Seasonal Variation and Assessment of Heavy Metal Contamination in the Sediments of Poovar Estuary, Kerala, South West Coast of India

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Abstract

Analysis of heavy metals in estuaries is significant due to its non-degradability, toxicity and accumulation in the body of organisms and thereby the body of humans through food chain. Poovar estuary is polluted now a days by the continuous discharge of sewage from agricultural lands and by other developmental activities. The sample sediments were collected from five stations for the assessment of heavy metals during a period of one year from February 2016 to January 2017. All the heavy metals analysed were present as maximum in the pre-monsoon season covering Feb, March, April and May of 2016. The mean concentration was in the order of Fe>Mn>Zn>Cu>Pb>Cd for all the three season. To assess the metal contamination Sediment Quality Guidelines were applied. The concentration of Fe exceeds the USEPA guidelines in all stations; concentration of Mn exceeds the USEPA guideline value in most of the stations. All other metal concentration was less than the USEPA guidelines. The metal contamination in the sediments was also evaluated by applying Contamination Factor (CF), Enrichment Factor (EF) and Pollution Load Index (PLI). As per the contamination factor low poisoning effect was observed in the estuary. Based on Enrichment Factor minimum to significant enrichment was observed for Mn, Zn, Cu and Cd and minimum to very high enrichment was observed for Pb.

Key words: Estuary, Heavy metal, Sewage, Anthropogenic, Concentrations

Introduction

The Poovar estuary (30.93 Ha) is located 2 km south of Kovalam in Thiruvananthapuram district. It is isolated but have spectacular beach, and is situated between 8°19' 3" N to 77°4' 7"E, and is formed by the confluence of river Neyyar. This is the southernmost estuary of Thiruvananthapuram district.A trading port in its early days; it is today an important tourist destination. Poovar is enveloped by most serene back water and opening in to the sea and has a dream golden sea beach. Poovar is basically a fishing village and estuary is situated adjacent to Poovar Island. Here the back water is formed by the action of waves and shore current creating low barrier island across the mouth of river flowing down. Coastal and estuarine ecosystem have been still are heavily influenced by human species. On the northern side of the estuary there are more than twenty tourist resorts are situating in and around the estuary .The drainage channels from the tourist resorts, paddy field and AVM Canal (Ananda Victoria Marthandavarma Canal), and open defecation near estuary and river side are the main sources for the flow of sewage and domestic wastes into the estuary. The villagers in and around the locality are using this estuary for their day to day activities. AVM canal water is used for retting activities and for washing purposes round the year.

Estuaries are important natural places which provide goods and services that are economically and ecologically indispensable. Often called nurseries of the sea, estuaries provide vital nesting and feeding habitats for many aquatic plants and animals. Estuarine sediments are the indicators of the quality of overlying water and its study is useful for the assessment of environmental pollution. The sediments are the ultimate sink of heavy metals that discharged in to the aquatic system [1, 2]. Heavy metals are the most common environmental pollutant and their presence in water and sediment indicate the presence of natural and anthropogenic contamination. Disposal of wastes containing bio pesticide, industrial wastes and land runoff are the main sources of natural and anthropogenic sources of heavy metals in the estuary [3, 4]. These heavy metals pollute water and reduce water quality [5, 6] and enters in to sediments.

The objective of the present study is to assess the concentration of heavy metals and its extent of contamination on poovar estuarine sediment.

Materials and Methods

The sampling stations in poovar estuary which are shown in Fig.1. Station 1 is Poovar estuarine mouth, station II is Mavilakadavu which is 5Km away from the estuarine mouth, station III is Kanjiramoodu bridge which is 8Km away from estuarine mouth, station IV is Parassery kadavu which is 11Km away from estuarine mouth, station V is Rameswaram temple bridge kadavu which is 14Km away from estuarine mouth.

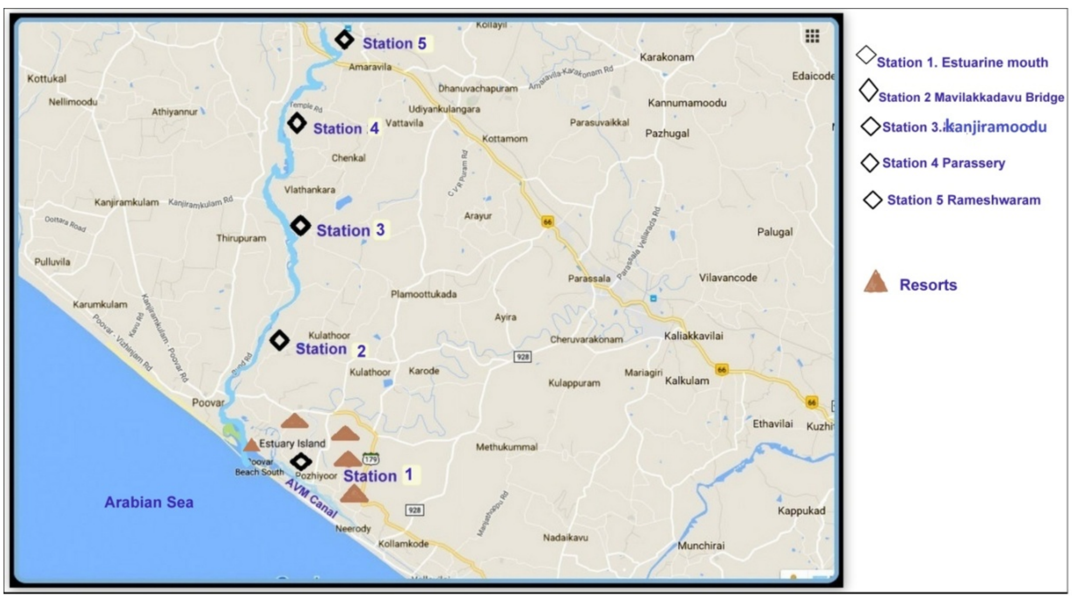

Fig: 1 Location map of the study area showing sampling station

Approximately 2Kg of the surface sediment samples were collected for a period of 12 months from Feb 2016 to Jan 2017 in clean polythene bags from all the five stations. The samples were dried in shade, powdered as fine particles and divided in to two fractions. One fraction taken in to the laboratory for the analysis of heavy metals. The analysis of heavy metal was done by using Atomic Absorption Spectrophotometer Perkin Elmer (AAnalyst 400) as per the standard methods prescribed by APHA.

Results and Discussion

Mean concentration of selected heavy metals seasonally in the surface sediments is given in Table 1. From the values it was observed that Fe was present in maximum in the study area followed by other metals. The mean concentration of metals was in the order of Fe>Mn>Zn>Cu>Pb>Cd for all the three season.

Table 1: Mean concentration of heavy metals in the sediments (ppm)

Season	Station	Fe	Mn	Zn	Cu	Pb	Cd
Pre monsoon (Average of four months)	I	220.12	13.45	3.05	2.94	0.99	BDL
	II	508.81	31.14	5.93	5.65	3.14	0.05
	III	750.87	52.99	5.64	5.21	3.55	BDL
	IV	694.19	48.47	5.71	5.03	4.83	0.04
	V	729.31	50.54	6.60	5.88	4.05	0.06
Monsoon (Average of four months)	I	89.56	7.18	1.78	1.37	BDL	BDL
	II	163.39	14.66	5.06	3.03	1.16	BDL
	III	185.45	32.54	3.73	2.86	1.16	BDL
	IV	156.19	26.83	3.73	3.00	1.74	BDL
	V	162.83	30.74	4.22	3.00	1.76	BDL
Post monsoon (Average of four months)	I	176.31	12.37	2.36	1.73	0.63	BDL
	II	310.90	20.84	5.51	5.51	2.55	BDL
	III	351.53	44.98	4.85	4.86	3.14	BDL
	IV	321.41	38.05	4.73	4.84	3.13	BDL
	V	331.46	38.92	6.13	5.79	2.65	0.03
Mean		343.49	30.91	4.60	4.05	2.30	0.01
TEC		20000	460	121	31.6	35.8	0.99
PEC		40000	1100	459	149	128	4.98

TEC–Threshold Effect Concentration; PEC – Probable Effect Concentration, BDL– Below Detectable Limit

From the table it was observed that the maximum concentration of all the metals was present in the pre - monsoon season and minimum values were noticed in the monsoon season. This may be due to the turbulence created by increase of flow during rainy season some sediment and heavy metals inside the aquatic system are displaced and carried away. As summer starts the raise in temperature and evaporation cause increase in heavy metal concentration in sediments. Of the various sampling stations the maximum concentration of Fe, Mn were found in the station III during all the three seasons, maximum concentrations of Zn and Cu were observed in station V during pre-monsoon season, maximum concentration of Pb was observed in station IV during pre-monsoon, maximum concentration of Cd was observed in station V during pre-monsoon season .

Assessment of Sediment Contaminations

(TEC/PEC Guidelines)

To assess the metal concentration in sediment Numerical Sediment Quality Guidelines were applied. The metal concentrations were compared with TEC/PEC guidelines. If the metal concentration present below TEC and above PEC harmful effects were observed. In the study area all the metal concentration that observed in all the stations in the three seasons were below to the proposed TEC values indicate there was no harmful effects from these metals.

USEPA/WHO Guideline

The chemical contamination in the sediments was evaluated by comparison with the sediment quality guidelines proposed by USEPA/WHO. These criteria are shown in Table 2.

Table2 SQGs and concentration of heavy metals (ppm) in the sediment samples of Poovar Estuary

Metal	Minimum	Maximum	Mean	Geochemical Background Mean shale concentration[1]	WHO SQGs*	USEPA SQGs*
Fe	89.56	750.87	343.49	46700	-	30
Mn	7.18	52.99	30.91	850	-	30
Zn	1.78	6.60	4.60	95	123	110
Cu	1.37	5.88	4.05	45	25	16
Pb	BDL	4.83	2.30	20	-	40
Cd	BDL	0.06	0.01	0.3	6	0.6

[1]Venkatesha Raju [3]; *Sediment quality guidelines.

In poovar estuary the highest concentration of Iron(750.87ppm) was observed in station III during pre-monsoon and minimum of (89.56ppm) was observed in station I during monsoon with an average of 343.49ppm .The values for Fe in all stations exceeds the USEPA guideline value indicates pollution in the study area. Iron is one of the most important essential plant nutrients and plays an important role in various metabolic processes such as photosynthesis, respiration, nitrogen fixation and detoxification of reactive oxygen species. Iron enters the aquatic environment from weathering as well as from human activities such as burning of coke and coal, sewage, corrosion of iron and steel etc. Iron pipes and cookware are also sources of iron accumulation and its target organs are the liver, cardiovascular system, and kidneys.

The common manganese compounds found in water is predominantly Mn^{2+} and Mn^{4+}. Manganese compounds are used in fertilizers, varnish and fungicides and as livestock feeding supplements. Manganese can be adsorbed onto sediment; the extent of adsorption depends on the organic content and cation exchange capacity. The maximum value of Mn (52.99ppm) was noticed in station III during premonsoon and minimum (7.18ppm) was observed in station I during monsoon season with an average of 30.91 ppm .The values observed in the pre- monsoon season except station I exceed USEPA guideline. During monsoon and post monsoon season the values exceeds the guideline value other than station I and II.

The value of Zinc was (6.60ppm) as maximum in the station V during premonsoon and minimum (1.78ppm) in station I during monsoon with an average of 4.60ppm and the values were less than WHO/USEPA guidelines indicates the estuary is free from Zinc pollution. The increase in concentration of Zinc in the sediment may be due to dredging activity. Sewage disposal may also increase the concentration of Zinc. Generally dissolved Zn is predominant in river water, whereas in estuaries a larger portion of the zinc is adsorbed to suspended particles where concentrations of suspended particles are higher. Zinc is potentially hazardous and excessive concentrations in sediment lead to phytotoxicity as it is a weed killer [7]. In fish Zinc gets accumulated in the digestive tract after exposure and will affect liver, spleen kidney [8].

The value of copper was maximum (5.88ppm) at station V during pre-monsoon and minimum (1.37ppm) at station I during monsoon with an average of 4.05ppm and the values were below to the WHO/USEPA guidelines indicates the estuary is free from Copper pollution. Copper is an essential element to human life, but, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritations. Higher concentration of free cupric ion is the most toxic form of copper in the aquatic environment for marine organisms [9].

The concentration of lead was maximum (4.83ppm) in station IV during pre-monsoon and minimum (BDL) at station I during monsoon with an average of 2.30ppm and the values were below to the WHO/USEPA guidelines indicates the estuary is free from Lead pollution. Presence of lead may be due to waste incineration or by the dumping wastes with lead soldered food cans or due to oil spillage. Lead is dispersed throughout the environment primarily as a result of anthropogenic activities. In the air lead in the form of particles are removed by rain or gravitational setting. The sink for lead is the soil and sediment because it is strongly adsorbed by the soil and sediment and generally retained in the surface sediments. Lead concentration may be attributed by the automotive exhaust, domestic sewage, agricultural runoff, dredging activities, leakage of unburnt leaded diesel, batteries, paint etc. Lead is second after arsenic in the case of poisoning effect. Its target organs are bones, brain, blood kidney, reproductive and cardiovascular system and thyroid gland [10].

The maximum value of Cadmium (0.06 ppm) was observed in station V during pre-monsoon and minimum was BDL with an average of 0.01ppm and the values were less than the USEPA guidelines indicates the estuary is free from Cd pollution. Anthropogenic input of Cd in sediment occurs by sewage sludge, Cadmium is used in the production of inorganic fertilizers from phosphate ores which constitute a major source of diffuse cadmium pollution [7, 11]. Cd may accumulate in the sediment through the disposal of waste containing Ni-Cd batteries. It is highly toxic to animals and carcinogenic to humans. When ingested by humans, cadmium accumulates in the intestine, liver and kidney. Cadmium has a range of negative physiological effects on organisms such as decreased growth rates and negative effects on embryonic development. Epidemiological evidence links Cd with sudden cardiac death[12]. The major anthropogenic includes industrial effluent discharge, municipal waste dumping, and man-made activities along the coastal environment. When ingested by humans it get accumulates in the intestine, liver and kidney. Cadmium usually settles down the bottom hence increased concentration in sediment than in water [13].

Contamination factor (C_f) and Degree of contamination (C_d)

Contamination Factor (C_f) analysis is another method for the assessment of heavy metal contamination in the estuarine sediment. This is calculate by using world shale average is taken as background value. The contamination factor was calculated by using the equation

C_f=Metal concentration in polluted sediment / Background value (shale) of the metal.
C_f< 1 refers to low contamination, $1 \leq C_f < 3$ means moderate contamination, $3 \leq C_f < 6$ indicates considerate contamination and C_f> 6 indicates very high contamination [14].

Hakanson's study also proposed that the numeric sum of the eight specific contamination factors expressed the overall degree of sediment contamination (C_d) using the following formula

$C_d = \sum C_{fi}$
i= 1 to n
C_d provide over all contamination in the particular stations by the metals.
The assessment of heavy metals based on contamination factor and degree of contamination is given in Table 3

Table 3 Contamination Factor and Degree of Contamination of Poovar Estuary

Season	Station	Fe C_f	Mn C_f	Zn C_f	Cu C_f	Pb C_f	Cd C_f	Degree of contamination (C_d)
Pre monsoon (Average of four months)	I	0.0047	0.0158	0.0321	0.0653	0.0495	0.0000	0.1674
	II	0.0109	0.0367	0.0624	0.1256	0.1570	0.1667	0.5593
	III	0.0161	0.0623	0.0594	0.1158	0.1775	0.0000	0.4311
	IV	0.0149	0.0570	0.0601	0.1118	0.2415	0.1333	0.6186
	V	0.0156	0.0532	0.0695	0.1307	0.2025	0.2000	0.6715
Monsoon (Average of four months)	I	0.0019	0.0084	0.0187	0.0304	0.0000	0.0000	0.0594
	II	0.0035	0.0172	0.0533	0.0673	0.0580	0.0000	0.1993
	III	0.0039	0.0383	0.0393	0.0636	0.0580	0.0000	0.2031
	IV	0.0033	0.0316	0.0393	0.0667	0.0870	0.0000	0.2279
	V	0.0035	0.0362	0.0444	0.0667	0.0880	0.0000	0.2388
Post monsoon (Average of four months)	I	0.0038	0.0146	0.0248	0.0384	0.0315	0.0000	0.1131
	II	0.0067	0.0245	0.0579	0.1224	0.1275	0.0000	0.339
	III	0.0075	0.0529	0.0511	0.1080	0.1570	0.0000	0.3765
	IV	0.0069	0.0448	0.0498	0.0978	0.1565	0.0000	0.3558
	V	0.0071	0.0458	0.0645	0.1287	0.1325	0.1000	0.4786

Maximum Contamination Factor was observed for all the metals in the pre- monsoon season. For all the metal the contamination factor was less than unity indicate low poisoning effect

Enrichment Factor (EF) and Pollution Load Index (PLI)

Enrichment Factor is another method used to assess the heavy metal contamination in the sediments. For the calculation of EF the normalising metal chosen was Fe since it is the most widely used reference element [4, 15, 16].

The formula used for the calculation of EF is
Enrichment factor = (Cn/Fe) sample/ (Cn/Fe) background, Where Cn is the concentration of element in sample and background value respectively [17].

Six categories are recognized: < 1 background concentration, 1- 2 depletion to minimum enrichment, 2 –5 moderate enrichment, 5 – 20 significant enrichment, 20– 40 very high enrichment and > 40 extremely high enrichment. EF values greater than 1.5 is a clear indication that the heavy metals derived from other sources suggesting environmental contamination by those particular heavy metals [18]. Measuring enrichment factor (EF) is an essential part of geochemical studies and is generally used to differentiate between the metals originating from anthropogenic and geogenic sources, and to assess the degree of metal contamination [19]. The elements derived naturally have an EF value nearly unity and those due to anthropogenic have high values [20].

Table 4 Enrichment Factor and Pollution Load Index of Sediments in Poovar Estuary

Season	Station	Fe	Mn	Zn	Cu	Pb	Cd	PLI
Pre monsoon (Average of four months)	I	1	3.3573	6.8122	13.8623	10.5009	0.0000	0.0000
	II	1	3.3627	5.7299	11.5250	14.4087	15.2971	0.0659
	III	1	3.8776	3.6929	7.2015	11.0386	0.0000	0.0000
	IV	1	3.8364	4.0440	7.5203	16.2450	8.9697	0.0754
	V	1	3.8076	4.4492	8.3678	12.9656	12.8066	0.0821
Monsoon (Average of four months)	I	1	4.4049	9.7714	15.8764	0.0000	0.0000	0.0000
	II	1	4.9299	15.2256	19.2471	16.5762	0.0000	0.0000
	III	1	9.6409	9.8850	16.0062	18.3814	0.0000	0.0000
	IV	1	9.4383	11.7409	19.9350	26.0145	0.0000	0.0000
	V	1	10.3728	12.7417	19.1220	25.2365	0.0000	0.0000
Post monsoon (Average of four months)	I	1	3.8549	6.5809	10.1811	8.3427	0.0000	0.0000
	II	1	3.6830	8.7132	18.3941	19.1501	0.0000	0.0000
	III	1	7.0304	6.7131	14.3572	20.8554	0.0000	0.0000
	IV	1	6.5046	7.2352	15.6267	22.7372	0.0000	0.0000
	V	1	6.4516	9.0924	18.1299	18.6667	14.0913	0.0574

The EF values for the sediment samples given in Table 4. From the table it was observed that the EF value of Mn and Zn , Cu and Cd varied in the range of 0<EF<20 for all the three season showing minimum to significant enrichment of the metal indicating anthropogenic effect mainly by the discharge from the agricultural fields that using fertilizers and sewages etc. The EF value Pb is between 0<EF<30 showing its minimum to very high enrichment indicating anthropogenic influences like discharge of unburnt petrol and other petrol leakages from vehicles in to the aquatic system.

Pollution Load Index

Pollution load index was calculated by using the formula

PLI= $(C_{f\,1} \times C_{f\,2} \times ..... \times C_{f\,n})^{1/n}$, where n is the number of metals and C_f is the contamination factor. Values are given in Table 4.

PLI>1 Indicates baseline pollution and PLI<1 indicates no pollution in the sediment samples. PLI>1 indicates deterioration of site quality[21]. Value equal to one indicates baseline pollution and value greater than one indicates progressive destruction in the sediment quality and the estuary. PLI values for all the stations in all the three seasons were less than unity indicate the estuary is free from pollution.

Conclusion

In the present study different heavy metal concentration of sediments were analysed for a period of twelve months from Feb 2016 to Jan 2017. The mean concentration of heavy metals found in the order of Fe>Mn>Zn>Cu>Pb>Cd for all the three season. Maximum concentration of the heavy metals was observed in the pre- monsoon seasons. From the results it was observed that the estuary and the nearby areas are contaminated due to sewage disposal and other developmental activities. Heavy metal concentrations in some areas exceeded the limit. If water and sediments get polluted it will enter into the body of aquatic organisms and there by enter in to the body of humans. So it is necessary to give more attention to protect estuary from pollution. More importantly measures should be taken to control estuarine pollution through anthropogenic activities. The discharges from the sources should be pre-treated to avoid this pollution without directly flowed in to the aquatic systems.

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