, 2018) [17] no scientific reports are found to date regarding the heavy metal pollution in waters of Gajanur reservoir. Therefore, an investigation was initiated with an objective of examining the concentrations of heavy metals in surface waters of River Tunga at Gajanur reservoir.

Materials and Methods

Study area

Table 1: Morphometric Features of Tunga Reservoir at Gajanur

Sl No	Morphometric Features	Dam after the Upper Tunga Project (2004 onwards)
1	Bund Length	364.8 m
2	Bund Width	5.5 m
3	Bund Height	584.04 m
4	Storage capacity	3244 mcft
5	Catchment area	2240 sq km

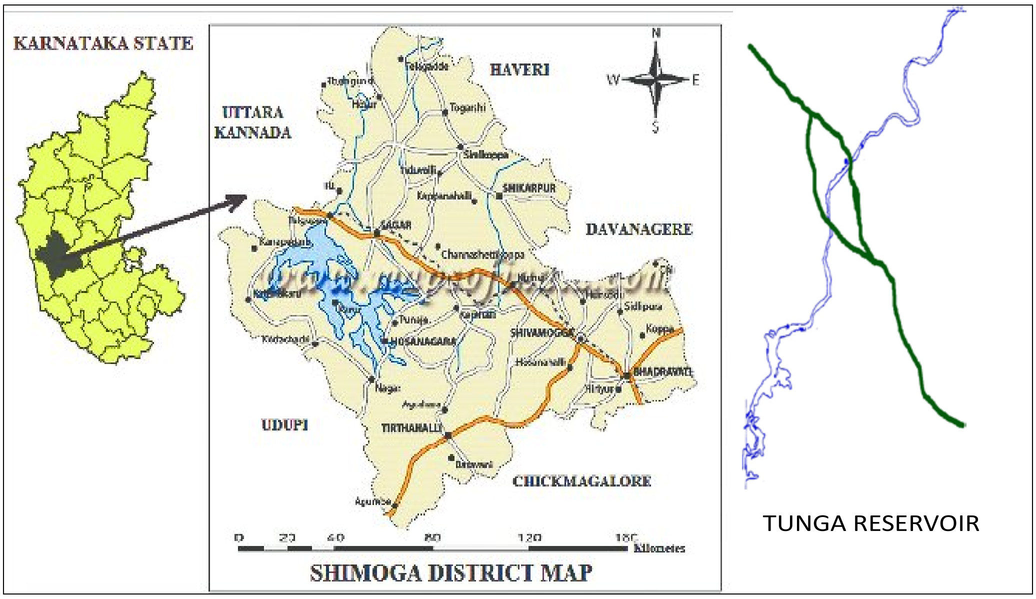

Fig 1: Study Area

Reservoir is constructed near Gajanur at a distance of 14.5 kilometers from Shimoga city between $13^{0}15^{I}$ North latitude and $75^{0}31^{I}$ East longitude across the River Tunga, which takes its origin in a place called Gangamoola of Chikkamagalur district on a hill-Varaha Parvata in Western Ghats of Karnataka and flows from the place of its origin to a distance of 130 kilometers across Shringeri, Koppa and Teertahalli before it reaches the reservoir at Gajanur. Table-1 gives the morphometric features of the reservoir. The catchment area constitutes hilly terrain with tropical deciduous and shrub jungle forest with an average annual rainfall ranges from 762 mm to 10795 mm. Upstream of the reservoir is unpolluted non discharge area and receives natural runoff. It is an S-shaped reservoir with 22 not so huge crest gates built in 1972 mainly to provide irrigational possibilities, flood controlling purpose and also as a source of drinking water for the people of Shimoga city and other adjoining rural areas. It is surrounded by lush green fields, plantations and forest with marginal emergent plants like *Marsilea quadrifolia*, *Cyperus rotundus*, *Polygonum hydropiper*, *Ipomoea aquatica* etc. The present study was conducted for a period of two years in order to assess the water quality of River Tunga in Gajanur reservoir by analysing the water samples for heavy metals such as Iron, Manganese, Lead, Copper and Zinc.

View of Reservoir outlet

Satellite View of Reservoir

Sampling & Analysis of water

Water samples were collected on monthly intervals for the analysis of heavy metals at a depth of one foot below the surface randomly at different places of the reservoir using plastic cans of two litres capacity and later mixed thoroughly for composite sampling. Standard methods of APHA (1995) [1] were followed during sampling, transportation and analysis of water samples. A litre of water is collected from a composite sample in a plastic container and preserved in deep freeze at -15 ± 5 °C with 2 ml /l of concentrated Nitric acid. 200 ml of water sample was digested using 5 ml of acid mixture (HNO_3 and $HClO_4$ in the ratio of 9:4) in a hot water bath. Later samples were filtered through Whatman No.42 filter paper and the volume is made up to 50 ml with distilled water. The samples were analysed for heavy metals using atomic absorption spectrophotometer (AA 240 FS, Varian) under specific wave lengths as follows; Iron - 279.5 nm, Manganese - 279.5 nm, Lead - 217 nm, Copper - 324.8 nm and Zinc - 213.9 nm. The data obtained was statistically analysed for mean, standard deviation and standard error by using SPSS 16.0 package in Microsoft office excel 2007. Inter relationships between the heavy metals and physico - chemical parameters was worked out by adopting Karl Pearson's correlation coefficient using SPSS 10.0 software.

Table 2: Descriptive Statistics of Heavy Metals

Sl No	Heavy Metal	Minimum	Maximum	Mean	Std Dev	Std Error
1	Iron	0.00	0.050	0.015	0.011	0.0023
2	Manganese	0.0	0.030	0.012	0.0051	0.0010
3	Lead	0.0	0.020	0.0096	0.0046	0.0010
4	Copper	0.001	0.001	0.0010	3.3061	6.753
5	Zinc	0.0	0.1	7.708	4.164	8.501

Table 3: Seasonal Variations of Heavy Metals

Sl No	Heavy Metals	Summer	Rainy	Winter
1	Iron	0.01 ± 0.02	0.01 ± 0.0	0.01 ± 0.01
2	Manganese	0.01 ± 0.0	0.02 ± 0.01	0.01 ± 0.0
3	Lead	0.01 ± 0.0	0.01 ± 0.0	0.01 ± 0.01
4	Copper	0.001 ± 0.0	0.001 ± 0.0	0.001 ± 0.0
5	Zinc	0.08 ± 0.05	0.09 ± 0.02	0.06 ± 0.05

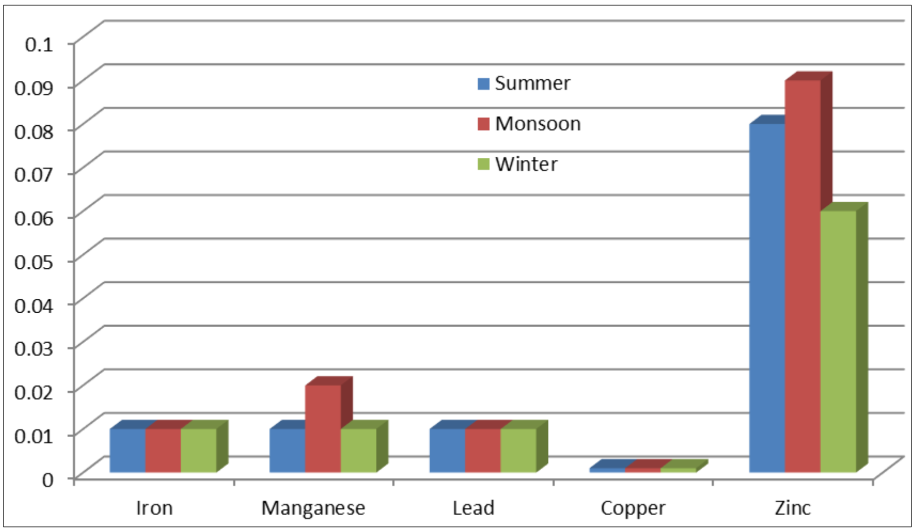

Fig 2: Seasonal Variations of Heavy Metals [mg/l]

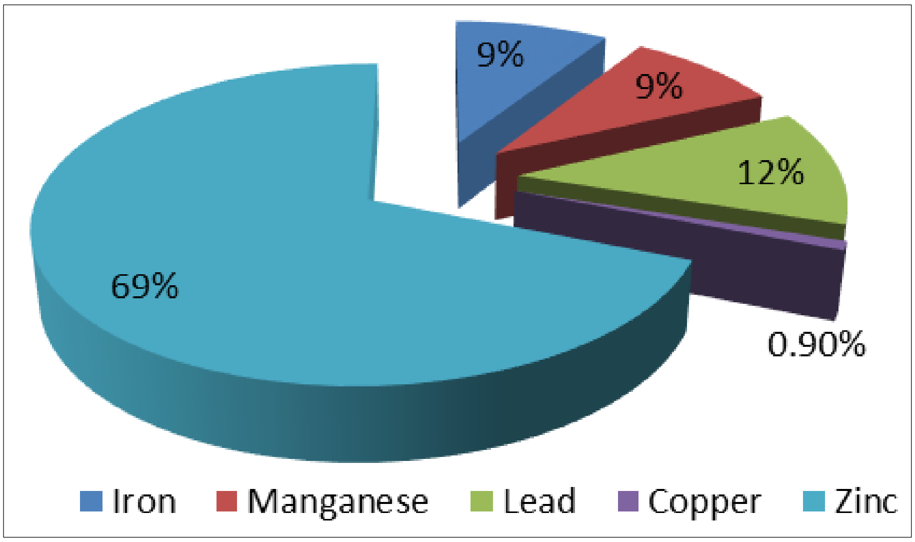

Fig 3: Relative Concentration of Heavy Metals

Table 4: Correlation Trends of Heavy Metals with Physico-Chemical Parameters

Sl No	Heavy Metal	Significant Positive Correlation	Significant Negative Correlation
1	Iron	Turbidity, Electrical Conductivity, Chloride, Total Solids, Total Hardness, BOD	PH, COD
2	Manganese	PH, Alkalinity, Sulphate, Phosphate, Sodium	Air & Water Temperature, Turbidity, Dissolved Solids, BOD, COD, Magnesium
3	Lead	Sulphate, Sodium	Air & Water Temperature
4	Copper	--	--
5	Zinc	Electrical Conductivity, Dissolved Oxygen, Calcium, Sulphate, Lead	--

Results and Discussion

Surface water samples collected were analysed for heavy metals and the range, mean, standard deviation and standard error of metals have been presented in table-2. Seasonal variations of the heavy metals were presented in table-3 and represented in figure-2. Correlation trend of heavy metals with water quality parameters fallowed by Karl-Pearson's matrix is shown in table-4. Out of the ten heavy metals investigated Arsenic, Cadmium, Mercury, Chromium and Nickel were totally absent which is due to absence of chemical industries responsible for heavy metal pollution along the upstream area of the river stretch. The values of metals analysed found in the increasing order as follows: Cu (0.9%), Mn (9%), Fe (9%), Pb (12%) and Zn (69%). Metals studied are found throughout the study period confirming that, heavy metals are naturally occurring in water. Similar observations have been made by Siong *et al.,* (2016) [23] while working on tropical hydroelectric dam in Sarawak, Malaysia. The probable sources of heavy metals in Tunga reservoir at Gajanur are lithogenic, anthropogenic and agricultural runoff. Hence, very low concentrations of heavy metals are seen and lies within the permissible limits of BIS and WHO.

Iron

Iron is one of the most abundant elements of the rocks and soil. Water bodies generally have higher concentrations of iron at the bottom due to the prevailing reducing conditions. Iron in excess of 0.3 mg /l causes staining of clothes and utensils and also causes vomiting in human beings. Iron in the present investigation constitutes 9% of the total heavy metal concentration and remains same in its concentration with that of Manganese (Figure-3).The values of iron varied from 0.0 to 0.05 mg /l with a mean of 0.015 mg /l (Table-2) and found within the permissible limits of WHO (0.1mg /l) and BIS (0.3 mg /l). Similar observations were been made by Jakir Hussain *et al.*, (2017) [8] while working on heavy metal contamination in Godavari river. Periodically the mean value of iron remained 0.01 mg/l in all the seasons (Table-2) which is contrary to the findings of Wasim *et al.* (2010) [10] who have recorded highest values of iron during winter season from river Ganga around Kolkata where, they have attributed this to the dilution during rainy season followed by the formation of metal chelates during winter. Concentrations of Iron showed positive correlations with the concentrations of physico - chemical parameters of the water such as turbidity, electrical conductivity, chloride, total solids, total hardness and biological oxygen demand, whereas PH and chemical oxygen demand showed a negative bearing on the concentrations of iron (Table - 4).

Manganese

Manganese, a copious metal on earth's crust found in association with iron compounds is indispensible for operational activity of the enzymes pyruvate carboxylases, dismutases, kinases, transferases, hydrolases and exists in 11 oxidative states (USEPA, 1994) [27]. Manganese in soil is mainly contributed by human activities, will erode in to surface waters and occurs in both dissolved and suspended forms (ATSDR, 2000) [2]. Manganese in drinking water is objectionable however, concentration below 0.05mg/l is acceptable subject to the local circumstances. Manganese concentration in waters of Tunga reservoir ranged between 0.0 to 0.030 mg/l with a mean value of 0.012 mg/l (Table-2) contrary to this Siong Fong Sim *et al,* (2016) [23] recorded higher concentrations of Manganese in Sarawak Dam, Malaysia. Similarly, Md. Wasim Aktar *et al.* (2010) [10] have recorded higher values of manganese in the range of 0.022 to 1.78 mg/l from Ganga River near Kolkota. Seasonally Manganese remained high during rainy and that of minimum was recorded during summer and winter (Table-3, Figure-2) may be due to agricultural runoff which is in conformity with the findings of Md. Wasim Aktar *et al.*, (2010) [10]. Table-4 of correlation trend according to Karl Pearson's correlation matrix revealed that physico-chemical parameters such as PH, alkalinity, sulphate, phosphate and sodium have a direct bearing on the concentration of manganese whereas, the concentration of manganese established a negative bearing with air and water temperature, turbidity, dissolved solids, biological oxygen demand, chemical oxygen demand and magnesium.

Lead

Lead is one of the commonly available toxic heavy metals found in the environment with no significant metabolic function either in plants or in animals and highly persistent in soils. Lead has a long term tendency to remain accessible to accumulate in the food chain. Lead is very toxic and accumulates in bones, brain, kidney and muscles of human body (Trivedy and Goel, 1984) [26]. It damages gastrointestinal and urinary tracts resulting in neurological disorder and brain damage. Concentration of Lead is varied between 0.0 to 0.020 mg/l with a mean value of 0.0096 mg/l (Table-2) owing to non discharge of any type of effluents in to the reservoir. In variance with our studies, Jakir Hussain *et al.,* (2017) [8] recorded maximum values of Lead (7.41 mg/l) much higher than the permissible limit from Godavari river. Similar findings were recorded by Harvey *et al.* (2015) [7] from Rupsha river and attributed it to the discharge of industrial and agricultural effluents. In the present investigation lead did not show significant difference among different seasons where it recorded 0.01 ± 0.0 mg/l in all the three seasons (Table-3 and Figure-2) whereas, Smriti Dwivedi and Tiwari (1997) [24], Solanki Hitesh and Pandit (2000) [25] and Saeed Shanbehzadeh *et al.* (2014) [19] observed high lead contents during summer and low during monsoon season. Similarly in variance with our findings Mohammad Ali *et al. (*2016) [11] have recorded 9.85 mg/l of lead during summer and according to toxicity reference value proposed by USEPA (1999) [28] they are of the opinion that the water of the river is unsafe for drinking and cooking which is not so in our studies. It is evident from table-4 that, concentration of Lead is positively correlated to Sulphate and Sodium at significant level whereas, its negative correlations were observed with air and water temperatures.

Copper

Copper is an essential trace element widely distributed in nature and rarely present in natural waters. Copper exists in soluble, particulate and colloidal forms in aquatic environments and is required for metabolic pathways. Mining, chemical weathering, steel production, agricultural practices and sewage are some of the sources of copper to natural waters. The concentration of copper beyond the permissible limit of 50 mg/l as laid down by BIS causes sporadic fever, hypertension and coma in human beings which turns in to carcinogenic or mutagenic in nature (Moore and Rama Moorthy 1984) [12]. Copper being a chief constituent of cytochrome oxidase and chlorophyll plays a significant role in plant metabolism. Dwivedi and Tiwari (1997) [24], Pande and Sharma (1998) [16] observed high content of Copper in the water bodies of their investigation. However, no such high Copper concentration was observed in the present study due to the absence of industrial effluents. Descriptive statistics of Copper is represented in Table-2. Very low concentration of Copper recorded in Tunga reservoir indicates that there is no significant source of pollution contrary to this Wang *et al.*, (2009) [29] recorded highest value of 114.84 mg/l from river Waingana and attributed it to the inlet of domestic sewage and farm runoff. The Copper contents in the present study showed no difference between seasons (Table-3 & Figure-2) whereas contrary to this Dwivedi and Tiwari (1997) [24] observed summer maxima. Figure - 3 represents the relative abundance of heavy metals which revealed that copper ranks the lowest of all other heavy metals investigated. Further, copper did not establish either positive or negative correlations with physico - chemical parameters at significant level (Table-4).

ZINC

It is one of the important trace elements primarily occurs in the form of silicates and oxides and plays a vital role in physiological and metabolic processes of organisms. Zinc enters water during chemical weathering of silicates and oxides. At high concentrations Zinc inhibits the growth of algae (Say & Whitton, 1978) [21]. At still higher concentrations it is toxic to organisms and imparts bitter taste to water. In the present investigation though, zinc is found to be the abundant metal it lies within the permissible limits of 5 mg/l as recommended by BIS for potability. Contrary to our results Munshi and Singh (1989) [13] and Munshi *et al*., (1989) [14] have recorded high concentrations of zinc (182 mg/l) in Subernarekha river water and they opined that the discharge of industrial waste from Hindustan Copper limited is responsible for high content of Zinc. Table-2 describes the descriptive statistics of zinc and it is evident from Table-3 that no significant difference was found with regard to concentration of zinc among the seasons which is confirmed by figure-2. Zinc recorded relatively higher concentrations than any other metals analyzed (figure-3). Water quality parameters such as electrical conductivity, dissolved oxygen, calcium, lead, sulphate showed direct bearing on the concentrations of Zinc at significant level (Table-4).

Conclusion

Based on the results Zinc is found to be abundant among the five metals analyzed and all the metals analyzed found within the permissible limits of drinking water standards laid down by BIS. Hence, concluded that there is no toxicity of these metals in reservoir waters. Metals studied are found throughout the study period in all the samples confirming that heavy metals are naturally occurring in waters of the reservoir and found in very low concentrations.

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