



Science

HEAVY METAL POLLUTION AND THE ENVIRONMENT IN TIRUCHENDUR TALUK AND SRIVAİKUNDAM TALUK

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DOI: <https://doi.org/10.5281/zenodo.345682>

Abstract

Heavy metals are naturally occurring elements that have a high atomic weight than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment. The maximum Zn concentration was noticed in the year 2012 as $24.47 \pm 0.57 \mu\text{g/l}$ in the water bodies of Tiruchendur and Srivaikundam taluk at station X. The highest Zn concentration was obtained in the water sediments as $272.33 \pm 5.01 \mu\text{g/g}$ at station 1 in the year 2012 and the concentration was high in the phytoplankton as $34.314 \pm 4.239 \mu\text{g/g}$ at station V in the year 2011.

During the year 2012, the Cu was found high as $22.53 \pm 15.70 \mu\text{g/l}$ at station III in the water bodies. In the sediments it was high as $63.03 \pm 13.85 \mu\text{g/l}$ at station XI during 2011. In the phytoplankton the maximum concentration was noticed at station VIII as $13.564 \pm 2.797 \mu\text{g/g}$ during 2011. During the year 2011 the highest concentration of Pb was emphasized at station VI as $11.31 \pm 1.63 \mu\text{g/l}$ in the water bodies. In the water sediments it was high at station V as $64.11 \pm 11.96 \mu\text{g/g}$ during 2011. In the phytoplankton, the concentration was measured highest at station II as $4.343 \pm 0.976 \mu\text{g/g}$ dry weight in the year 2012.

All the heavy metals such as Zn, Cu and Pb were exceeded the Shale reference background value. This review provides an analysis of their environmental occurrence and potential for human exposure.

Keywords: Heavy Metals; Atomic Weight; Technology.

Cite This Article: Esther Isabella Eucharista. (2017). "HEAVY METAL POLLUTION AND THE ENVIRONMENT IN TIRUCHENDUR TALUK AND SRIVAİKUNDAM TALUK." *International Journal of Research - Granthaalayah*, 5(2), 252-265. <https://doi.org/10.5281/zenodo.345682>.

1. Introduction

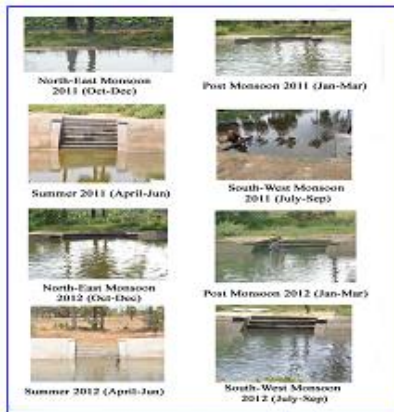
In the recent past, there have been increasing interests and regarding heavy metal contaminations in the environments, apparently due to their toxicity within the aquatic systems Tijani *et al*

(2005). Trace amounts of heavy metals are always present in freshwaters such as weathering of rocks resulting into geo-chemical recycling of heavy metal elements in these ecosystems (Muwanga, 1997; Zvinowanda *et al.*, 2009).

Trace elements may be immobilized and thus could be involved in absorption, co-precipitation and complex formation (Okafor and Opuene, 2007); Mohiuddin *et al.*, 2010). Occasionally they are co-adsorbed with other elements as oxides, hydroxides of Fe, Mn, or may occur in particulate form (Awofolu *et al.*, 2005; Mwiganga and Kansime, 2005).

Heavy metals drain into aquatic ecosystems from anthropogenic sources, such as industrial waste water discharges, sewage waste water, fossil fuel combustion and atmospheric deposition (Linnik and Zubenko, 2000 ; Campbell, 2001 ; Lwanga *et al.*.,2003 ; ElDiwani and El Rafie, 2008 ; Idrees, 2009).

High population density, shortage of monsoon rainfalls and increasing water depletion, many fresh water bodies in Indian cities are now polluted and disappearing (Karmakar, 2007). This study therefore aimed to determine the distribution and concentration of trace metals in sediments with different sediment characteristics from 6 stations in Tiruchendur taluk and 6 stations in Srivaikundam taluk during 2011 to 2012 (Figure -1).



Seasonal views of Station I
(AUTHOORANGAL CHANNEL)



Seasonal views of Station II
(KADAMBA POND)



Station III
(Church open well)



Station IV
(Pragasapuram open well)



Station V
(Merchant street bore well)



Station VI
(East Street bore well)



Seasonal views of Station VII
(Srivaikundam channel)



Seasonal views of Station VIII
(Arumugamangalam pond)



Station IX
(Open Well Inside Therasa School)



Station X
(Open Well primary health centre)



Station XI
(Muslim St Bore Well)



Station XII
(Infront of Therasa School Bore well)

Figure 1: Different study stations in Tiruchendur taluk and Srivaikundam taluk

2. Objectives

- To analyse the characteristic features of metals such as Zn, Cu and Pb.
- To evaluate the standard mean deviation.
- To compare the values of metals with Shale reference background.

3. Methodology

The trace metal analysis of water, sediment and phytoplankton 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.

$$\text{Absorbance} = \text{Log}^{10} I^0/I^t = KCL$$

Where I^0 = 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 month for two years (2011 & 2012) using pre-cleaned and acid-washed polyethylene bottles. Care was taken to minimize the exposure of samples to the atmosphere. The sample was acidified with supra-pure grade nitric acid (5 ml of 1M acid per litre of sample) and stored in the refrigerator at constant low temperature to avoid evaporation.

Calibration and Determination of Blank

Eight aliquots (400 ml) of metal – free water were taken in a pre-cleaned separating funnel. The pH of the solution was adjusted between 2 – 3 by adding 1 M HCl (2 ml). APDC (Ammonium Pyrolidine Dithiocarbonate) solution 10 ml was added and shaken well. After 30 seconds 15 ml 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 (5 ml) and MIBK solvent (10 ml). The MIBK layer was discarded and the metal-free water was retained for blank determination and calibration.

The metal stock solutions of Cu, Zn and Pb were diluted (1 ml each) to 100 ml with water containing 1 ml of concentrated HNO₃. Again 10 ml of the solution was diluted to 100 ml with water containing 0.5 ml of concentrated HNO₃. This working standard solution contained 1 mg metal Cu / Zn / Pb ml.

Eight aliquots (400 ml) of metal-free water were taken in pre-cleaned separating funnels and spiked (in duplicate) with 0.0 (blank) 0.5, 1.0 and 2.0 ml of mixed working standard. To each funnel APDC solution (10 ml) was added. The funnel was shaken for 30 seconds. 15 ml 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 500 ml capacity. The aqueous layer was once again extracted with 5 ml APDC and 10 ml MIBK solvent. 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 0.2 ml 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. 19.8 ml of water was added with the help of an Eppendorf pipette. The aqueous layer was collected and stored in 50 ml polythene bottle for analysis.

The absorbance of the aqueous solutions of blanks and standards was measured in Hitachi Flame Atomic Absorption Spectrophotometer (Z-7000).

4. Sample Analysis

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

Heavy Metal Analysis in Sediment

Sediment samples were collected and kept in a pre-cleaned and acid-washed polythene container. Collection was made every month for a period of two years (2011 and 2012). The metals such as copper, zinc and lead were analysed using the method of Peerzada and Dickinson (1988) by using Hitachi (Z-7000) Flame Atomic Absorption Spectrophotometer.

Heavy Metal Analysis in Phytoplankton (Knauer & Martin,1973)

The collected phytoplankton samples were cleaned with metal-free double distilled water. The samples were dried in an oven at 60⁰C till a constant weight was obtained. Ground and redried samples (250 mg) were digested with HNO₃ and H₂O₂. After centrifugation to remove silica fractions, the solution was diluted and stored for analysis. Blank digestions were also carried out.

5. Statistical Analysis

Sediment Pollution Indices

The geo-accumulation index (I-geo) and pollution load index (PLI) were employed to assess the pollution of metals in the sediment of Tiruchendur and Srivaikundam taluk water resources. The average of the four season values were considered as the final value in each stations.

Geo-Accumulation Index (I-Geo)

Geo-accumulation index was determined by the following equation according to Muller (1969) which was described by Adel Mashaan Rabee *et al.*, (2011).

$$I\text{-geo} = \log_2 (C_n / 1.5 B_n)$$

Where,

C_n = Measured concentration of heavy metal in the Tiruchendur and Srivaikundam taluk water sediments.

B_n = Geochemical background value in average shale (Turekian and Wedepohl, 1961) of element n. The factor 1.5 is used for the possible variations of the background data due to lithological variations.

The Pollution Load Index (PLI)

The pollution load index (PLI) is obtained as concentration factors (CF). This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. With the PLI obtained from each place (Soares *et al.*, 1999). Generally pollution load index (PLI) as developed by Tomlinson *et al* (1980), which is as follows:

$$CF = C \text{ metal} / C \text{ background value}$$
$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \dots \times CFn)}$$

Where,

CF = contamination factor, n = number of metals

C metal = metal concentration in polluted sediments

C Background value = background value of that metal.

The PLI value of > 1 is polluted, whereas < 1 indicates no pollution (Harikumar *et al.*, 2009). The world average concentration of Cu (45 µg/g), Pb (20 µg/g) and Zn (95 µg/g) reported for Shale were considered as the background value.

6. Results and Discussions

ZINC (Zn)

The maximum Zn concentration was noticed in the year 2012 as 24.47±0.57µg/l in the water bodies of Tiruchendur and Srivaikundam taluk at station X (Figure 3). The highest Zn concentration was obtained in the water sediments as 272.33±5.01 µg/g at station 1 in the year 2012 and the concentration was high in the phytoplankton as 34.314±4.239 µg/g at station V in the year 2011(Figure 6). Accumulation of Zn may be due to organic matter like phosphate chemical fertilizers from the agricultural fields, vehicular emissions and domestic discharges. Large concentrations of zinc cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.

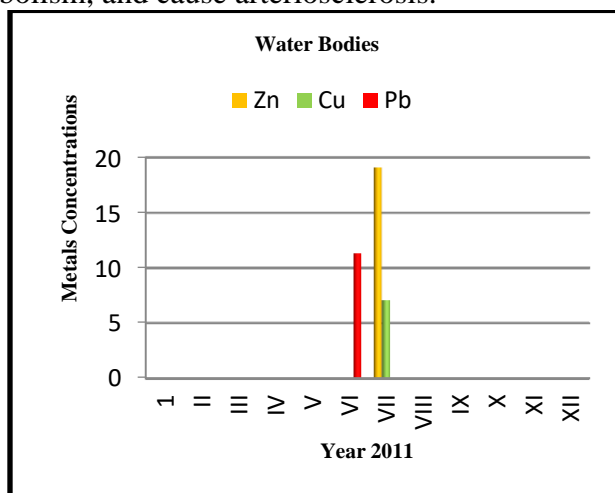


Figure 2: Heavy metal concentrations for water bodies in Tiruchendur and Srivaikundam taluk during 2011

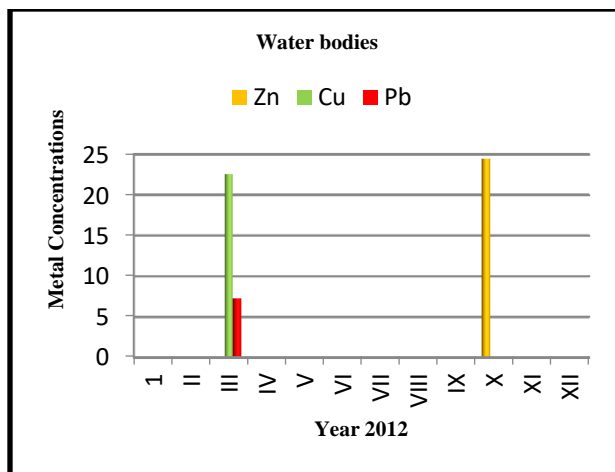


Figure 3: Heavy metal concentrations for water bodies in Tiruchendur and Srivaikundam taluk during 2012

COPPER (Cu)

During the year 2012, the cu was found high as $22.53 \pm 15.70 \mu\text{g/l}$ at station III in the water bodies. In the sediments it was high as $63.03 \pm 13.85 \mu\text{g/l}$ at station XI during 2011 (Figure 4). In the phytoplankton the maximum concentration was noticed at station VIII as $13.564 \pm 2.797 \mu\text{g/g}$ during 2011. The retention of copper metal perhaps through the wet and dry depositions of domestic and agricultural waste discharges into the aquatic environment. Excessive copper intake can cause nausea, vomiting, abdominal pain and cramps, headache, dizziness, weakness, diarrhea, and a metallic taste in the mouth.

LEAD (Pb)

During the year 2011 the highest concentration of Pb was emphasized at station VI as $11.31 \pm 1.63 \mu\text{g/l}$ in the water bodies. In the water sediments it was high at station V as $64.11 \pm 11.96 \mu\text{g/g}$ during 2011. In the phytoplankton, the concentration was measured highest at station II as $4.343 \pm 0.976 \mu\text{g/g}$ dry weight in the year 2012 (Figure 7). The sedimentation of Pb metal concentration probably the chemical fertilizers from the agricultural field and sewage, domestic disposal into the aquatic environment. Pb toxicity leads to anaemic both by impairment of haemoglobin biosynthesis and acceleration of red blood cell destruction in human beings. Lead also depresses sperm count. The lead has been known to inhibit growth of microalgae.

All the heavy metals such as Zn, Cu and Pb were exceeded the reference background value.

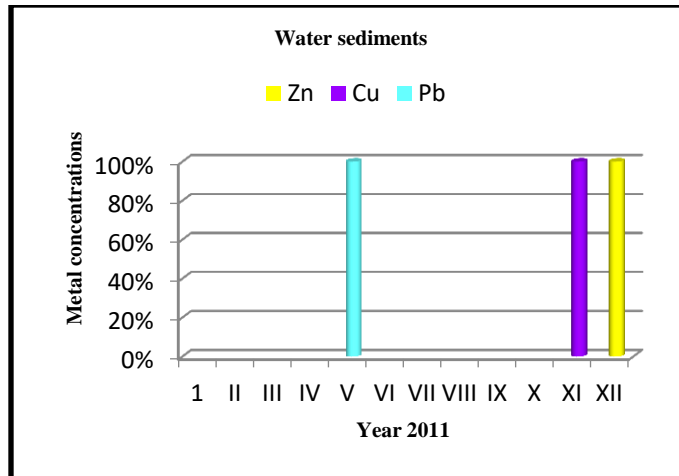


Figure 4: Heavy metal concentrations for water sediments in Tiruchendur and Srivaikundam taluk during 2011

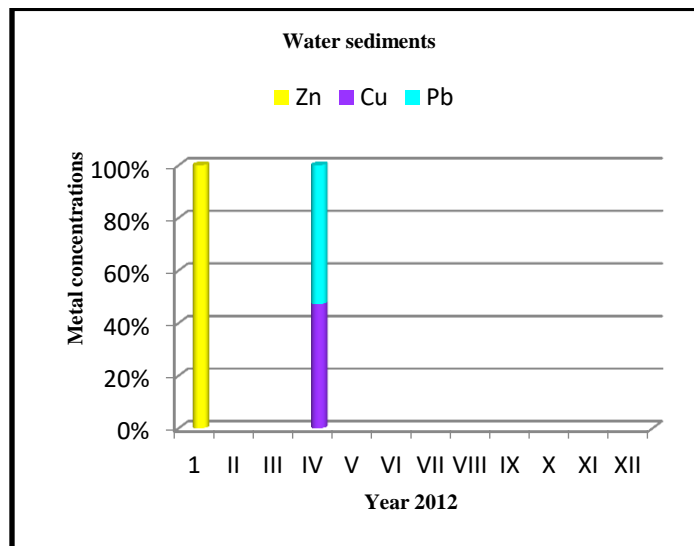


Figure 5: Heavy metal concentrations for water sediments in Tiruchendur and Srivaikundam taluk during 2012

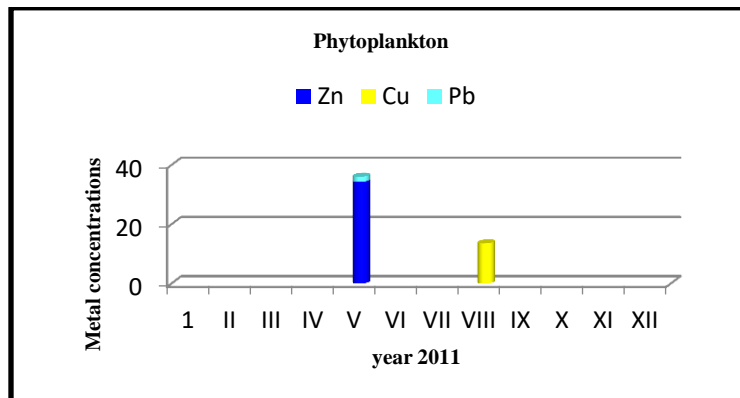


Figure 6: Heavy metal concentrations for phytoplankton in Tiruchendur and Srivaikundam taluk during 2011

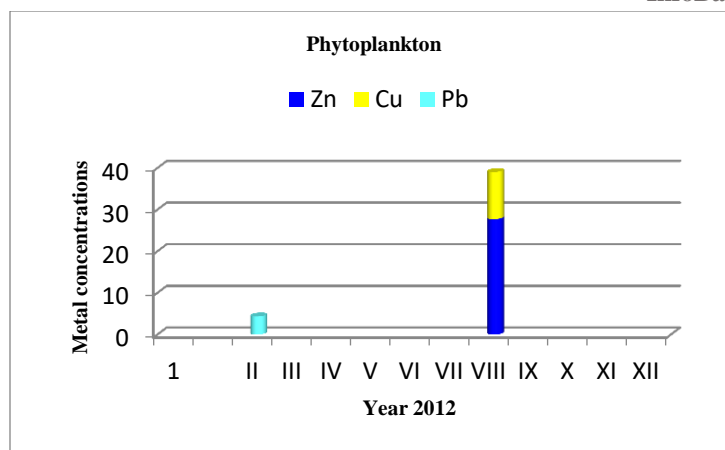


Figure 7: Heavy metal concentrations for phytoplankton in Tiruchendur and Srivaikundam taluk during 2012

Pollution Load Index (PLI)

The contamination Factor sediment quality index showed that the CF values of metals such as Zn, Cu and Pb were low (<1) in the water bodies (Table 1&2). Whereas in the water sediments during the year 2011, at stations II to IX and XI, XII the CF values were < 3 belongs to class 2 (moderate CF) (Table 3). The pollution status in the year 2012 (Table 4) indicated that stations from 1 to VIII belongs to CF class 2 (moderate CF) and the remaining stations fall on class 1 indicated low CF. Consequently, the CF values for metals like Zn, Cu and Pb in the phytoplankton (Table 5 &6) falls on class 1 indicated low CF in both the years (2011 to 2012).

Table 1: Geo-accumulation index (I_{geo}), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk water bodies during 2011

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	-1.86	0.19	-2.16	0.03	-7.09	0.00	0.00
II	-2.45	0.13	-2.03	0.03	-6.80	0.40	0.11
III	-2.03	0.17	-1.72	0.04	-6.84	0.39	0.13
IV	-4.11	0.06	-1.84	0.04	-6.78	0.32	0.09
V	-2.68	0.11	1.69	0.15	-6.78	0.00	0.00
VI	-3.17	0.11	1.62	0.15	-6.68	0.56	0.20
VII	-2.42	0.20	2.46	0.15	-4.43	0.00	0.00
VIII	-2.65	0.17	2.57	0.15	-4.80	0.01	0.06
IX	-2.84	0.15	1.48	0.11	-4.85	0.00	0.00
X	-2.56	0.18	0.56	0.10	-4.10	0.00	0.00
XI	-3.20	0.11	0.06	0.12	-3.12	0.00	0.00
XII	-3.19	0.11	0.52	0.10	-3.01	0.00	0.00

Table 2: Geo-accumulation index (I_{geo}), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk water bodies during 2012

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	-3.18	0.11	-2.30	0.45	1.79	0.34	0.25
II	-2.84	0.15	-2.65	0.36	1.24	0.35	0.26
III	-3.20	0.11	-2.18	0.50	2.25	0.36	0.27
IV	-2.56	0.18	-2.35	0.44	3.50	0.33	0.29
V	-3.19	0.11	-2.24	0.48	1.69	0.35	0.26
VI	-2.69	0.16	-2.42	0.42	1.62	0.34	0.28
VII	-2.75	0.16	-2.78	0.33	2.46	0.34	0.26
VIII	-2.51	0.18	-3.17	0.25	2.57	0.28	0.23
IX	-2.75	0.15	-2.68	0.23	1.48	0.35	0.22
X	-2.06	0.25	-1.84	0.41	0.56	0.34	0.32
XI	-2.42	0.20	-1.78	0.43	0.06	0.32	0.30
XII	-2.42	0.20	-1.97	0.38	0.52	0.34	0.29

Table 3: Geo-accumulation index (I_{geo}), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk water sediments during 2011

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	-2.16	0.33	-2.68	0.23	-0.18	1.32	0.46
II	-0.13	1.36	-1.84	0.41	0.49	2.10	1.05
III	0.04	1.54	-0.84	0.83	0.92	2.84	1.53
IV	-0.71	0.91	-1.13	0.68	0.74	2.50	1.15
V	0.31	1.85	-0.38	1.15	1.10	3.20	1.89
VI	-0.46	1.09	-1.42	0.55	0.29	1.83	1.03
VII	-0.04	1.46	-1.15	0.67	0.45	2.05	1.26
VIII	0.29	1.83	-0.62	0.97	0.94	2.87	1.72
IX	0.33	1.88	-1.00	0.75	1.00	2.99	1.61
X	-0.56	1.02	-1.78	0.43	0.26	1.80	0.92
XI	0.82	2.64	-0.10	1.40	0.77	2.56	2.11
XII	0.86	2.71	-0.94	0.78	0.71	2.46	1.73

Table 4: Geo-accumulation index (Igeo), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk water sediments during 2012

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	0.93	2.86	-0.76	0.88	0.79	2.60	1.87
II	0.82	2.65	-0.36	1.17	0.60	2.28	2.06
III	0.09	1.60	-1.08	0.71	0.47	2.08	1.33
IV	0.87	2.74	-0.34	1.18	0.99	2.98	2.12
V	0.61	2.30	-0.79	0.87	0.90	2.79	1.77
VI	0.17	1.68	-0.36	1.16	0.94	2.87	1.77
VII	0.09	1.59	-0.45	1.09	0.83	2.67	1.66
VIII	-0.24	1.26	-0.64	0.96	0.79	2.58	1.46
IX	-0.72	0.91	-1.97	0.38	-0.28	1.23	0.75
X	-0.68	0.93	-1.86	0.41	0.56	2.20	0.94
XI	-1.69	0.46	-2.45	0.27	0.06	1.56	0.57
XII	-1.17	0.66	-2.03	0.36	0.52	2.15	0.79

Table 5: Geo-accumulation index (Igeo), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk for phytoplankton during 2011

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	-4.31	0.23	-5.77	0.14	-5.15	0.06	0.31
II	-3.47	0.19	-4.80	0.11	3.71	0.04	0.27
III	2.16	0.11	2.59	0.06	2.50	0.03	0.18
IV	-4.59	0.25	-6.50	0.16	-5.28	0.06	0.34
V	-6.54	0.36	1.01	0.25	-6.93	0.08	0.44
VI	-5.80	0.32	-9.41	0.23	-5.51	0.06	0.41
VII	-2.20	0.12	3.11	0.07	1.91	0.02	0.20
VIII	-6.13	0.33	1.22	0.30	-6.19	0.07	0.46
IX	1.76	0.00	-8.31	0.02	-3.79	0.04	0.00
X	-6.21	0.00	-4.93	0.01	-6.69	0.08	0.00
XI	1.95	0.01	1.09	0.02	-5.40	0.06	0.05
XII	2.09	0.01	-9.96	0.02	1.51	0.01	0.05

Table 6: Geo-accumulation index (Igeo), Contamination factor and Pollution Load Index (PLI) values of heavy metals in Tiruchendur and Srivaikundam taluk for phytoplankton during 2012

Stations Number	Zn(I-geo)	CF	Cu(I-geo)	CF	Pb(I-geo)	CF	PLI
I	-3.72	0.20	-4.08	0.10	-4.44	0.05	0.10
II	-3.03	0.16	-4.62	0.11	1.74	0.21	0.15
III	1.89	0.10	1.78	0.04	-4.08	0.05	0.05
IV	-4.05	0.22	-6.27	0.15	-4.44	0.05	0.11
V	-4.89	0.27	-8.78	0.21	-4.83	0.06	0.15
VI	-3.86	0.21	-8.61	0.21	-4.42	0.05	0.13
VII	1.76	0.09	-3.12	0.07	-5.24	0.06	0.07
VIII	-5.28	0.29	1.02	0.25	-5.56	0.06	0.16
IX	-8.06	0.00	-9.69	0.02	-5.43	0.06	0.00
X	-4.15	0.00	-8.66	0.21	-5.24	0.06	0.00
XI	1.66	0.00	-6.68	0.16	1.04	0.13	0.00
XII	1.66	0.00	-8.91	0.21	1.17	0.14	0.00

7. Future Recommendations

- Discharge of effluents into the fresh water bodies used for drinking purposes must be prohibited; this might be enforced in penalizing those who disobey.
- Natural resources should be protected from unwanted anthropogenic activities.
- Survive under boundary lines of the fresh water resources are to be clearly demarked to prevent further human encroachment.
- A comprehensive programme of periodical monitoring and analysis of fresh water resources is necessary to assess the water quality for sustainable development.
- Inlets and outlets should be checked frequently to avoid blockages.
- Non-biodegradable objects should not be thrown into the fresh water resources.

8. Conclusion

A comprehensive analysis of published data indicates that heavy metals such as zinc, copper and lead, occur naturally. However, anthropogenic activities contribute significantly to environmental contamination. These metals are systemic toxicants known to induce adverse health effects in humans. In many areas of metal pollution, chronic low dose exposure to multiple elements is a major public health concern. Elucidating the mechanistic basis of heavy metal interactions is essential for health risk assessment and management of chemical mixtures. Hence, research is needed to further elucidate the molecular mechanisms and public health impact associated with human exposure to mixtures of toxic metals.

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