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### **ORIGINAL RESEARCH ARTICLE**

# Seasonal distribution of heavy metals in Vellar estuary, Mudasalodai and Muzhukuthurai Coastal Waters, South East Coast of India

## K. Santhi and C. Prabhahar\*

Department of Zoology, Annamalai University, Annamalai Nagar -608 002, Tamil Nadu, India

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### ABSTRACT

In this present research work, the heavy metal contamination in Vellar estuary, Mudasalodai and Muzhukuthurai coastal waters, South east coastal of India were evaluated in this study, heavy metals such as copper, zinc, lead, iron, chromium and cadmium were analyzed in the water samples. The metals concentration in water during the present study period showed pronounced spatio-temporal variations. The spatio- temporal variations of heavy metals at different stations were due to the variations in point sources. Occurrence of higher levels of heavy metals at all the three stations may be due to agricultural runoff, effluent discharge from the discharge of tanneries and distilleries at the upstream of vehicular emissions the river and to the air-borne due to the recently developed East Coast Road (ECR). The sample analysis was done by microwave assisted digestion and atomic adsorption spectrophotometer (AAS).

**Key words:** Vellar estuary, Mudasalodai, Muzhukuthurai, Coastal waters, Heavy metals and Atomic absorption spectrophotometry (AAS).

#### INTRODUCTION

Heavy metals are considered as major resources of pollution in natural water. These have received considerable attention because of the inherent toxicity to the living aquatic forms. The toxicity of heavy metals in water is affected by pH, hardness, alkalinity and organic materials <sup>[1]</sup>. Another type of toxic pollution comes from heavy metals such as cadmium, mercury and lead. Recently, a high toxic chemical called TriButylTin (TBT) is used in paints to protect boats from the ravaging effects of the ocean. Mineral, containing heavy metallic elements are of widespread occurrence in rocks and soils, when they weathered, cations of the heavy metals are liberated and find their way into surface waters and soil waters <sup>[2]</sup>. Lead, copper and zinc have been extensively mined and whose environmental levels have been strongly influenced by man, all are toxic to living animals and are considered as serious pollution <sup>[3]</sup>. The aquatic ecosystem metallic compounds occur in low concentration. Heavy metals may come from natural sources, leached from rocks and soils according to their geochemical mobility and also from anthropogenic source as the result of human land occupation and industrial pollution <sup>[4]</sup>.

Depending on their solubility, these metals may eventually associated with be suspended particulate matter or accumulate in the bottom sediments. The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems, with the accumulation of metals in the target organs<sup>[2]</sup>. Trace elements are essential to life but at high concentration may become hazardous. Heavy metals such as cadmium, arsenic and lead several problems can cause in aquatic environments due to their persistence, toxicity and tendency to accumulate in tissue<sup>[5]</sup>.

The trace amount of chromium is necessary for the entire organism as it is needed for the proper utilization iron and conversion of into haemoglobin. Excessive discharge of chromium into the aquatic environment can have an adverse effect both on animals and man who eat these animals as food. In animals, it reduces fertility <sup>[6]</sup>. The copper is an essential trace element, which is widely distributed in nature and also widely used in metal industries. Copper sulphate mixed with lime is used as a fungicide. Medicinally copper sulphate is used as an emetic, it is also used as an antiparasitic agent based on its astringent and caustic actions. Copper levels in human body vary with age. Copper levels in brain increase with age and Cu levels are high in new borns than in adults <sup>[7]</sup>. The cadmium contamination of water may also come from use of metallic and plastic pipes, while super phosphate fertilizers, sewage sludge and automobile tyres also contain some amount of this toxic metal. The main problem with Cd in human nutrition is that the body does not completely excrete whatever Cd is absorbed. Cd in water at 10 ppm level can kill fishes in one day while at 2 ppm level they will be killed in 10 days. Hardness and salinity of water provides some degree of protection <sup>[8]</sup>. The human exposure to lead occurs primarily through drinking water, airborne lead-containing particles and lead based paints. Several industrial processes create lead dust and fumes. Lead is airborne for a period of 10 days it falls into the ground and becomes distributed in soils and water sources. It may cause fatigue, irritability, processing difficulties, information memory problems, a reduction in sensory and motor reaction<sup>[9]</sup>.

The zinc is nutritionally an essential element and is required for the activity of a number of enzymes. Mining, processing and smelting of ores for the extraction of zinc constitutes the chief source of zinc pollution in the environment. Zinc content in aquatic invertebrates in fresh unpolluted water ranges between 25-200 mg per litre. Above 40 ppm level this metal imparts a faint but definite metallic taste and milky appearance to fresh water <sup>[10]</sup>. The increased loads of nutrients, heavy metals and other compounds like pesticides, fertilizers have resulted from changes in land use and anthropogenic development of the river basins. Since, rivers constitute the main inland water resources for domestic, industrial and irrigation purposes, it is imperative to prevent and control the river pollution and to have reliable information on the quality of water for effective management <sup>[11]</sup>.

## MATERIALS AND METHODS

Heavy metals in the water samples were analyzed by adopting the procedure of <sup>[12]</sup>. Water samples were collected at monthly intervals (for a period of 12 months from July 2012 to June 2013) and were collected in pre cleaned and acid washed polypropylene and acid washed polypropylene bottles of one litre capacity and were immediately kept in an ice box and transported to the laboratory to avoid contamination. Water samples were then filtered through a Millipore filtering unit using a Millipore filter paper (pore size 0.45 µm). The filtered water samples were re concentrated with APDC-MIBK extraction by following the procedure of <sup>[12]</sup>. The heavy metals in water were analyzed in air-acetylenemic absorption spectrophotometer (AAS-Model 802), undisturbed surface sediment samples were collected using a grab sampler placed in plastic containers for transport to the laboratory. Sample preparation for chemical analyses involved procedures for sub sampling during drying, sieving crushing and storage. All these steps were followed by adopting the methods explained in <sup>[13]</sup>. Sediments samples were collected on a monthly basis in 2 stations using a Petersen's grab for one consecutive year. The samples were taken from the mid portion of the grap to avoid the metal contamination and brought to the laboratory in clean polythene bags. The samples were shade dried and the course material such as pebbles, coarse organic fibres and shells were removed. The remaining material was crushed, sieved (0.5)mm sieve) and homogenized before being split into sub samples. The collected samples were ground to fine powder using pestle and Mortar and dried in an oven at 60°C for 24hrs. One gram of powder sample was digested with hydrochloric acid and nitric acid-perchloric acid (HCl, HNO<sub>3</sub>, and HCl<sub>4</sub>) mixture at a ratio of 10:5:1 (25, 12.5, 2 ml) at 300°C following the method of Parasons et al. <sup>[14]</sup> the digested residues were dissolved and filtered. A small aliquot was injected into atomic absorption spectrophotometer (AAS) Perkin Elmer Model A400 the qualified values for zinc, copper, iron, cadmium, chromium and lead. The standards are expressed in  $\mu g/g$ . The reagent blanks were run for each set of samples and also analyzed for both water and sediment samples. The analytical precision was reported in AAS better than  $\pm$  10%. The following are the instrument condition for trace metal analyses <sup>[13]</sup>.

## **RESULTS AND DISCUSSIONS**

Results of heavy metals in sediment at station1 minimum (19.36 mg/l) concentration of copper was recorded during summer season and the maximum (67.21 mg/l) during post monsoon season. At station 2, minimum Cu concentration of (24.49 mg/l) was recorded during pre monsoon and the maximum (75.22 mg/l) during monsoon season. At station 3, it was minimum 3.8 (mg/l) during post monsoon and the maximum

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(15.75mg/l) during monsoon season. At station 1, throughout the study period, the lead in water was found to be minimum (0.58 mg/l) during post monsoon and maximum (1.9 mg/l) during the monsoon season. At station 2, the lead in water was minimum (0.83 mg/l) in summer and maximum (2.15 mg/l) during the pre - monsoon season. At station 3, it was minimum (0.14 mg/l) during post monsoon season and maximum (0.83 mg/l) during the monsoon season. The heavy metal lead was found to be high at station 2. At station 1, concentration of Iron in water ranged from 0.33 mg/l to 0.99 mg/l. Minimum concentration (0.33 mg/l) was recorded during summer season and the maximum (0.99 mg/l) during the monsoon season. At station 2, concentration of Iron in water ranged from 0.11 mg/l to 0.94 mg/l with minimum concentration (0.11 mg/l) during pre monsoon season and the maximum (0.94 mg/l) during monsoon – season. At station 3, minimum concentration (0.2 mg/l)was recorded during pre monsoon season and the maximum (0.31 mg/l) during the monsoon season. In general, minimum concentration of Iron in water was recorded during the summer and the maximum during the monsoon season at all the stations. The zinc was found to be high at station 1. The station 1 registered minimum (0.97 mg/l)and the maximum (3.97 mg/l) values of chromium in water during post monsoon and monsoon seasons respectively. The station 2 registered minimum (1.03 mg/l) and maximum (1.44 mg/l) values of Cr in water during summer and monsoon seasons respectively. The station 3 registered minimum (0.71 mg/l) and maximum (8.71 mg/l) values of Cr in water during pre monsoon and monsoon seasons respectively. In general, post monsoon season recorded maximum values of Cr in water at all the stations. The chromium was found to be high at station 3. At station 1, cadmium was minimum (0.91 mg/l) during the summer season and the maximum (1.93 mg/l) during monsoon season. At station 2, minimum (1.01 mg/l) during the post - monsoon season and maximum (1.65 mg/l during the summer seasons. At station 3, it was minimum (0.19 mg/l) during post monsoon – and maximum (0.99 mg/l) during the pre - monsoon seasons. The lead was found to be high at station 1. The analyzed concentrations of heavy metals in the coastal waters during different seasons were geographically represented in (Fig 1-6). ANOVA between heavy metals in the coastal water showed

a significant value whereas within the metals insignificant.

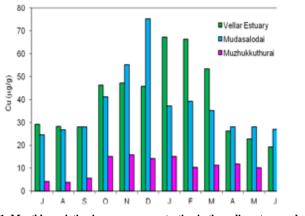


Fig 1: Monthly variation in copper concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

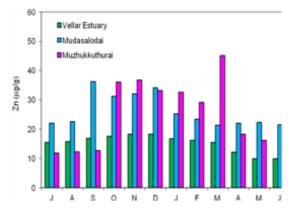


Fig 2: Monthly variation in zinc concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

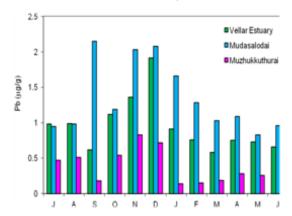


Fig 3: Monthly variation in lead concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

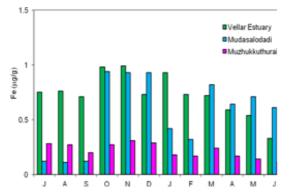


Fig 4: Monthly variation in iron concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

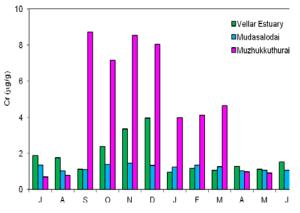


Fig. 5: Monthly variation in chromium concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

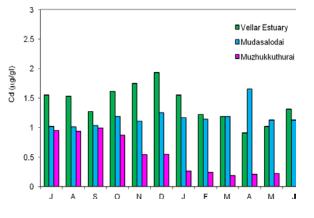


Fig 6: Monthly variation in cadmium concentration in the sediments recorded at station 1, station 2 and station 3 from July 2012 to June 2013

The analyzed concentration coefficient value between the heavy metals in the coastal waters during the season July 2012 to June 2013 and presented respectively.

The copper is a fundamental micronutrient to all forms of life in enzyme activity or random rearrangement of natural protein. These results agree with those obtained <sup>[15,16]</sup> who had revealed that the increase is anticipated to industrial, drainage and sewage effluents. Also, it may be due to elevated metal- binding protein synthesis as recorded <sup>[18]</sup>.

The zinc is an essential element and is a common pollutant as well. Mining smelting and sewage disposal are major source of zinc pollution. Fish take it up directly from water, especially by mucous and gills <sup>[15]</sup>. The high accumulation of zinc in studied fish liver agrees with. In present study iron contamination in river water may be due to industrial effluent and automobile activities performed on the bank of river <sup>[16]</sup>. The lead concentration was more during the monsoon in both stations due to various sources of pollution paints, diesel, fuel combustions pipes and solder discarded batteries and natural deposits <sup>[17]</sup>. The chromium pollution in industrial discharge and geological mining sites, both stations show chromium concentrations high in monsoon A number of toxic elements are season. introduced into the aquatic environment from the effluents coming from the large industries, resulting biodiversity and changes in water quality <sup>[18]</sup>. The Cu and Cd concentrations were high during the post monsoon season. Zn and Pb concentrations were high during the stations, Cu and Cd concentrations were high during the postmonsoon season. Zn and pb concentrations were high during the pre-monsoon, summer and postmonsoon<sup>[20]</sup>.

The higher concentration of metals observed during monsoon could be attributed to the heavy rainfall and subsequent river runoff, bringing much industrial and land derived materials along with domestic, municipal, and agricultural wastes, which include residues of heavy metal containing pesticides <sup>[19]</sup>.

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