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Original Research Paper

Evaluation of The Trace Metal Contamination in Sediments of The Urban Water Channels in Thrissur City, South India

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ABSTRACT

Present study endeavours to estimate the domain of trace metal contamination in the sediments of water channels of Thrissur city. The major trace elements present in the study area were reviewed and in addition the organic carbon content in the sediments confined to the urban channels was also determined. Thrissur is a newly constituted corporation and is momentarily undergoing nimble urbanization which sequentially place aggravated trace metal pollution. This is habitually caused by land run off, dredging and other linked anthropogenic activities. The discharge of such urban effluents into the natural channels might have contributed to add up accumulation of metals. Correlation with the standard geochemical background values, it is palpable that the average total concentration of lead and zinc are fairly high. Cadmium concentration was found to be inflated in some locations. The contamination factor determined for Ni, Zn, Pb and Cd signify that, these may induce contamination in the sediments. From the correlation studies it is accomplished that, there exists a positive relationship among cadmium, nickel and zinc and that speak to a common source.

INTRODUCTION

Water channels will ordinarily serve as corridors for the transit of terrigenous metal rich materials to the sea (Sharp et al. 1984). Historically, urbanization advanced principally in the vicinity of waterways and hence increased formation of anthropogenic loads in most cities. Sediments in urban waterways, act as vectors of metal transfer and metal storage, and may largely influence the ecosystems (Taylor 2007). The impact of heavy metal pollution in water bodies could be hefty by virtue of a variety of inputs (Nriagu & Pacyna 1988). Potential land based sources of heavy metals encompass river inputs, local runoff and atmospheric deposition (Galloway 1979). Erosion of bedrock and soil also leads to accumulation of sediments of past or ongoing natural and anthropogenic processes. The interpretation of sedimentary metal concentrations is, however, not straightforward, since the concentrations commonly show spatial and temporal variations as a response to natural processes (Paula Kuusisto-Hjort 2009). Monitoring of the contamination of sediments with heavy metals is of prime interest due to their influence on groundwater and surface water. The buildup of trace metal contaminants in sediments can pose solemn environmental tribulations to the neighbouring areas. Trace metal contamination in sediment could influence the water quality and bioaccumulation of metals in aquatic organisms, ensuing in potential threat to human health (Harikumar & Jisha 2010). Data retrieved from the study of sediments offer valuable information on the impact of human activity on ecosystem. Thus, the significance of trace element detection of the sediments in streams, canals and wetlands in Thrissur city have gained significance. The channels and the wetlands in the urban centres amass considerable quantity of waste containing toxic metals from sources such as corporation wastewater flowing through canals, household garbage and vehicular discharge. The aspiration of this study is to assess the degree of trace metal content in sediments and also to evaluate the impact shaped due to this pollution.

STUDY AREA

Thrissur is one of the fastest growing cities of the state. It is situated in the midland topographic region of Kerala, with an extended part encroaching the Palakkad plains and bound with in the drainage basin of Kecheri and Karuvannur rivers. The study area also includes a wetland system which is known popularly as Thrissur Kole wetlands. It acts as a natural drainage system for Thrissur city in particular and Thrissur District at large. The Kole wetland is one of the largest, highly productive and vulnerable wetland ecosystems (Jeena 2010) and has been affirmed in Ramsar Convention as an area to be protected. Large scale developmental actives are going on at the expense of this wetland and this crafted great stress to the water environment. Both Karuvannur and Kecheri rivers drain the Kole lands of the area. Kecheri river joins the Chettuva *Puzha* on the northern portion and Karuvannur River joins the Canolly canal. Sampling and analysis was carried out on the sediments collected from minor channels and canals in the city as well.

MATERIALS AND METHODS

Ten sampling locations including streams, canals and wetlands (Fig. 1) were selected for the collection of sediments, in which the streams and canals are running through the city where large scale urbanization is incident. Sediment sampling was done during post monsoon season (Harikumar & Jisha 2010) and the sampling locations were Puzhakkal Thodu (L1), Puzhakkal (L2), Peringavu (L3), Cheroor (L4), Kokkali (L5), Irumbu palam (L6), Karyattukara (L7), Chettupuzha (L8), Ayyanthol (L9) and Nedupuzha (L10).

Sediment samples were grabbed from the mid portion of the stream, which was quickly packed in air tight polythene bags (Kruopiene 2007). Later, required amount of samples was taken out and oven dried at 45°C for 48 hours and grinded using mortar and pestle. Subsequently sieve analysis was performed using 125 A.S.T.M mesh. The lower particle size fraction was homogenized by grinding in a mortar (Saha & Hossain 2011). An amount of 0.5g of finely powdered bulk sediment was digested with perchloric and hydrofluoric acid in 1:3 proportion in a clean dry teflon crucible and heated in a sand bath until emission of fumes stops. An amount of 5 mL of double distilled water was added to it and filtered the solution until the digestion of the sample is completed. The retrieved solution is made up to 50 mL and this was accordingly used for geochemical analysis (Varian 1989).

The organic carbon in the bulk sediments was determined by titrimetric method (Brian 2002). For the determination of trace metals such as Cu, Mn, Ni, Cr, Pb, Fe, Cd and Zn, the acid extraction method (Jackson 1967) was performed and trace metal concentration was determined by atomic absorption spectroscopy (AAS) (Varian 1989) and (Forstner & Salomonus 1980). All the reagents and chemicals used were of analytical grade

RESULTS AND DISCUSSION

The background and toxicological reference values for sediments, along with average values obtained for the trace metal concentration of the study area are summarized in Table 1. It is visible from the results (Table 2) that the average total concentration of all the trace metals except lead and zinc were quite below the geochemical background values.

The highest concentration of Cu is 0.63μg/kg in the sediment. The mean concentration of Cu is slightly lower than

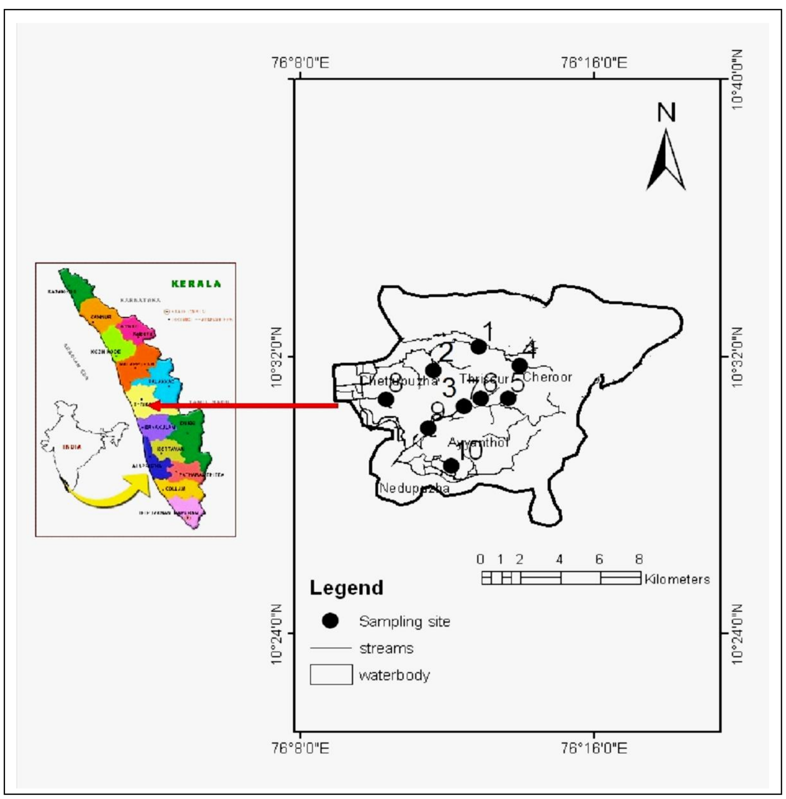

Fig. 1: Map showing sediment sampling site.

Table 1: Average value of trace metal concentration compared with geochemical background values.

Trace metal	Geochemical background (μg/ kg) Shale standard	Continental crust	Study area Maximum (μg/ kg)
Copper	45	55	0.63
Nickel	68	76	31
Cadmium	0.3	0.2	0.06
Lead	20	12.5	26.27
Zinc	95	70	85.4
Chromium	90	100	0.67

the average concentration in shale as proposed by Turekian & Wedepohl (1961). Presence of Cu is found in all locations in accountable amount. Even slight occurrence of Cu indicates an input of organic deposition in those sites, which might have contributed by the urban waste water sediment deposition. Lead is observed only at four locations with a highest concentration of 26.21μg/kg, whereas at other locations the presence of Pb is not traceable. Puzhakkal thodu - 26.21μg/kg, Puzhakkal-22.65μg/kg and Ayyanthol 18.27 μg/kg, are the locations, which were identified with Pb concentration greater than 16μg/kg, are adjacent to the huddle of the settlement in the city. Pb is considered as a good gauge of pollution created by urban runoff. The use of petrol is mainly responsible for the lead pollution especially in urban area. The highest concentration of Zn is 85.4μg/kg. The concentrations of Zn in the sediment shows anomalous variation and found to be maximum at locations such as Puzhakkal thodu-77.3μg/ kg, Puzhakkal - 85.4 μg/kg, Irumbu palam - 82.1μg/kg and Ayyanthol - 74.6μg/kg, all of which are confined to the urban zone. While considering urban areas independently, domestic construction, car related sources and untreated wastewater are the main sources of Zn. Presence of cadmium was found only in three locations that too in minimal amount. Elements like Pb, Cd and Zn exhibit extreme toxicity even at trace levels. The possible sources of Cd include leachates from defused Ni-Cd batteries and Cd plated items.

Pollution assessment: Metal pollution in urban environment is usually caused by land runoff, mining activities, dredging and other allied anthropogenic inputs. Traces of heavy metals such as Pb, Mn, Fe and Cr have been identified as deleterious to aquatic ecosystems and human health. In the present study, an attempt has been made to evolve an overall idea about the extent of heavy metal pollution in the small streamlets using appropriate statistical tools like enrichment factor (EF) and contamination factor (CF).

Enrichment factor (EF): A common approach to estimate how much of the sediment is impacted with heavy metal is done by calculating the EF of metal concentrations and then comparing it with uncontaminated background values. Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material. EF is a convenient measure of geochemical trend and is used for making comparisons between areas. The EF method normalizes the measured heavy metal content with respect to a sample reference such as Fe, Al or Zn (Mediola et al. 2008). The EF of heavy metals in sediment can be calculated using the following formula: (Huu et al. 2010).

$$EF = [C_{metal}/C_{normalizer}] \text{ sediment } / [C_{metal}/C_{normalizer}] \text{ (Earth's crust)}$$

Where C_{metal} and $C_{normalizer}$ are the concentrations of heavy metal normalized in sediment and in unpolluted control.

Iron was chosen as the element of normalization because natural sources (98%) immensely dominate its input (Tippie 1984) and also anthropogenic sources of Fe are negligible as compared to the natural sources (Mohan 1995, Padmalal et al. 2004). The crustal abundance data of Bowen (1979) were used for all EF values. A value of unity denotes neither enrichment nor depletion relative to the Earth's crust.

EF can be used to differentiate between the metals originating from anthropogenic activities and those from

Table 2: Trace metal with organic carbon (OC) and iron concentration in sediment (μg/kg).

No.	Fe^{2+}	Ni^{2+}	Cr^{2+}	Zn^{2+}	Cu^{2+}	Mn^{2+}	Pb^{2+}	Cd	O C (%)
1	95.01	31.02	0.73	77.3	0.45	12.26	26.21	0.04	3.42
2	94.88	20.05	0.14	85.4	0.49	11.13	22.65	0.06	4.56
3	82.88	0.35	0.01	34.9	0.32	12.24	13.84	-	3.27
4	73.92	0.56	0.13	2.41	0.15	13.24	-	-	1.34
5	65.54	0.14	0.29	2.99	0.09	9.53	-	-	0.96
6	73.07	26.23	0.38	82.1	0.38	7.99	-	0.05	1.41
7	81.73	0.02	0.13	-	0.17	6.19	-	-	0.74
8	78.72	0.09	0.19	74.6	0.14	4.21	-	-	0.42
9	68.43	0.08	0.67	5.9	0.63	7.09	18.27	-	2.78
10	85.62	-	-	-	0.02	10.09	-	-	0.47

Table 3: Enrichment factor (EF) for the trace elements.

Location	Ni	Cr	Zn	Cu	Pb	Cd
1.	0.2	0.035	0.54	0.42	1.03	9.52
2.	0.1	0	0.60	0.48	0.89	14.28
3.	0	0	0.28	0.03	0.62	0
4.	0	0	0.02	0	0	0
5.	0	0	0.03	0	0	0
6.	0.2	0	0.75	0.04	0	11.90
7.	0	0	0	0	0	0
8.	0	0	0.63	0	0	0
9.	0	0	0.05	0.07	0.99	0
10.	0	0	0	0	0	0

Table 4: Concentration factor (CF) for trace elements (Ni, Zn, Pb, Cd).

Location	Ni	Zn	Pb	Cd
1.	0.4	0.8	1.3	0.13
2.	0.3	0.8	1.1	0.2
3.	0	0	0	0
4.	0	0	0	0
5.	0	0	0	0
6.	0.4	0.8	0	0.2
7.	0	0	0	0
8.	0	0.7	0	0
9.	0	0	1	0
10.	0	0	0	0

Table 5: Correlation coefficient (CC) matrix of physico-chemical characteristics and trace metal concentrations of sediment samples.

	Fe	Ni	Cr	Zn	Cu	Mn	Pb	Cd	OC
Fe	1								
Ni	.613	1							
Cr	.191	.363	1						
Zn	.760	.577	.121	1					
Cu	-.145	.216	.659*	.092	1				
Mn	.750	.545	.196	.545	.028	1			
Pb	.121	.635*	.300	.591	.006	.875**	1		
Cd	-.161	.543	.293	.654*	.238	.065	.260	1	
OC	.821*	.464	.301	.320	.568	.920**	.574*	.423	1

natural processes, and also to assess the degree of anthropogenic influence. Five contamination categories were recognized on the basis of EF as follows (Sutherland 2000).

Enrichment factor (E.F)	*Contamination category*
< 2	Deficiency to minimal enrichment
2-5	Moderate enrichment
5- 20	Significant enrichment
20- 40	Very high enrichment
> 40	Extremely high enrichment

As the EF values increase, the contributions of the anthropogenic sources also increase (Sutherland 2000). The sediments of the study area were subjected to detailed EF analysis using the average crustal abundance of these elements (Mason & Moore 1982). Table 3 shows the EF computed for the sediments of the study area. Except Cd at three locations, all other trace metals exhibit EF values lower than 2 indicating that these elements are at depleted level than the crustal averages. These stations had comparatively the lowest EF value for all elements. There is a possibility that heavy metals are released from sediments at locations which were identified with trace element occurrence. Hence, at three locations such as Puzhakkal thodu (L1), Puzhakkal (L2) and Irumbu palam (L6), enrichment of Ni, Pb, Zn and Cu was identified. These locations are influenced by waste discharges from the urban centres in close proximity. Highest EF value was shown by Cd at three sampling points, L1-9.5, L2-14.2, L6-11.9. According to Khan, EF values <5 are considered as significant enrichment. As the EF were high for these metals in these locations, it is a clear indication that these spots where a strong influence of anthropogenic input do happen. Areas with EF values <1 should be viewed with caution as they imply preferential release of these metals, making them bio-available (Harikumar & Jisha 2010).

Contamination factor (CF): CF analysis is another important tool for the assessment of heavy metal pollution of the sediments. For CF computation, the values like Fe, Ni, Zn, Pb and Cr are normalized using the corresponding average metal values of shale reported by Turekian and Wedepohl (1961). This is because, the world shale average is considered as the background value.

The level of contamination of sediment by a metal is often expressed in terms of a CF calculated using the following equation,

CF = Metal content in the sediment/background level of the metal

Where, $CF < 1$ refers to low contamination, $1 \geq CF \geq 3$ means moderate contamination, $3 \geq CF \geq 6$ indicates considerable contamination, and $CF > 6$ specify very high contamination. The CF values for the trace elements such as Ni, Zn, Pb and Cd in the study area are given in Table 4. It was found that the traces of Ni, Zn and Cd have produced low level contamination at locations L1, L2 and L6. However, Pb has created moderate pollution at Puzhakkal thodu, Puzhakkal and Ayyanthol with C.F > 1.

Correlation coefficient: Trace metal data were subjected to correlation analysis and analysis of variance (ANOVA) to determine the association and the spatial variation (Yule & Kendall 1993). After verification of the normal distribution of the dataset a Pearson correlation coefficient was used to determine the correlation between the analysed elements. This was performed with the aid of SPSS 16.

Regression analysis was used to geochemically normalize the dataset and simultaneously ascertain the "normal" or background relationship between Fe^{2+} and a target metal in order to analyse anthropogenic enrichment. Outliers were identified using regression analysis. Residuals of each regression (metal/Fe^{2+} and metal/OC) were analysed for normality. If a normal distribution was not achieved, sites with residuals greater than two standard deviations (positive or negative) were eliminated following the method developed by Schiff & Weisberg (1999). The result of the CC of the elements in the sediments is given in Table 5. Except Cr and Zn, all other trace metals show good to excellent positive correlation with percentage of OC of the sediments. OC shows positive correlation with Fe (r = 0.82), Mn (r = 0.92), Cu (r = 0.568), Pb (r = 0.574), Cd (r = 0.723) and Ni (r = 0.464). This implies that the presence of organic matter has a commanding influence on the accumulation of trace metals in sediments (Harikumar & Jisha 2010). The high significance of the correlations of OC with other metals indicate anthropogenic source. The positive correlation of Fe with OC (r = 0.82) indicates that a part of Fe is incorporated in organic matter rich very fine particles that have greater ability to fix the Fe and other cations by adsorption. From the correlation data (Table 5), it can be distinguished that Fe shows significant positive correlation with Mn (r = 0.75) and Ni (r = 0.613). Zinc has positive correlation with Mn (r = 0.545) , Pb (r = 0.591), Cd (r = 0.654), Fe (r = 0.76) and Ni (r = 0.577). The positive relationship exists between Zn and other metals like Mn, Pb, Fe, Ni and Cd which mark to a common source for all these metals. Ni has got positive correlation with all the elements as well as OC. The association of Ni with Fe suggests their deposition along with iron oxides of hydrogenetic origin. In addition to the above, direct adsorption of Ni by OC can also fix substantial amount of this element in sediments. In the study area, Pb shows significant correlation with Ni (r = 0.635), Zn (r = 0.577) and Mn (r = 0.545). The possible source of Pb can be clay minerals. Some amount of Pb, which is transported into the sedimentary environments, is being adsorbed on clay minerals and ferric hydroxides. Mn shows positive correlation with Pb (r = 0.875), Fe (r = 0.75), Ni (r = 0.545), OC (r= 0.92) and Zn (r = 0.577). Cadmium shows positive correlation with Ni (r = 0.543) and Zn (r = 0.654). The positive relationship prevails between Cd and other metals like Ni and Zn fleck to a common source for all the above discussed metals.

CONCLUSION

The present study, affirms that the augmented concentration of trace metals such as lead and zinc in the populated urban areas of the Thrissur city is owed to anthropogenic clout. The allocation of other trace metals in the urban sediments was relatively trivial. However, cadmium was found to be embellished in sediments at exiguous locations. The CF calculated for the heavy metals such as Ni, Zn, Pb and Cd divulge that the contamination of these heavy metals generated low to moderate contamination. Thus, to avoid the astringent of heavy toxic metal pollution in the urban water system, conspicuously in the proximity of urban settlement exposed to anthropogenically derived metal inputs it becomes ultimately imperative to implement fitting monitoring and remediation procedures to avert the city from elevated cumulative concentration of trace metal aggregation.

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