Human and Ecological Risk evaluation of Toxic Metals in the Water and Sediment of River Cauvery

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Abstract- The River Cauvery is considered to be the main source of drinking water supply. Deterioration of drinking water quality continues to be a major problem. Hence, the present study aimed at analyzing toxic metals such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni) and Lead (Pb) using Atomic Absorption Spectrophotometer in the surface water and sediment collected from twenty different locations of river Cauvery. The mean concentrations of Pb, Cr and Cd in water exceeded the permissible limit and concentrations of Ni, Cr and Pd showed contamination of sediment samples of river Cauvery. The study on the Pollution Load Index (PLI) has also confirmed low to moderate level of contamination. The correlation between metals and hazard quotient revealed significant health risk to the local human population by Pb through intake of water. Acute risk to aquatic organisms due to Pb and Cd concentration in water from the study area is also predicted.

Index Terms- Heavy Metals; Water; Sediment; Health Risk; Ecological Risk Quotient

I. Introduction

Drinking water is constantly associated with multitude of health-related concerns as a result of contamination by both chemical and biological pollutants. Due to the adverse effects on human and the environment, chemical pollutants such as heavy metals, pesticides, PCBs, PAHs are of foremost importance. Over the last few decades heavy metal pollution in rivers has become a matter of great concern, not only because of the threat to public water supplies, but also the risk arising due to human consumption of fishery resources as a result of accumulation through food chain (Terra *et al.*, 2008). Elevated levels of heavy metals in rivers, lakes and ponds are considered to be precarious because they are the main source of drinking water as well as habitat for aquatic ecosystem in the developing countries (Ochieng *et al.*, 2008). The occurrence of metals in the aquatic environment may cause potential threat to aquatic life and cause severe toxicity to the aquatic ecosystem since most of the organisms are not adapted to contract them when they prevail in such an environment above the threshold concentrations (Hodson, 1981; Turner *et al.*, 1986). The essential metals available in the aquatic environment are taken up by fish through water, food and sediment. However, similar to essential metals, non- essential ones are also taken up by fish and accumulated in their tissues (Kalay and Canli, 2000). The surface sediment contamination with metals could directly influence the quality of water resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health. Sediments act as sinks and sometimes potential sources of various contaminants in aquatic systems (Christophoridis *et al.*, 2008).

Most of the heavy metals are extremely toxic because, as ions or compounds, they are soluble in water and can be readily accumulated into plant or animal tissue (Kennish, 1992). They displace the vital elements thereby hindering their biological function. At the present it is impossible to live in an environment free of heavy metals. There are many ways by which these toxins can be introduced into the body such as consumption of foods, beverages, skin exposure, and the inhaled air. To the general population, the dietary intake is the main exposure pathway. The high exposure of these metals through any means of dietary intake will have confirmative negative effects to human health (Pan *et al.*, 2013). The risk assessment of heavy metal ions in human even at trace levels is important, especially in the occupational and environmental exposure to toxic metals (Sung and Huang, 2003).

The study was carried out in the River Cauvery. The River Cauvery flows through a densely populated area from the Coorg in the Western Ghats to the river mouth at the Bay of Bengal. River Cauvery covers a drainage area of approximately 90,000 Sq.Km. in the southern part of the Indian sub-continent. The urbanized cities such as Erode, Karur, Tiruchirappalli, Thanjavur and Kumbakonam situated on the bank of River Cauvery in Tamil Nadu may contribute a huge load of municipal sewage and industrial effluents. Metals have also been found to be used in various industries such as electroplating, ceramics, dyeing and fertilizers used in the agricultural field. Many Dyeing industries are located on the bank of the Cauvery River. Industries in Kadayampatty, Komarapalayam, Erode and Pallipalayam, through which the Cauvery flows, discharge huge quantities of effluents into the river and pollute it. Due to the degree of heavy metals present in the modern dyes, even in low concentration may pose serious threat to aquatic life and food web. Extensive irrigation is being carried out in Thanjavur district on the banks of the River Cauvery and fertilizers are being used in abundance. Apart from industrial waste and agricultural, the municipalities also dump sewage in to the river. The river is being incessantly polluted with metals due to multifarious anthropogenic activities. Plethora of human activities both in and near bank of the rivers and lakes as well as the catchment may ultimately affect the quality of water. Many of the activities are as old as the human civilization and have therefore been ignored as a part of sociocultural milieu of the human society. Numbers of studies have been done on trace element concentrations from various aquatic ecosystems (An and Kampbell, 2003; Chandrasekar *et al.*, 2003; Karadede *et al.*, 2004; Mendil *et al.*, 2006; Yang *et al.*, 2007). However, during the past few decades, these activities have become intensive resulting in serious impacts on human health. Hence, the present study aimed at assessing heavy metals in water and sediment of River Cauvery and risk caused to the local human population and resident aquatic organisms through water.

II. MATERIALS AND METHODS

Using high density polyethylene plastic containers (1L capacity) pre-rinsed with nitric acid, water samples were collected from twenty locations in the River Cauvery (Figure 1). The surface sediments were collected using Van veen grab and stored in clean polyethylene bags. The water samples were preserved immediately after sampling by acidifying with 1.5 ml concentrated nitric acid and transported to the laboratory using ice boxes. In the laboratory, water and sediment were stored at 4ºC

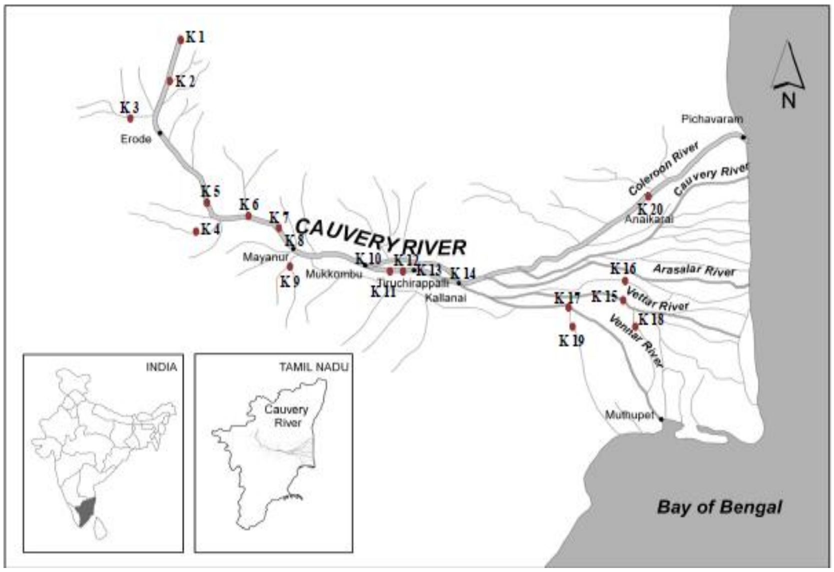

Figure 1: Map showing sampling locations in River Cauvery

The water samples were taken as such for the extraction. Heavy metal extraction in water was done by USEPA method 3010 A. The sediment samples were dried in hot air oven at 120°C. After complete drying, it was grounded and sieved for fine fraction in a sieve (mesh size 63µm). USEPA method 3050B was followed for extraction of metals from sediment.

Atomic Absorption Spectrophotometer (Perkin Elmer AA 800) with hollow cathode lamp was used for the analysis of Ni, Cr & Cu and Graphite Furnace with Electrodeless discharge lamp and flame mode was used for Pb and Cd. The position of the monochromator, proper slit width and cathode current was optimized. Air-acetylene is used as fuel and flow rate is maintained at 4L/min, using a heat combustion value of 1450 BTU per cubic feet. The heat given off would be approximately 12,300 BTU per hour and the temperature of the flame is about 2300°C. Appropriate standards at different concentrations of each element was aspirated and analyzed to obtain a linear graph. The samples were then aspirated and the concentration of each element was determined directly. Duplicates were also simultaneously carried out. Blanks were analyzed for all types of samples. The precision of the sample preparation was checked using Certified Reference Materials (CRMs) spiked with concentration of metals. The calibration standard was checked at the beginning and end of the analysis for each group of samples to ascertain that instrument calibration had not drifted.

The health risk of metals through drinking water from River Cauvery was assessed. The measured concentration of heavy metals in water from the River Cauvery was taken for calculating the risk.

$$\text{Hazard Quotient} = \frac{C_w \times IR_w \times EF \times ED}{RfD \times BW \times AT} \times 10^{-3}$$

Where, C_w -concentration in water; IR_w - daily water ingestion rate (Adult: 95th percentile – 2 L/day: 50th percentile - 1.4 L/day; Child: 95th percentile – 1.08 L/day: 50th percentile – 0.38 L/day); EF - exposure frequency (365 days/year); ED - exposure duration (70 years), equivalent to average life time; RfD - oral reference dose (mg/kg/day); BW- body weight (adult - 70 kg; child – 30 kg); AT - average exposure time (noncancer risk- 30 years x 365 days/year); and 10^{-3} the unit conversion factor.

The measured environmental concentrations (MEC) of metals were used for assessing ecological risk quotient (ErQ). Effective concentration (EC_{50}) or Lethal concentration (LC_{50}) values were used for the calculation of the PNEC [PNEC = (LC_{50} or EC_{50})/ assessment factor]. To overcome the uncertainty from the extrapolation from single species toxicity to ecosystem toxicity (including interactions between toxicants) PNEC values were calculated by dividing the lowest short term $L(E)C_{50}$ (lethal/effect median) of the most of the sensitive species by an appropriate assessment factor.

$$\text{Ecological Risk Quotient (ErQ)} = \text{MEC/ PNEC}$$

The assessment factor addresses a number of uncertainties such as (i) Interspecies variation (biological variance), (ii) Short-term to long-term toxicity extrapolation (iii) Laboratory data to field extrapolation. Assessment factor of 1000 is assigned if at least one short-term L(E)C50 from each of three trophic levels of the base-set (fish, *Daphnia* and algae), 100 if one long-term NOEC (either fish or *Daphnia*), 50 if two long-term NOECs from species representing two trophic levels (fish and/or Daphnia and/or algae) and 10 is assigned for Long-term NOECs from at least three species (normally fish, *Daphnia* and algae) representing three trophic levels are available (CEC, 1996).

III. RESULTS AND DISCUSSION

The mean and range of Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni) and Lead (Pb) in water samples from River Cauvery were represented in Figure 2. The metals were found to be in the order of Pb> Cr> Ni> Cd in River Cauvery. Cu was below detection limit in the water samples. The mean concentration of Pb in water samples of River Cauvery was 0.12 mg/L. Generally, the concentrations of Pb in the surface water will be typically low but levels may increase after alkaline sewage mixes with the surface water (Rahbar *et al.*, 2002). Lead solubility is principally controlled by $PbCO_3$ hence highly alkaline waters can have higher Pb concentrations (Hem, 1989). The mean concentration of Pb in this study is higher than the Pb in South Channel (0.005 mg/L) of Salado River Basin, Argentina (Gagneten *et al.*, 2007) and To Lich River, Vietnam (0.002 mg/L; Kikuchi *et al.*, 2009). Based on the drinking water standards (Table I) of World Health Organization (WHO) and Bureau of Indian Standards (BIS) our results showed the contamination of surface water with Pb. The chromium levels in the present study ranged from 0.001 to 0.034 mg/L in River Cauvery. Comparable level of Cr was also reported in Asa river, Nigeria (0.04 mg/L: Eletta, 2007). The mean concentration of Cr (0.02 mg/L) in Cauvery River is below the WHO and BIS permissible values for drinking water quality. But the level is slightly higher than the Criterion maximum concentration (CMC) and Criterion continuous concentration (CCC) of USEPA (Table I). The concentration of Ni ranged from 0.006 - 0.024 mg/L with an average concentration of 0.011 mg/L was observed. Sources of Ni in water include effluents and sludge from sewage treatment plants. Industries like ceramics, steel and alloys, electroplating, and refractory are also the contributors of Ni to surface/ground water. The mean concentrations are less compared to earlier reports in Indian rivers like river Ganges at West Bengal (0.038 mg/L: Kar *et al.*, 2007); streams near Ranipet industrial area, Tamil Nadu (0.04 mg/L: Gowd and Govil, 2008) and also substantially below the drinking water quality guidelines of WHO and BIS and freshwater quality criteria of USEPA (Table I). The concentration of Cd varied from BDL to 0.006 mg/L in the River Cauvery, it has both natural and anthropogenic sources. Cadmium is a relatively mobile element. Environmental levels are greatly enhanced by the industrial operations as Cd is commonly used as pigment in paint, plastics, ceramics and glass manufacture (Gowd and Govil, 2008). Mean concentration in River Cauvery is comparable to the Indian river, Florida, USA (0.006 mg/L: Trocine and Trefry, 1996) and Madanzhe river, South Africa (0.005 mg/L: Okonkwo and Mothiba, 2005). It is apparent from the present study that the concentrations may be due to the multifarious anthropogenic activities along the course of the River Cauvery.

Table I: Acceptable level (mg/L) of some heavy metals in natural waters

Limit	**Cd**	**Cr**	**Ni**	**Pb**
MPL	0.003	0.05	0.02	0.01
TC	0.01	0.05	0.05	0.1
BIS	0.01	0.05	NA	0.05
WA	0.001	NA	NA	0.04
Freshwater Quality Criteria				
CMC	0.002	0.016	0.47	0.07
CCC	0.0003	0.011	0.052	0.003
This Study				
River Cauvery (Mean)	0.003	0.02	0.011	0.12

MPL- Maximum permissible Limit in drinking water (WHO, 2004); TC- Threshold concentration for aquatic life tolerance (safe for most fishes) (Burrel, 1974); BIS-Bureau of Indian Standards (BIS, 1991); WA - World Average of trace elements in unpolluted rivers; CMC - Criterion maximum concentration (USEPA, 2006); CCC- Criterion continuous concentration (USEPA, 2006); NA- Not available

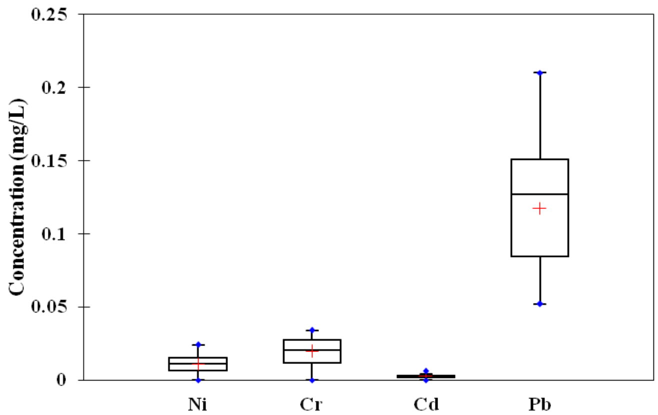

Figure 2: Metal concentrations and its variations in water samples from River Cauvery

The mean and the range of metals in the surface sediment of River Cauvery were represented in Figure 3. Cd was below detection limit in all the locations of River Cauvery. Similar to the present investigation Mwamburi (2003) also observed the presence of Cd in water and its absence in sediment. The order of metals in the surface sediment in the river was Cr > Ni > Cu> Pb. In aquatic system, metals are transported or settled on the surface of suspended sediments or particulate matter. Because of their strong affinity to particles, metals tend to get accumulated as suspended matter or settled immediately on bottom sediments. Among the metals, Pb is least mobile and 90% is present mainly in the residual fraction (Routh and Ikramuddin, 1996; Morillo *et al.*, 2002). The mean concentration of Pb in River Cauvery (14 mg/Kg) is about 5 fold greater than the level reported in the upstream of the same river (Abida *et al.*, 2009) but less compared to ISQG standards TEL (Threshold Effect Level) and PEL (Probable Effect Level).

The range of Cr observed in the sediment samples of River Cauvery was 28 -145 mg/Kg which is on par with the concentration reported in the River Ganges, India (121 -200 mg/Kg: Singh *et al.*, 2003) but several folds higher compared to upstream of the river Cauvery in Karnataka, India (BDL -18.24 mg/Kg: Abida *et al.*, 2009). According to Canadian Sediment Quality Guidelines, the threshold effect level (TEL) of chromium is 37.3 mg/Kg and Probable Effect Level (PEL) is 90 mg/Kg. The mean concentration of Cr in River Cauvery is found to be exceeding the TEL (Table II), indicating the possibility of adverse effects. In river and lakes, chromium will absorb to the sediment and become immobile. Only a small part of the chromium will eventually dissolve and ends up in water (Gowd & Govil, 2008). In compliance with this statement the present investigation showed higher levels of Cr in sediment than in water. The mean concentration of Ni in River Cauvery was 17 mg/Kg.

Table II: Comparison of results with recommended trace element standards in sediment (mg/Kg)

Limits	Ni	Cr	Cu	Pb
Standard Values				
BV	26	73	56	18
US	NA	NA	33	19
Limits				
TEL (ISQG)	NA	37.3	35.7	35
PEL	NA	90	197	91.3
PL	20	22	34	15
US EPAToxicity classifications				
Non Polluted	<20	NA	<25	<40
Moderately Polluted	20 - 50	NA	25 – 50	40 – 60
Heavily Polluted	>50	NA	>50	>60
NOAA				
ERL	20.9	NA	34	46.7
ERM	51.6	NA	270	218
This Study				
River Cauvery (Mean)	16.7	58.5	22.7	13.9

BV - Background Values of metals in India (Chandrasekhar *et al.*, 2003); US - Unpolluted Sediment (Kumar *et al.*, 2010); ISQG - Interim Sediment Quality Guidelines (CCME, 2002); TEL- Threshold Effect Level & PEL - Probable Effect Level; PL - Permissible Limit (Chandrasekhar *et al.*, 2003); ERL - Effects low range; ERM - Effects mean range; NA - Not available

The concentration is few folds higher than the New Calabar River, Nigeria (3.2 mg/Kg: Horsfall & Spiff, 2001). The concentration of Ni in river Cauvery ranged from 3.4 to 26.3 mg/Kg (Fig. 3). The Ni in the present investigation is over the range reported by Abida et al. (2009) (0.05 – 5.25 mg/Kg) in the upstream of River Cauvery. The Cu concentration in river Cauvery ranged from 0.7 to 164 mg/Kg and greater than the earlier reports in Ganges river at Kanpur, India (15 – 17 mg/kg: Beg & Ali, 2008) and ponds in the eastern Kolkata India (27 – 64 mg/Kg: Kumar *et al.*, 2010). The mean Cu concentration (22.7 mg/Kg) in the river Cauvery is several folds in excess of earlier reports by Abida et al. (2009) from upstream of the river (0.56 mg/Kg) and below TEL and PEL (Table II) suggesting less or no risk to the aquatic organisms.

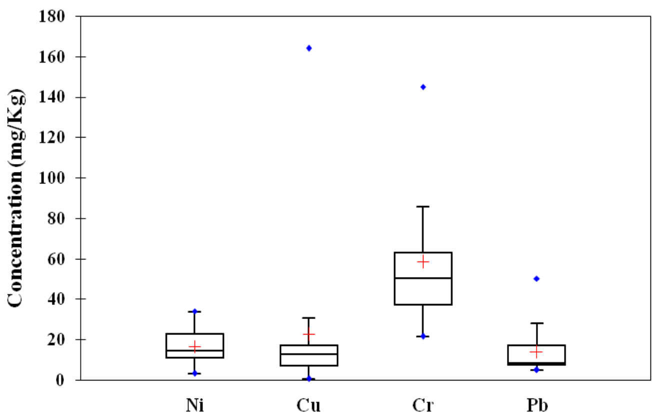

Figure 3: Metal concentrations and its variations in sediment samples from River Cauvery

Contamination factor (CF) is defined as the ratio of observed concentration of metal over background value of the trace element in sediment, and calculated using following formula;

$$CF = \frac{\text{Observed concentration of trace elements (mg/Kg)}}{\text{Background value of the trace elements (mg/Kg)}}$$

The index for pollution assessment is pollution load index (PLI) is obtained by measuring the elements contents, and deriving contaminating factors by reference to the baseline trace element levels i.e background value of metals in India (Chandrasekhar *et al.*, 2003). Pollution load index (PLI), for a particular site, has been evaluated by the method proposed by Tomlinson et al. (1980). This parameter is expressed as:

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots\ldots\ldots \times CFn)^{1/n}$$

here, n is the number of metals, CF < 1 refers to low contamination, CF 1 to 3 means moderate contamination, CF 3 to 6 indicates considerable contamination, and CF > 6 indicates very high contamination (Puyate *et al.*, 2007). The calculated CF values based on background values in India for metals Ni, Cu, Cr and Pb were 0.64, 0.4, 0.8 and 0.77 respectively and the PLI was 0.63. The CF for all metals is less than 1 that implies less contamination. PLI values >1 would cause health risks to sediment dwellers. In the present investigation PLI values in River Cauvery is slightly greater than 0.5. Even PLI >0.5 would cause at least minimum hazard to the aquatic organisms indicating low to moderate pollution of the river.

Health risk assessment is a very important tool to evaluate the consequences of human action and also measures the adverse effect to public health (Ukoha *et al.*, 2014). The health risk assessment or the non-cancerous effects of heavy metals due to consumption of water has been calculated for both children and adults. An evaluation of non cancer risk to human health associated with the consumption of drinking water containing metals was undertaken and the results were represented in Figure 4. The average concentration of each metal was applied to evaluate the risk level. The RfD for Ni, Cr, Cd and Pb was 0.02, 0.05, 0.0005 and 0.004 mg/kg/day respectively. The safety range of health risk (hazard quotient) was below unity. The hazard quotient (HQ) resulting from the exposure to Pb was predicted high through drinking water for child and adult 2.5 and 2.3, respectively at 95th percentile from River Cauvery. The HQ of Pb in River Cauvery is above unity which indicates that the concentration of Pb in the drinking water in the study area may pose health threat. The hazard quotients of all other metals such as Ni, Cr and Cd are closer to unity suggesting that these pollutants could pose minimum hazard to local residents. The difference in age and exposure conditions might also contribute to risk. The result of the present investigation suggests higher risk to child than adult. Eventhough, the upper bound (95th percentile) consumption of drinking water is low for a child (1.08 L/day) than an adult (2 L/day) based on the body weight it may be a potential health hazard to child. The HQ of Cd (0.003) derived by Wu et al. (2009) in the water from Yangtze river, China for adult at 95th percentile was lower than the present study in River Cauvery (0.46). The HQ of Ni for child in this study is well above the HQ (0.0026) observed by Huguet et al. (2009) in Ebro river, Spain.

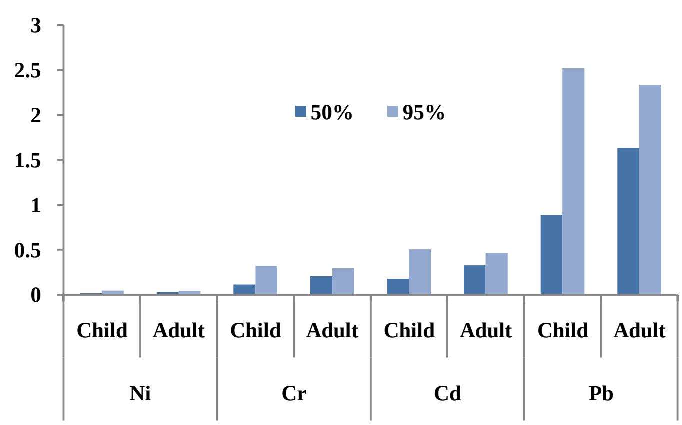

Figure 4: Hazard Quotient of metals through drinking water from River Cauvery, India

Ecological risk quotient (ErQ) was conducted to evaluate the likelihood risk arising from the exposure to heavy metals that adversely affect aquatic organisms. The MEC: PNEC (assessment factor) approach is a generic conservative approach assuming the presence of the most sensitive species. To derive a PNEC using the assessment factor approach, preferably, toxicity data on at least the three selected trophic levels (e.g., algae, crustaceans, and fish) were considered for evaluation of risk to the aquatic environment. The assessment factor is applied to extrapolate from laboratory single-species toxicity test data to multi-species ecosystem effects. The mean concentration of Ni, Cr, Cd and Pb were used to assess the aquatic toxicity. The ecological risk quotient of all the metals in River Cauvery was greater than unity (Table III). Eventhough, slightly higher than unity the risk quotient of Ni and Cr is considered to be non-acceptable risk. The ErQ of Cd and Pb in River Cauvery implies a severe acute risk to all the three categories (fish, zooplankton and phytoplankton). It has long been recognized that heavy metals in the environment have a particular significance in the eco-toxicology, since they are highly persistent and can be toxic even in traces (Langston, 1990).

Table III: Ecological Risk Assessment of metals to phytoplankton, zooplankton and fish in River Cauvery

Metals	Toxicity Levels			Assessment Factor	PNEC (µg/L)			MEC (µg/L)	Ecological Risk Quotient (ErQ)		
	Phyto plankton	Zoo plankton	Fish		Phyto plankton	Zoo plankton	Fish		Phyto plankton	Zoo plankton	Fish
Cd	8^{**}	14^{**}	2.1^{**}	100	0.08	0.14	0.02	3	37.5	21.43	150
Pb	7940^{**}	4400^{**}	10^{**}	50	159	88	0.2	120	0.75	1.36	600
Ni	100^{**}	1000^{**}	50^{**}	50	2	20	1	19	9.5	0.95	19
Cr	350^{**}	22^{**}	100000^{**}	10	35	2.2	10000	11	0.31	5	0.001

NA – Not Available; * - NOEC; ** - LC_{50}/EC_{50} ; MEC- Measured Environmental Concentration

IV. CONCLUSION

The mean concentration of Pb, Cr and Cd exceeded the permissible limit and concentration of Pb was found to be far exceeding the permissible limits in the water samples of River Cauvery. The high concentration of metals in water can be gradually accumulated on the sediments and in due course it may get transferred to aquatic organisms. The calculation of the CF and PLI based on background value in India also proved that the sediment of River Cauvery has been polluted from low to moderate. The results of the present study provided useful information to understand the risk to the aquatic ecosystem; also transfer of toxic metals to human through drinking water from the contaminated sites. Based on the findings it can be concluded that regular surveillance and evaluation of metals input into the riverine system from the nearby sources is mandatory to circumvent unfavorable impacts on environment in the future.

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