



# Seasonal Variations of Heavy Metal in Seawater and Sediment from Uppanar Estuary, Cuddalore Coast, India

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**Abstract:** The current study was carried out to estimate of heavy metal concentration in seawater and sediment samples from industrial area of Uppanar estuary, Cuddalore. Seawater and sediment samples were collected in two different stations during four seasons (post monsoon, summer, pre monsoon and monsoon). The heavy metal concentration was higher in sediment samples were compared with water samples in monsoon season compare with other seasons. The order of heavy metal concentration in seawater and sediment samples was  $Fe > Cu > Zn > Cd > Cr > Ni$ .

**Keywords:** Uppanar estuary, Seawater, Sediment, Cuddalore coast, Heavy metal

The contamination of aquatic and terrestrial ecosystems with heavy metals is a major environmental problem. Some of these metals are potentially toxic or carcinogenic at sufficient concentrations and can cause serious human health hazards if they enter the food chain. A lot of input eventually accumulates in the estuarine zone and continental shelf, which are important sinks for suspended matter and associated land-derived contaminants. (Masindi 2018, Walker et al., 2012). The pollution of aquatic and terrestrial ecosystems with heavy metals is a major environmental trouble. Some of these metals are potentially toxic or carcinogenic at enough concentrations and can cause serious human health hazards if they enter the food chain. Heavy metals in the sediment are essential to assess the extent of metal pollution. The distribution of heavy metals in solution has widely been recognized as a major factor in the geochemical behavior, transport and biological effects of these elements in natural waters (Karthikeyan et al., 2004, Ananthan et al., 2006, Karthikeyan et al., 2007).

The majority of the heavy metals are essential for growth of organisms, but are only required in low concentrations (Akpoveta et al., 2010). The increasing concentration of heavy metals leads to bioaccumulation of metals in fauna and flora if the rate of uptake of heavy metals by the organisms is more than the excretory phase. Heavy metals are not biodegradable, so they accumulate in primary organs in the body and over time begin to fester, leading to various symptoms of diseases (Siyanbola et al., 2011). Thus, untreated or incompletely treated industries effluent can be harmful to both aquatic and terrestrial life by unfavorably affecting on the natural ecosystem and long term health

effects. Such accumulation takes place by biological and geochemical mechanisms (Karbassi and Amirnezhad 2004). Evaluation of heavy metal concentration in the coastal waters can be made by using indicator organisms which accumulate pollutants proportionally to their environmental condition (Thangaradjou et al., 2010).

Heavy metals have been renowned to interact with nuclear proteins together with DNA which cause specific damage. Two types of damages may be caused by direct and indirect damage. In direct damage, conformational changes occur to the biomolecules, due to the metal. The heavy metal causes indirect damage, which is a result of the production of immediate oxygen and nitrogen species which comprise of the hydroxyl and superoxide radicals, hydrogen peroxide, nitric oxide and other endogenous oxidants. Heavy metals also activate signaling pathways (Valko et al., 2005). These are the basic steps used in sewage treatments depending on what the sewage contains and where it is being process. Several controls have been set up due to the problems caused by sewage exclusion into the rivers and seas without being treated. Severe regulations have been placed and better technology has been developed to decrease the amounts of pollutants that are unnerved in the waters (Walker et al., 2012).

Chromium is a cancerous and toxic element and is used in many industries that pose a threat to regional climates. In assessment to natural chromium emissions from the environment, ferrochrome industry emissions are at the highest level (Coetzee et al., 2020). Nickel is a naturally abundant element and has extensive industrial uses. It is emitted from both natural and anthropogenic sources into the

atmosphere (Li et al., 2016a). It has many unpleasant effects on humans, and causes allergies, nasal and lung cancer, and kidney and cardiovascular diseases owing to the inhalation of contaminated air (Genchi et al., 2020, Lu et al., 2005). The present study focus on the level of dissolved trace metals in coastal water off Cuddalore.

## MATERIAL AND METHODS

**Study area:** The Uppanar estuary is situated in Cuddalore (Lat. 11°43'N, Long. 79°46' E). (Fig. 1) is at an average height of about 1 m above sea level. It is brief through the Industrial coastal town of Cuddalore on the southeast coast of India. The major 55 industries along the Uppanar estuary contain chemicals; beverage industrialized, tanneries, oil, soap, paint production, etc. Two different sampling sites have been selected for this study.

**Sampling site I- Uppanar estuary (SIPCOT):** The Uppanar estuary runs following 1 km away from the mouth of the estuary SIPCOT (State Industrial Promotion Corporation of Tamil Nadu) industrial complex is located in Cuddalore which consists of many chemicals, plastics, soap, pharmaceutical industries, etc. This open type of estuary receives treated and untreated industrial waste containing toxic wastage. In addition to the estuary to receives also domestic and municipal waste in Cuddalore old town.

**Sampling site II- Sea mouth region (Fishing harbor):** The station 2 adjacent to the mouth of the estuary located on near

the Cuddalore old town all the discharged industrial, municipal, agriculture and domestic waste are mixed and diluting the sea mouth region.

**Sample collection and maintenance:** The sample collection was made during forenoon from January to December 2012 for four seasons viz. post-monsoon (January-March), summer (April-June), pre-monsoon (July-September) and monsoon (October-December) from two sites in using wide mouth polyethylene bottle regularly. The collected seawater sample safely transported to the laboratory condition in ice box and preserved refrigerator for 4°C till their use. The sediment samples (1 meter depth) were scraped in pre cleaned zip lock polyethylene cover after collection the sediment samples were brought to the laboratory condition and air dried for 5 days awaiting reaches a stable weight.

**Heavy metal analysis in seawater samples:** The collected seawater samples taken 1 liter were filtered through Whatman filter paper No. 42 and adjusted to pH 2 with HNO<sub>3</sub> taken in a separating funnel. 10 ml (3% w/v) of a freshly prepared solution of ammonium-pyrolidine dithiocarbamate (APDC) added into the funnel, and the mixture was shaken by a mechanical shaker for 10 min. Further, 25 ml of iso-butyl methyl ketone (MIBK) added to this mixture and shaken for 15 min. The phases were allowed to separate. The top organic phase was collected. The bottom aqueous phase again shaken with 25 ml of MIBK, and the organic phase obtained then pooled with an earlier one. The pooled organic phase mixed with 2 ml of 50% HNO<sub>3</sub> and shaken vigorously for 10 min to separate the bottom acid layer and make up 25 ml of metal free distilled water (Jonathan et al., 2008).

**Heavy metal analysis in sediment samples:** Heavy metal extraction in sediment samples with slightly modified. The dried sediment samples were ground well in a mortar and pestle it weighed in 1.00 g of dried sediment sample was taken with a mixture of 1,5 and 2 ml of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO<sub>4</sub>. The mixture was boiled on a hot plate, evaporated to near dryness. At the end of the digestion, the samples were making up 25 ml of metal free double distilled water and filtered through Whatman No.42 filter paper. The filtered sample was aspirated into the Atomic Absorption Spectrophotometer (AAS) and the reading was taken and the quantified metals are expressed in parts per million (ppm).

**Statistical analysis:** All the data were analyzed statistically apply using software PAST (version 3) and SPSS (version 16) for the studied parameters.

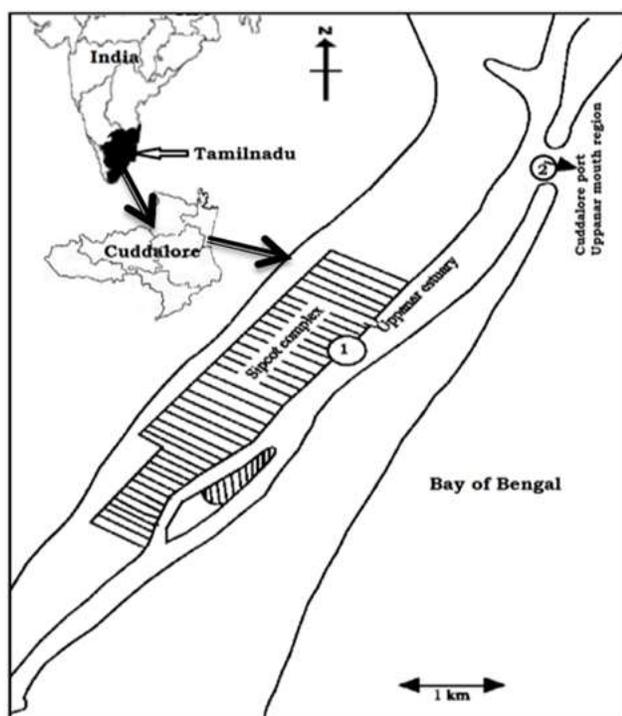


Fig. 1. Sampling sites on the Cuddalore coast

## RESULTS and DISCUSSION

**Seasonal variations of heavy metals in seawater samples:** Iron concentration of seawater sample value

varied from 2.53 ppm to 3.21 ppm (St. 1) and 2.21 ppm to 2.89 ppm (St. 2). The highest was during the monsoon season and lowest value during the summer season. The seasonal correlation matrix indicated for Fe with Cu and cadmium in the sediment is highly significant in St.I. Copper in water values ranged from 1.86 to 2.19 ppm (St. 1) and 1.72 to 2.01 ppm (St. 2). The highest value observed during post-monsoon and monsoon season and the lowest value was during the summer season.

Zinc in water content varied from 1.65 to 2.10 ppm (St. 1) and 1.53 to 2.01 ppm. The highest was observed in post-monsoon and monsoon season and the lowest during the summer season. Cadmium in sea water values ranged from 1.38 to 1.53 ppm (St. 1) and 1.32 to 1.46 ppm (St. 2). The maximum was observed during the monsoon period and the smallest value was observed during the summer season. Chromium in water concentration varied from 1.42 to 1.65 ppm (St.1) and 1.36 to 1.56 ppm (St.2). The highest was recorded during monsoon season and the lowest was observed during the summer and pre-monsoon seasons. Nickel in sea water values ranged from 1.21 to 1.31 ppm (St.1) and 1.18 to 1.28 ppm (St.2). The high nickel value was observed during the monsoon period and the lowest value was observed during the summer season in both study sites (Table 1).

**Seasonal variations of heavy metals in sediment samples:** Higher metal values recorded in sediment samples were compared with water samples. The iron present in the sediment sample varied from 2.50 to 4.80 ppm (St.1) and 2.20 to 4.20 ppm (St.2). The highest was observed during the monsoon season and lowest during the summer season. The amount of copper present in the sediment sample ranged from 1.86 to 2.21 ppm (St.1) and 1.69 to 2.05 ppm (St.2). The highest values were observed during the monsoon season and lowest value was observed during the summer season. Zinc concentration of sediment samples varied from 1.68 to 2.25 ppm (St.1) and 1.00 to 1.25 ppm

(St.2). The highest were observed during the monsoon season and lowest during the summer and pre-monsoon seasons. The amount of cadmium present in the sediment sample ranged from 1.31 to 1.51 ppm (St.1) and 1.26 to 1.41 ppm (St.2). The highest cadmium was observed during the monsoon season and lowest during the summer season. Chromium concentration in sediments varied from 1.48 to 1.67 ppm (St.1) and 1.42 to 1.56 ppm (St.2). The high chromium concentration was observed during the monsoon season and lowest during the summer season. Nickel concentration in the sediment sample values ranged from 1.33 to 1.63 ppm (St.1) and 1.27 to 1.52 ppm (St.2). The highest value was observed during the monsoon season and lowest during the pre-monsoon season (Table 2).

The concentrations of heavy metals in water and sediment varied depending on their incidence and seasonal difference. Generally, the natural source of heavy metal pollution in coastal waters through land derived run-off, chemical and mechanical weathering of rocks. The components were also washed from the atmosphere through rainfall, windblown dust, forest fire and volcanic particles (Sankar et al., 2010). The highest concentration of heavy metals was observed in sediment sample as compared with water samples. The high concentration of heavy metals in sediment samples depends on the migration of the water column downwards in sediment. Highest metal contents were Fe, Cu and Zn in monsoon and post monsoon season. Maximum iron concentration observed in monsoon closely followed by a post monsoon season. The season of abundance of metal is due to run off water into the sampling sites. This was substantiated in sediment sample which also exhibited similar trends of results. The correlation matrix of water samples during all seasons was significantly different. The correlation matrix indicated that iron with copper and cadmium in the sediment were significant ( $r=0.96$ ;  $r=0.98$ ) in St.I (Table 3).

The copper (Cu) is a normal element which is widely

**Table 1.** Heavy metals in water sample (Mean  $\pm$  Standard deviation)

Heavy metals	Stations	Fe	Cu	Zn	Cd	Cr	Ni
Post monsoon	S1	3.10 $\pm$ 1.0	2.12 $\pm$ 1.07	2.09 $\pm$ 0.99	1.49 $\pm$ 0.98	1.57 $\pm$ 0.95	1.24 $\pm$ 0.94
	S2	2.65 $\pm$ 1.0	1.98 $\pm$ 0.95	2.00 $\pm$ 0.90	1.39 $\pm$ 0.89	1.51 $\pm$ 0.87	1.19 $\pm$ 0.87
Summer	S1	2.53 $\pm$ 1.0	1.86 $\pm$ 0.93	1.65 $\pm$ 0.89	1.38 $\pm$ 0.87	1.42 $\pm$ 0.84	1.21 $\pm$ 0.83
	S2	2.21 $\pm$ 1.0	1.72 $\pm$ 0.86	1.53 $\pm$ 0.83	1.32 $\pm$ 0.81	1.36 $\pm$ 0.79	1.18 $\pm$ 0.78
Pre monsoon	S1	2.60 $\pm$ 1.0	1.96 $\pm$ 0.96	1.76 $\pm$ 0.91	1.41 $\pm$ 0.89	1.51 $\pm$ 0.87	1.25 $\pm$ 0.86
	S2	2.32 $\pm$ 1.0	1.82 $\pm$ 0.88	1.65 $\pm$ 0.84	1.35 $\pm$ 0.83	1.43 $\pm$ 0.81	1.21 $\pm$ 0.80
Monsoon	S1	3.21 $\pm$ 1.0	2.19 $\pm$ 1.10	2.10 $\pm$ 1.02	1.53 $\pm$ 1.0	1.65 $\pm$ 0.97	1.31 $\pm$ 0.96
	S2	2.89 $\pm$ 1.0	2.01 $\pm$ 1.02	2.01 $\pm$ 0.95	1.46 $\pm$ 0.94	1.56 $\pm$ 0.91	1.28 $\pm$ 0.90

spread in soils and rock sand in rivers and the sea. High copper value was observed during the monsoon season and lowest value was observed during the summer season in both St.1 and St.2. The copper concentration at the outfall increased twofold compared to the outlet due to the anthropogenic activity, agricultural run-off; industrial and domestic waste water into the river. Copper is released into water as a result of ordinary weathering of soil and discharges from industries and sewage treatment plants (Hutchinson 2002). Copper concentration in downstream was several times higher than the raw effluents and may be attributed to domestic sewage and runoff from extensive farmed areas (Wu et al., 2008). Copper has a positive correlation coefficient with iron (Table 3).

Zinc concentration has always had a tendency to couple

with organic carbon. Decomposition of the organic substance release heavy metals reverse to sediments and accumulated, and this process might be responsible for the strong association of zinc and copper with organic carbon (Bardarudeen et al., 1996). The highest organic carbon observed during the post-monsoon and monsoon seasons coincide with the elevated level of zinc and copper in sediments. Besides, the release of heavy metals through the influx of land-derived contaminant increased the level of zinc and copper despite they are meagre in amount.

Generally, zinc and copper are good indicators of anthropogenic inputs.

High cadmium ranges were observed in monsoon and lowest in summer season, which could be attributed to the particulate fractions derived from the river run-off caused by

**Table 2.** Heavy metals in sediment sample (Mean ± Standard deviation)

Heavy metals	Stations	Fe	Cu	Zn	Cd	Cr	Ni
Post monsoon	S1	4.3±1.0	2.18±1.0	2.25±1.0	1.42±1.0	1.58±1.0	1.52±1.0
	S2	3.6±1.0	2.0±1.0	2.10±1.0	1.38±1.0	1.49±1.0	1.43±1.05
Summer	S1	2.5±1.0	1.86±1.0	1.68±1.0	1.31±1.0	1.48±1.0	1.38±0.81
	S2	2.7±0.57	1.69±1.0	1.61±1.0	1.27±1.0	1.41±1.0	1.35±1.06
Pre monsoon	S1	2.9±1.0	1.87±1.0	1.79±1.0	1.39±1.0	1.51±1.0	1.33±0.88
	S2	2.2±1.0	1.78±1.0	1.63±1.0	1.31±1.0	1.42±1.0	1.27±1.0
Monsoon	S1	4.8±1.0	2.21±1.0	2.13±0.95	1.51±1.0	1.68±1.0	1.61±1.36
	S2	4.2±1.0	2.25±1.0	2.10±1.0	1.42±1.0	1.57±1.0	1.52±1.0

**Table 3.** Correlation-coefficients matrix (r) of heavy metals in seawater and sediment samples during different seasons at station I

	Water sample							Sediment sample					
	Heavy metals	Fe	Cu	Zn	Cd	Cr	Ni	Fe	Cu	Zn	Cd	Cr	Ni
Water sample													
Fe	1.00												
Cu	0.893	1.00											
Zn	0.690	0.719	1.00										
Cd	0.986 <sup>*</sup>	0.938	0.784	1.00									
Cr	0.770	0.965 <sup>*</sup>	0.784	0.857	1.00								
Ni	0.847	0.625	0.823	0.845	0.545	1.00							
Sediment sample													
Fe	0.975 <sup>*</sup>	0.967 <sup>*</sup>	0.679	0.982 <sup>*</sup>	0.873	0.735	1.00						
Cu	0.887	0.999 <sup>***</sup>	0.687	0.929	0.960 <sup>*</sup>	0.598	0.966 <sup>*</sup>	1.00					
Zn	0.706	0.756	0.998 <sup>***</sup>	0.802	0.821	0.806	0.707	0.726	1.00				
Cd	0.994 <sup>***</sup>	0.935	0.730	0.997 <sup>***</sup>	0.835	0.825	0.989 <sup>*</sup>	0.928	0.750	1.00			
Cr	0.687	0.919	0.808	0.793	0.990 <sup>*</sup>	0.500	0.799	0.910	0.844	0.762	1.00		
Ni	0.860	0.574	0.682	0.821	0.441	0.975 <sup>*</sup>	0.728	0.552	0.664	0.818	0.369	1.00	

\*\*correlation is significant at the 0.05 and 0.01 level

**Table 4.** Correlation-coefficients matrix (*r*) of heavy metals in seawater and sediment during different seasons at station 2

	Water sample						Sediment sample						
	Heavy metals	Fe	Cu	Zn	Cd	Cr	Ni	Fe	Cu	Zn	Cd	Cr	Ni
Water sample													
Fe	1.00												
Cu	0.899	1.00											
Zn	0.770	0.737	1.00										
Cd	0.995**	0.932	0.739	1.00									
Cr	0.781	0.945	0.839	0.808	1.00								
Ni	0.894	0.652	0.832	0.844	0.588	1.00							
Sediment sample													
Fe	0.971 <sup>†</sup>	0.968 <sup>†</sup>	0.706	0.990**	0.849	0.765	1.00						
Cu	0.938	0.995**	0.738	0.964 <sup>†</sup>	0.915	0.710	0.988 <sup>†</sup>	1.00					
Zn	0.774	0.764	0.998**	0.749	0.868	0.812	0.724	0.761	1.00				
Cd	0.981 <sup>†</sup>	0.878	0.631	0.986 <sup>†</sup>	0.704	0.825	0.970 <sup>†</sup>	0.922	0.637	1.00			
Cr	0.715	0.904	0.839	0.742	0.994**	0.535	0.787	0.866	0.869	0.624	1.00		
Ni	0.866	0.564	0.685	0.813	0.436	0.974 <sup>†</sup>	0.725	0.639	0.659	0.833	0.365	1.00	

\*\*correlation is significant at the 0.05 and 0.01 level

monsoonal flow, and occurrence of relatively higher percentage of particulate matter could be due to the heavy rainfall and river run-off received from industrial and land-derived contaminants along with domestic and municipal waste which includes heavy metal-containing pesticides (Karthikeyan et al., 2004, Ananthan et al., 2005,2007). Cadmium has a positive correlation with iron in St.1 and St.2 water samples (Table. 3) and also in sediment samples. Cd is a component of pesticides and fertilizers. The volatilization of Cd from fertilized agricultural lands introduces significant amounts of Cd into the atmosphere, which, through runoff, gets into the aquatic ecosystem (Annema et al., 2016).

The highest chromium and nickel were observed during monsoon season and lowest value was recorded in summer season at both stations. The high chromium during monsoon could be attributed to the Palar river discharge as it carries tannery and distillery effluents from the upstream (Velsamy et al., 2013). Lowest chromium concentration recorded during summer season might be due to the smaller amount or lack of rainfall, which eventually reduces the quantity of river flow.

The estuaries are highly active systems from both a physical and chemical point of view. Sharp gradients in parameters such as temperature, salinity, pH and dissolved oxygen induce considerable biochemical activity and the behaviour of trace elements in the estuarine ecosystems (Wang et al., 2007, Satheeskumar 2011). Dissolved heavy metals such as copper and zinc present in a maximum quantity at relatively high salinity and decreased seawater Cadmium.

## CONCLUSION

The heavy metal concentration in the seawater and sediments from the Uppanar estuaries has recognized that Cu, Zn, Cd, Cr and Ni are present by the change degrees of absorption. It is supposed that the level of absorption that the defect of above metals will continue to increase in Uppanar estuary. In the current study all the metals are originate in higher concentration in the upstream side of the estuary, anywhere additional industries are united along the estuary areas. In this area majority of the industrial wastage, agricultural wastes which are treated or unprocessed waste is released into the estuary, the water flow in this area is stagnant or flow of water will be smaller quantity, which lead to contamination and destroy the ecosystem. Contamination of irrigate by the chemical substance has critically affected the human healthiness because most of these heavy metals cause serious illness.

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