# **EVALUATION OF THE STATUS OF HEAVY METAL** CONTAMINATION AND TEXTURE OF SEDIMENTS IN THE POONTHURA ESTUARY, SOUTHWEST COAST OF INDIA



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Abstract: The present study focuses on the heavy metal contamination in the sediments of Poonthura Estuary, along the southwest coast of India. It is one of the most polluted estuaries in the Thiruvananthapuram district. Over a period of time, Poonthura estuary has been under severe ecological degradation due to the disposal of municipal sewage, land drainage and industrial effluents. On the basis of geographical features and noticeable ecological differences, four stations were selected. Sediment sampling was made for a period of one year and temperature, pH, heavy metal concentration and texture of the were analysed. Marked spatial and seasonal variations in textural characteristics were observed in the Poonthura estuarine system. The main constituents of station 1 and 2 were sandy-clayey-silt and clayey-silty-sand respectively. Heavy deposition of silt fractions noticeable in this region may be attributed to the large amount of drainage reaching here through Parvathy Puthanar canal. Iron content obtained in the sediment ranged between 5100 -55000 ppm and it indicates severe pollution of the estuary by iron. Highest values of copper (160 ppm) might be due to the contamination by Parvathy Puthanar canal and river Karamana. Chromium concentration indicate that the system is moderately polluted. The entire estuary is polluted with lead (10- 60 ppm). Iron, copper, nickel and lead concentrations obtained were under heavily polluted classification levels and chromium showed moderate levels of pollution. In the present study higher concentrations of copper and chromium was observed in clayey-silt zones. Analysis of variance was also done for heavy metals . In the present study the spatial distribution of heavy metals showed considerable fluctuation from upstream to bar mouth. Heavy metals belong to the most hazardous waste products as their toxicity is high and they may get accumulated in tissues. Presence of high levels of heavy metals like copper, nickel, lead and iron, also strongly emphasized the unhealthy condition of the estuary mainly due to industrial and anthropogenic activity.

Key words: Heavy metal, Poonthura estuary, Contamination, Pollution, Sediment, Texture, Industrial waste.

## **INTRODUCTION**

Estuarine and coastal areas are among the most importantplaces for human inhabitants. Estuary is an integral part of all coastal zones and forms natural buffer zone between marine and limnetic region with very little wave action. No two estuaries are alike, mainly due to the constantly changing river discharge and land drainage. They are generally zones of deposition of sediments and are therefore structurally dynamic.Sediment characteristics are not only being influenced by the dynamics of the estuarine system (Baeta et al., 2005), but are also related to human disturbances (transportation, industries, drainage, unscientific aquaculture) of the habitat.With rapid urbanizationand industrialization, heavy metals are continuously carried to he estuarine and coastal sediments at a rapid rate, from upstream of tributaries.

Heavy metal contamination in sediment could affect thewater quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem. Metal composition in the sediment may be controlled by natural andanthropogenic processes (Nesbitt, 1979). Rivers and streams can transport land-based source of pollutants in surfacewater runoff to coastal and estuarine environments. Lateral variations in thedistribution of metals has provided evidence that chemical composition of surface sediments act as a guide to local pollution centres. The sediment of an estuarine system is very important, as it influences the types of organisms living there, especially the plants and benthic animals. The trace metals when introduced into the system do not remain

in water column, but it get precipitated or adsorbed by suspended particulate matter and form part of sediment. Accumulation of trace metals in aquatic sediments become toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity (Praveena *et al.*, 2007).

Sediments are complex mixtures of a number of solid phases that may include the loose sand, clay, silt, organic matter, metal oxides etc. and other soil particles that settle at the bottom of the water body (Davies and Abowei, 2009). Even though the sediments act as sink, the metals may re-enter into the water column by various physical, chemical and biological processes. Groot et al. (1971) have shown that there is a distinct relationship between the sediment particle size and the concentration of various metals including Cu, Zn and Pb. The process of metal accumulation in residue is controlled by and related to the amount of fine grain particles (Cranston, 1976).Clay minerals with its comparatively high cation exchange capacity play a vital role in mobilizing the trace metals. Sediment analysis of aquatic enviro-nment has greater attention in the world's scientific scenario due to growing awareness of environmental pollution and its impact on ecosystem.

This study intends to evaluate the degree of anthropogenic influence on heavy metal concentration in the sediments. Poonthura estuary is one of the most polluted estuary in the Thiruvananthapuram city. Few studies have been conducted to characterise pollution status of heavy metals of this estuary.Some heavy metals in sediments of the Poonthura estuary had been partially reported by KSCSTE (2010). However, the extent and horizontal distribution of heavy metals in sediments from thewhole estuary is still unknown.Over a period of time Poonthura estuary is under severe ecological degradation due to the disposal of municipal sewage, land drainage and industrial effluents.

Thestudy was performed to (1) identify estuarine sediment characteristics (2) to quantify and explain the spatial distribution of heavy metal contaminants in surface sediments and (3) to evaluate degree of contamination of heavy metals in surface sediments of the Poonthura estuarine system.

#### MATERIALS AND METHODS

The study was carried out in Poonthura estuary, one of the important coastal wetlands of Kerala, situated in Thiruvananthapuram district. It is located at the south west coast of India between  $8^{\circ}25' - 8^{\circ}30'$  North latitude and  $76^{\circ}55' - 77^{\circ}00'$ 



Fig. 1. Map showing the study area

East longitude (Fig. 1). It is a semi-closed shallow estuary with an approximate area of 97.59 ha. Karamanariver branches into two at the Thiruvallam bridge and flows down enclosing an island called Edayar and joins the sea at Panathurapozhi. The tidal reaches of the river is designated as the Poonthura estuary. Parvathy Puthanar, the most severely polluted canal in the city, which connects the Velilake and the Poonthura estuary joins at Moonnattumukku. On the basis of geographical features and noticeable ecological differences, four stations were selected for the present investigation. Station1-Moonnattumukku, Station<sub>2</sub> Therya-muttom, Station<sub>3</sub> –Panathura pozhi and Station 4- Aruthamoola.

Sediment sampling was made for a period of one year. The sediment samples were collected every month from the four stations by using a Van Veen Grab. The temperature, pH, heavy metal concentration and texture of the sediments were analysed. The sediment temperature was measured at the site by an accurate Celsius thermometer. A 1:3 sediment suspension in distilled water was prepared and used for determining the sediment pH by an Elico pH meter. A part of washed and dried samples were used for the textural analysis by the combined sieving and pipette method suggested by Krumbein and Pettijohn (1938). The heavy metal (iron, copper, chromium, nickel, lead and cadmium) concentrations were analysedusing an Atomic Absorption Spectrophotometer following the methods of Grasshoff et al., 1983. The results of this investigation were compared to the sediment quality guidelines of USEPA standards. The metal contamination in the sediments was also evaluated by applying contamination factor, C<sub>f</sub> (Hakanson, 1980). Simple correlation matrices between the various sediment parameters and analysis of variance (ANOVA) of each parameter between stations, months and seasons were analysed.

#### **RESULTS AND DISCUSSION**

The study focussed on the variation of sediment pH, temperature, texture and some heavy metals. The temporal and spatial variability of trace metals in estuarine sediments result from the cyclic changes in the fresh and sea water

conditions of temperature, pH, salinity and suspended particles. pH of the sediment is an important parameter for the existence of a phase, its speciation and toxicity depends on the pH of the sediments. Soil texture and pH influence the mobility of the metals. This study, reports the spatial distribution and pollution status of heavy metals in the surface sediments of the Poonthura Estuarine system.

Sediment temperature did not show any definite pattern in its distribution without wide spatial variations. Maximum temperature was obtained during premonsoon and minimum during monsoon periodat allstationsexcept at station I, where the temperature was maximum during postmonsoon and minimum during monsoon. The sediment temperature ranges from 26.0° C to 32.0°C.

The major factors governing the pH of soil include the concentration of reduced metals like iron, manganese as well as carbonates, carbonic acid and humic acid (Patrick and Mikkelsen, 1971). Sediment pH was found to be generally towards the acidic side at all stations. There was not much variation in pH between the seasons.

Seasonal variation of sediment temperature, pH and heavy metal (Fe, Cu, Cr, Ni, Pb, and Cd) concentrations are given in Table 1. Comparison of the results of the present study with USEPA standards 1977 and 2008 (Table 2) shows that the concentration found in most samples greatly exceeded the natural levels.

Several parameters such as sediment composition, nature and source of pollution influence the level of heavy metals in sediments. Iron is found in all natural waters both in oxidised and reduced forms. Among the heavy metals iron is an important transition element. It is required for both plants and animals and can be toxic at high concentrations. Iron was the most abundant element in the sediments analysed. Data on concentration of iron showed significant variation in spatial distribution. All stations except station 3 depicted high iron content in all seasons. Maximum iron concentration obtained was 55000 ppm in station 4 which indicates severe pollution of the estuary by iron.

Parameters	Station	Premonsoon	Monsoon	Monsoon Postmonsoon			
Temp.(℃)	1	30.13±1.03	29.5±1	29.63±0.48	29.75±0.84		
	2	31.13±0.63	30±0.82 29.13±0.63		30.08±1.06		
	3	30.63±0.75	29.25±1.66	30.25±1.71	30.04±1.44		
	4	31±0.41	28.13±2.02	29±0.41	29.38±1.67		
p <sup>H</sup>	1	6.20±0.18	5.70±0.36	6.65±0.52	6.20±0.53		
	2	6.48±0.32	5.95±0.34	6.23±0.27	6.20±0.36		
	3	7.13±0.75	6.70±0.66	6.85±0.24	6.90±0.57		
	4	6.88±0.67	6.43±0.19	6.45±0.31	6.60±0.45		
Fe (%)	1	2.16±1.03	3.19±1.28	2.96±0.60	2.77±1.02		
	2	2.54±1.10	2.37±1.58	3.8±1.29	2.90±1.38		
	3	0.68±0.17	1.03±0.22	0.98±0.09	0.89±0.22		
	4	4.33±1.58	4.03±1.23	4.35±1.28	4.23±1.25		
Cu (ppm)	1	70±46.90	94.25±37.40	127.5±27.54	97.25±42.36		
	2	22.5±15	25±12.91	62.5±30.96	36.67±27.08		
	3	15±5.77	20±14.14	10±0	15±9.05		
	4	40±8.16	32.5±9.57	30±8.16	34.17±9.00		
Cr (ppm)	1	38.33±17.21	46.25±13.84	41.25±6.80	42.27±11.92		
	2	32.5±9.57	34.5±13.92	55.5±17.92	40.83±16.84		
	3	28.75±14.36	42.5±12.58	42.5±9.57	37.92±13.05		
	4	38±9.09	30±16.33	25±19.15	31±15.05		
Ni(ppm)	1	18.5±7.55	19.25±8.5	25.5±13.96	21.08±9.96		
	2	15.5±6.40	21.5±17.84	21.5±3	19.5±10.45		
	3	10±0	17.5±9.57	10±0	12.5±6.23		
	4	62.5±27.54	75±12.91	57.5±35.94	65±25.76		
Pb(ppm)	1	22.5±9.57	32±5.42	27.5±9.57	27.33±8.63		
	2	40±8.16	27.5±12.58	45±5.77	37.5±11.38		
	3	50±20	55±5.77	55±5.77	53.33±11.55		
	4	45±5.77	35±5.77	42.5±5	40.83±6.69		

Table 1. Seasonal variations of geochemical parameters

Copper is an essential element for all living organism but is toxic at high concentrations. Spatial distribution of copper content in sediments showed significant fluctuation. Station I registered very high concentrations of copper followed by station 2, but station 3 near the bar mouth recorded lowest values throughout the year except June. There is a gradual decrease in copper concentration from the upstream towards the bar mouth. In the Poonthura estuary maximum copper concentration recorded was 160 ppm and it indicates that the system is heavily polluted with copper. Chromium is very harmful to living organisms. The maximum concentration of chromium was observed in sediments at station 1&2. A uniform spatial distribution pattern of chromium was noticed

in the riverine and estuarine regions in the present study. Maximum concentration of chromium was 72 ppm, this reflects that the system is moderately contaminated with Chromium.

Nickel is a highly toxic element even at low concentrations. A study conducted by KSCSTE (2010) in Karamana river basin reported that the system was heavily polluted with heavy metals and the concentration of nickel was high in this zone. In the present investigation the highest value of nickel concentration obtained was 90 ppm at station 4 and this showed severe pollution with nickel but the other stations were moderately polluted. Lead is also toxic metal and the concentration of lead was maximum at station 3 during postmonsoon period. The

Heavy Metal (ppm)	Not polluted	Moderately polluted	Heavily polluted	Obtained concentration
Fe	<17000	17000-25000	>25000	5100-55000
Cu	<25	25-75	>75	10-160
Cr	<25	25-50	>50	10-72
Ni	<20	20-50	>50	10-90
Pb	<40	40-60	>60	10-60
Cd			>6	Not detectable

Table 2. Classification as per U.S. EPA, 1977,2008

Table 3. Contamination Factor and Degree of Contamination

Station	(	Contamin	Degree of			
	Fe	Cu	Cr	Ni	Pb	Contamination
1	0.77	3.04	0.42	0.43	1.37	6.03
2	0.81	1.15	0.42	0.40	1.88	4.66
3	0.25	0.47	0.39	0.26	2.67	4.04
4	1.12	1.07	0.32	1.33	2.04	5.88

concentration of lead was less in monsoon period since the estuary breaks and merges with sea. In the Poonthura estuary, the maximum concentration of lead obtained was 60 ppm which is classified as heavily polluted.Cadmium is a non-essential element and highly toxic to man and several other organisms at extremely low concentration. Cadmium concentration was also analysed in all the stations during the present investigation, but was below detectable level. Present study showed that station 1,2&4 are heavily polluted with Fe, station 1 with Cu, station 4 heavily polluted with Ni and station 3 with Pb.

The contamination factor ( $C_f$ ) and the degree of contamination ( $C_d$ ) are used to determine the contamination status of sediment in the present study. The contamination factor is calculated according to the equation

C<sub>f</sub>=Measured concentration/Background concentration

Where, Background value of the metal= world surfacerock average given by Martin and Meybeck (1979). Degree of contamination ( $C_d$ ) was defined as the sum of all contamination factors. Calculated contamination factor ( $C_f$ ) and degree of contamination ( $C_d$ ) for this study is shown in the Table 3.

The degree of contamination maximum (6.03) in station 1. Contamination factor, ( $C_f>6$  indicates very high contamination) found highest in station 3 for Pb. The order of degree of contamination of tested heavy metals in Poonthura estuary: Cu>Pb>Ni>Fe> Cr> Cd.

There may be an increase in the quantity of heavy metals including iron due to the concentration from municipal solid waste waters, urban runoff and industrial effluents. Heavy metal such as Fe, Cu, Ni, and Pb showed significant variation in spatial distribution. Parvathy Puthanar is an artificial canal which connects Poonthura estuary and the Veli lake which receives industrial effluents from Travancore Titanium Industry, English Indian Clay Factory Ltd., and Trivandrum Rubber Works. This canal is the most severely polluted canal in Thiruvananthapuram. It receives waste water drainage from the city and from the banks of the canal, sewage spill from the Valiyathura sewage farm, sanitary and household wastes, hospital and hotel wastes. These wastes stagnate in parts of the Poonthura estuary during most of the year. Karamana river also brings in city waste and industrial effluents into the estuary.

Data on sediment quality such as its textural characteristics, chemical composition, are useful in assessing the water quality and management of ecosystem. Hence the analysis of sediments

Stn.	Sediment	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Annual
	texture			0								•		Mean
	Sand	38.8	28.6	29.6	45.5	46.1	41.5	39.7	29.1	32.1	32.1	28.6	30.4	35.2
1	Silt	50.2	65.3	64.5	49.1	47·3	47.7	47.2	50.3	45.6	39.9	38.6	51.6	49.8
	Clay	11.1	6.1	5.9	5.4	6.6	10.9	13.1	20.7	22.2	28.0	32.9	18.0	15.1
2	Sand	48.8	47.2	42.7	50.4	53.1	48.4	52.7	53.2	52.5	49.8	46.8	42.4	49.0
	Silt	44.2	48.3	48.5	44.1	42.3	47.1	40.5	40.9	35.4	35.2	40.8	45.6	42.7
	Clay	7.0	4.5	8.8	5.5	4.6	4.6	6.8	5.9	12.1	15.1	12.4	12	8.3
	Sand	81.1	85.1	82.7	89.1	92.6	72.6	64.2	67.1	61.3	59.2	57.1	76.2	74.0
3	Silt	14.1	12.0	12.6	9.5	7.0	24.1	31.6	29.5	35.8	37.0	39.1	20.9	22.8
	Clay	4.8	2.9	4.7	1.3	0.3	3.3	4.2	3.4	2.9	3.8	3.7	2.9	3.2
4	Sand	65.2	63.2	64.4	56.2	55-3	60.8	58.1	64.9	56.3	61.6	60.4	57.6	60.3
	Silt	28.8	30.7	29.6	38.7	40.6	35.9	37.4	29.6	36.3	32.3	33.9	36.3	34.2
	Clay	6.o	6.1	5.9	5.1	4.1	3.3	4.5	5.5	7.4	6.1	5.7	6.1	5.5

Table 4. Sedimenttexture in stations - percentage of sand, silt and clay

is an effective way to assess the magnitude of pollution (Forstner and Wittman,1981).The particle size distribution of the study area are given in Table 4.

Grain size is one of the basic attributes of sediments and its determination is essential to delineate the sedimentary environments. Marked spatial and seasonal variations in textural characteristics were observed in the Poonthura estuarine system. The main constituents of station 1 and 2 were sandy-clayey-silt and clayeysilty-sand respectively. Heavy deposition of silt fractions noticeable in this region may be attributed to the large amount of drainage reaching here through Parvathy Puthanar canal. The allochthonous material reaching the station 1 was subject to bio-degradation which resulted in the high percentage of silt apart from the death and decay of vegetation. Station 3 which is near to the bar mouth was sandy. Sediment in station 4 is silty-sand almost throughout the period of study, with small amount of clay. Clay minerals have ability to absorb or release heavy metal ions (Farrah et al., 1980). Maximum sand deposition in all the stations was during monsoon season and the minimum was during premonsoon. At station 1, composition of sand varied from 28.56% to 46.11%. Silt was the major component and ranged from 38.57% to 65.32%. This station showed highest composition of clay with a minimum of 5.38% to 32.87%. Sand as well as silt showed narrow monthly variation of 42.4% to 53.22% and 35.16% to 48.54% respectively at station 2. Composition of clay ranged from 4.53% to 15.08%. Sediment in station 3 was mainly sandy, showing a monthly variation of 57.12% to 92.63%. Silt composition varied from 7.04% to 39.14% and clay was the smallest fraction with a minimum of 0.33% to 4.78%. Station 4 was also mainly silty sand with small amount of clay. Percentage of sand in sediment at this station varied from 55.34% to 65.16%. Silt composition varied from 28.83% to 40.58% and clay was present from a minimum of 3.31% to 7.36%.

Analysis of variance was also done for heavy metals where iron, copper, nickel and lead

 Table 5.
 Analysis of variance of sediment temperature, pH and heavy metals

Sources	df	Temp.	pН	Fe	Cu	Cr	Ni	Pb
Stations	3	1.049	8.114**	11.870**	21.840**	1.336	24.555**	13.389**
Seasons	2	8.303**	3.605*	0.760	2.573	0.743	0.673	1.036
Months	3	0.935	0.782	0.0235	0.351	1.074	0.697	0.191

showed 1% variance between stations, whereas temperature showed 1% level and pH showed 5% significant level within seasons (Table 5).

Simple correlation matrices between the various sediments parameters and analysis of variance (ANOVA) of each parameter between stations, months and seasons were analysed. Iron, copper, nickel and lead showed highly significant variations within stations but not much variation between stations and between seasons.

#### CONCLUSIONS

A comparison with sediment quality guideline indicated that there may be some eco toxicological risk to the aquatic forms. The average concentrations of heavy metals in Poonthura estuary exceeded acceptable limits for sediment pollution. Concentrations of Cu, Pb, Fe and Ni showed pollution levels classified as heavily polluted. In the estuarine sediments, the absence of any significant correlation of the heavy metals with other sedimentary parameters and their strong interdependence revealed the possibility that the input is not through the natural weathering processes. There is no doubt that high concentrations of certain heavy metals found in sediments analysed are the result of industrial and urban pollution. The present study which revealed the presence of high levels of heavy metals strongly emphasized the unhealthy condition of the estuary and hence the need for taking urgent measures to prevent further deterioration.

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