Distribution of Some Heavy Metals in Water Bodies and Water Sediments of the Tamirabarani River at Eral, Tamil Nadu, South India.

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ARTICLE INFO	ABSTRACT
	Heavy metals contamination in river is one of the major quality issues in developing countries and metals enter these aquatic systems mainly through natural inputs such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal. In the month of March CF > 6 in Copper indicated extremely contaminated as 9.333 in the water bodies. In the water bodies the month of March indicated that it is very high extremely polluted emphasized as 10.62 pollution load index. In the water sediments regarding in the month of March pointed out the pollution load index that it is very high extremely polluted as 17.28. The highest copper concentration was noticed in the water bodies during the month of March as 420±2.40 mg/l and the zinc as 260±3.04 mg/l which exceeded the shale value. The highest copper concentration was noticed in the water sediments during the month of March as 750±2.40mg/l and the zinc as 380±3.20 mg/l which exceeded the shale value. The Lead metal concentration was observed as 10 mg/l during all the months.

Introduction

A person can live without food for a month, but only for a week without water. Nothing will quench thirst the way water can. Water is the essential part of the modern day life. The identification and quantification of the heavy metal in water and sediments are important environmental issues (Manoj *et al.,* 2012). The contamination of surface water by heavy metals is a serious ecological problem as some of them are toxic even at low concentration, are non-biodegradable and bio-accumulate through food chain (Abdullah, 2013). In order to protect the aquatic life community, comprehensive methods for identifying and assessing the severity of sediment contamination have been introduced over the past 10 years (Van de Guchte, C, 1992; HU, Ying, *et al.,* 2012).

But no significant studies have been under taken to investigate the heavy metal pollution in the Eral River. Hence, a periodical assessment is necessary for monitoring the water quality. In the present investigation an attempt is made to study the heavy metals in the water bodies and water sediments in Eral River. Therefore, the objectives of this study are given below.

❖ To analyse the heavy metal concentration such as Zn, Cu and Pb.
❖ To evaluate the standard deviation.
❖ To evaluate the pollution load index.
❖ To assess the heavy metal contamination factor.
❖ To compare the heavy metal values, with shale reference background values and BIS.

Study Area

The Thamirabarani river is located between latitude 8.63˚N and longitude 78.20˚E. The main drains of the river, believed to originate from Manimutharu and Papanasam, passes through many residential communities including Kallidaikuruchi, Seranmahadevi, Tirunelveli, Vallanadu, Konkarayakurichi, Srivaikundam, Eral and Punnaikayal (Figure-1). Further the water flows through the pipelines to the Dharangadhara Chemical Industry. The rain fall range of January was 8Mm. The total length of the study area is 1.80m and the total area is covered as $50 \times 36 \times 9.6$ cm. In the Eral town there are about 9478 populations are dwelling. The bridge is surrounded on two sides by major roads with high vehicular emission (Figure-2) .In addition; the water is used for washing of vehicles, washing clothes, bathing, sewage and dumping of domestic wastes. The Thamirabarani River is a habitat to many species of plants and animals serves as the major sources of water for fishing, vegetable crops irrigation in Eral town.
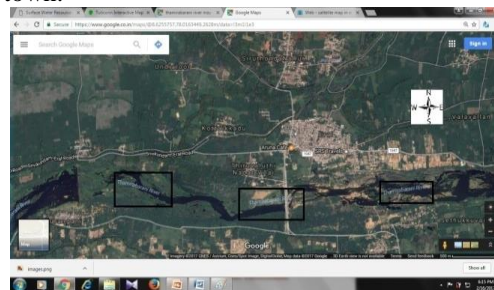

Figure 1. Location map of the study area.

Figure 2. Study area and sampling site in Eral.

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Methodology

The trace metals analysis of water and sediment has been determined by Atomic Absorption Spectrophotometer. Flame spectrophotometer is an analytical technique used for qualitative and quantitative determination of the metal in a sample. In Atomic Absorption Spectrophotometer the magnify of the free atoms in the commonly used flames were in the ground states but the flames did not have enough energy to excite these atoms. The decrease in energy (absorption) was then measured.

The absorption is proportional to the concentration of free atoms in the flame given by Lambert Beer Law:

$$Absorbance = Log^{10} I^0/I^t = KCl$$

Where

I^O = Intensity of incident radiation emitted by the light source.
I^t = Intensity of transmitted radiation (amount not absorbed).
C = Concentration of sample (free atoms).
K = Constant (can be determined experimentally).
L = Path length.

This is the most common method where interference effects are known to be absent. Using the blank solution as zero in the instrument performs the calibration. The standards were then analysed with the lowest concentration first and the blank run between the standards, to ensure the base line (zero point).

Heavy Metal Analysis in Water

Water samples were collected every three months from January 2017 to March 2017 using pre-cleaned and acid – washed polyethylene bottles Care should be taken to minimize the exposure of samples to the atmosphere. The sample was acidified with Supra-pure grade nitric acid (5ml of 1m acid per litre of sample) and stored in refrigerator at constant low temperature to avoid evaporation.

Calibration and Determination of Blank

Eight aliquots (400ml) of metal-free water were taken in a pre-cleaned separating funnel. The pH of the solution was adjusted between 2-3by adding1m HCl (2ml). APDC (Ammonium Pyrolidine Dithicarbomate) solution 10ml was added and shaken well. After 30 seconds 15ml of MIBK (Methyl Isobutyl Ketone) was added and shaken vigorously for 2 minutes. The MIBK layer was discarded and it was extracted again with APDC solution (5ml) and MIBK solvent (10ml).The MIBK layer was discarded and the metal- free water was retained for blank determination and calibration.

The metal stock solution of Cu, Pb and Zn were diluted (1ml each) to 100 ml with water containing 1ml of concentrated HNO3.This working standard solution contained 1mg metal Cu/Pb/Zn/ml. Eight aliquots (400ml) of metal free water were taken in pre-cleaned separating funnels and spiked (in duplicate) with 0.0 (blank) 0.5, 1.0and2.0ml of mixed working standard. To each funnel was shaken for 30 seconds.15ml of MIBK was added and shaken vigorously for 2 minutes. The solution was allowed to stand for 20 minutes for phases to separate.

The aqueous layer was collected in a clean polythene bottle of 500ml capacity. The aqueous layer was discarded and the MIBK solvent was added to the separating funnel containing the first extract. The combined extract was washed with Milli-QR water and the aqueous layer was discarded carefully. For each extraction 0.2ml of concentrated nitric acid was added to the combined MIBK extract and it was shaken vigorously. Then it was allowed to stand for 20 minutes. 19.8ml of water was added with the help of an Eppendorf pipette. The aqueous layer was collected and stored in 50ml polythene bottle for analysis. The absorbance of the aqueous solutions of blanks and standards were measured in Hitachi Flame Atomic Absorption Spectrophotometer (Z-700).

Sample Analysis

Duplicate aliquots of the sample (400ml) were measured and the pH was adjusted between 2-3with 1m HCL in separating funnels and the extraction procedure was followed as mentioned for standards.

Heavy Metal Analysis in Sediment

Sediments sample were collected and kept in a pre-cleaned and acid – washed polythene container. Collection was made every three months from January 2017 to March 2017.The metal such as Cu/Pb/Zn were analysed using the method of Peerzada and Dickinson (1988)by using Hitachi (Z-7000) Flame Atomic Absorption Spectrophotometer.

Statistical Analysis

Determination of contamination factor (CF)

CF for each metal was determined as described below

$$CF = \frac{Observed\ metal\ concentration}{Background\ concentration\ of\ the\ same\ metal}$$

Determination of Pollution Load Index (PLI)

Pollution load index for each site was determined following the method proposed by Tomlinson *et al., (1980)*

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots \ldots \times CFn)}$$

Where,

CF is the contamination factor and n is the number of parameters.

Average shale standard for different metals reported by Turekian and Wedepohl (1961) was taken as background concentration throughout the study. The world average concentration of Cu (45µg/g), Pb (20µg/g), Zn (5000 µg/g), and reported for shale were considered as the background value.

Results

Contamination Factor

Water Bodies

It consists of four grades ranging from low contamination factor to very high contamination factor. (Table 1) In the month of January CF < 1 in Copper, Lead and Zinc indicates low contamination in the water bodies. Likewise in the month of February CF < 3 in the Copper indicates moderately contaminated whereas the CF < 1 in Lead and Zinc indicates low contamination in the water bodies. In the water bodies Copper is moderately contaminated.   Like wise in the month of March CF > 6 in Copper indicates extremely contaminated whereas the CF < 1 in Lead indicates low contaminated and CF < 2 in Zinc indicated moderately contaminated in the water bodies.

Water Sediments

It consists of four grades ranging from low contamination factor to very high contaminated factor (Table 1). In the month of January CF <1 in Copper, Lead and Zinc indicates low contaminated in the water sediments. Likewise in the month of February CF < 6 in Copper indicates extremely contaminated .Whereas in Lead the CF < 1 in indicates low contaminated CF < 2 in Zinc indicates moderately contaminated in the water sediments.

Likewise in the month of March CF > 6 in copper indicates extremely contaminated where as CF < 1 in Lead indicates low contaminated and CF < 3 in Zinc indicates considerable contaminated in the water sediments.

Table 1. Index Classification of Contamination Factor.

CF Values Hakanson(1980)	Class	Sediment quality
CF < 1	1	Low CF
$1 \leq CF < 3$	2	Moderate CF
$3 \leq CF < 6$	3	Considerable CF
$CF \geq 6$	4	Very high CF

Pollution Load Index

Water Bodies

The pollution Load Index represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample (Barakat *et al.,* 2012) The values of pollution load index (Table 2 & Table 3) were found to be unpolluted to moderately polluted in the month of January in the water bodies. In the water bodies regarding in the month of February pointed out that it is moderately to strongly polluted. In the water bodies the month of March indicates that it is very high extremely polluted.

Table 2. Index Classification Of Pollution Load Indexes (Pli).

PLI Values Muller(1981)	Class	Sediment quality
≤ 0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to extremely polluted
5-6	6	Extremely polluted

Water Sediments

The values of pollution load index were found to be moderately polluted in the month of January in the water sediments .In the water sediments regarding in month of February and March pointed out that it is very high extremely polluted (Table 4).

Table 4. Contamiantion Factor And Pli For Studied Heavy Metals In Water Sediments At Eral Thamirabarani River.

Months	CF (Cu)	CF (Pb)	CF(Zn)	PLI
January	0.888	0.5	0.736	1.58
February	8	0.5	1.473	7.0
March	16.66	0.5	4	17.28

Table 5. Mean Concentration Of Heavy Metals In Water Bodies.

| S.N O	Metals	January	February	March	Shale value	BIS
1	Cu (mg/l)	10 ±0.96	130 ±1.92	420±2.40	45	50
2	Pb (mg/l)	10 ±1.20	10 ±2.30	10±2.38	20	10
3	Zn (mg/l)	10 ±0.96	50 ±2.70	260±3.04	95	5000

The total mean concentrations for the sampling site found in water bodies in the study are shown in (Table 5). The highest copper concentration was noticed during the month of March as 420± 2.40mg/l. The Lead metal concentration was observed as 10mg/l during all the months. Zinc metal contents were ranging from 10± 0.96 mg/l to 260± 3.04 mg/l. The highest Zinc concentration was noticed during the month of March 260± 3.04 mg /l.
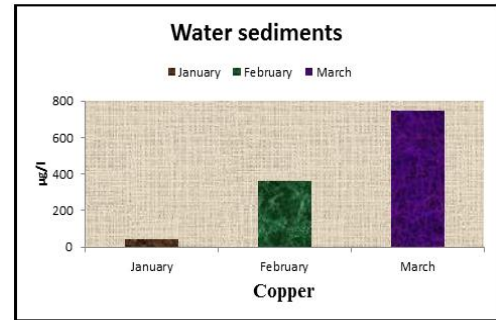
Figure 3. Graph showing analysis of heavy metals Concentration in water sediments from January to March 2017.

Copper metal contents were ranging from 40 ±1.58 mg/l to 750± 2.40 mg/l. The highest copper concentration was noticed during the month of March as 750± 2.40mg/l (Fig.3).
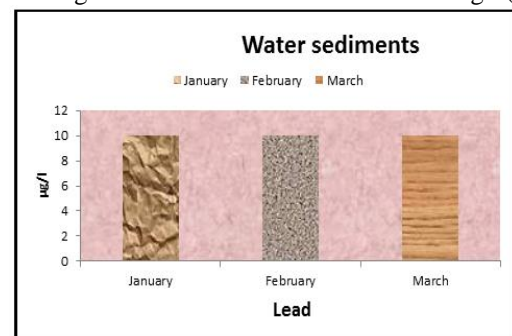
Figure 4. Graph showing analysis of heavy metals Concentration in water sediments from January to March 2017.

The Lead metal concentration was observed as 10mg/l during all the months (Fig.4).
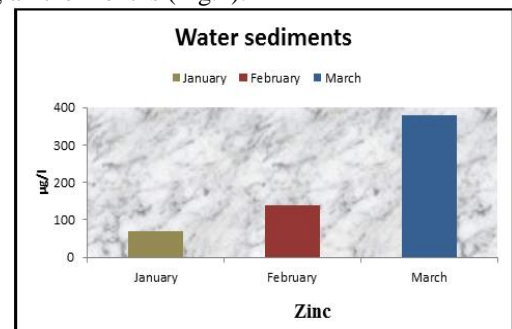
Figure 5. Graph showing analysis of heavy metals Concentration in water sediments from January to March 2017.

Zinc metal contents were ranging from 70± 1.58 mg/l to 380± 3.20 mg/l (Fig.5). The highest Zinc concentration was noticed during the month of March 380± 3.20 mg /l.

Discussion

The maximum concentration of copper may be due to water supply systems through distribution of pipelines to the DCW chemical industry. Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage stomach and intestinal irritation (J.R Turnland, 1988).

During the study period the minimum concentration of lead might be due to less vehicular emissions, less corrosive deposition level of pipe lines to the DCW industry and minimum usage of pesticides the agricultural field by the farmers.

The highest concentration of zinc observed during the study could be as a result of human activities around the riverbanks include washing of household wares, washing of automobiles, dumping of domestic discharges and agricultural use of pesticides and insecticides. Very high concentration of zinc may cause harmful effects (Lark *et al.,* 2011). Zinc influences growth rate and bone development. The chronic health effect of zinc includes cancer, birth effect, organ damage, disorders of the nervous system and damage to the immune system (Priti saha and Biswajit Paul, 2016).

Recommendations

➢ The most widely used conventional methods for removing heavy metals from waste water include ion exchange, chemical precipitation, reverse osmosis, evaporation and membrane filtration.

➢ Activated carbon has been using for the removal of lead and other heavy metals especially when associated with organic particulate matter in water.

➢ Saw dust, an in –expensive material has been utilized as an adsorbent for the removal of copper from waste water.

➢ The Zn ions were successively desorbed from Botrytis cinerea (B.cinerea) bio mass using 10mM HCL solution.

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