Pollution Characteristics of Soils and Sediments of Thoothukudi City

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Abstract: ***Thoothukudi city in the state of Tamil Nadu situated in southern India has drawn widespread attention in the recent past because of concerns over deteriorating environmental conditions. As a step towards addressing this issue, a scientific study of soils, and both lake and marine sediments was conducted. Concentrations of Si, Al, Fe, Ca, K, S, Ti, Mn, Cr, Ni, Cu, Zn, and Pb were analysed in the collected samples. Geo-accumulation indices and enrichment factors were computed for individual samples. Pollution load indices were computed for each site, component and as a composite whole for the region. Enhanced quantities of Pb and Cu were found in soils and lake sediments. Highest geo-accumulation was evidenced for the elements S and Pb in all the components. Pollution load indices based on heavy metals indicate that each of the components and the region can be classified as unpolluted to moderately polluted.***

Keywords: contamination of soils and sediments, enrichment factors, geo-accumulation, pollution load index,Thoothukudi city.

I. INTRODUCTION

Thoothukudi city (also known as Tuticorin) is situated in Tamil Nadu,South India. It is spread over an area of 353.07 km^2 and has a population of 410,760 as of 2011 (GoI, 2011). It is an industrial city with many large-scale industries, a busy port, and a fishing harbour. Owing to its rapid industrialisation and resultant urbanisation the environmental components of the city are under stress. Therefore, it is important to understand the chemical and physical characteristics of various environmental components periodically in order to assess their environmental condition. In this paper, a study of pollution owing to certain elements in soil and lake and marine sediments is described. Jayaraju et al. (2009) described the metal pollution in coarse sediments of Thoothukudi coast. They found that Cd, Cu, Pb, and Zn were the contaminants found in sediments. Asha et al.(2010)reported Fe, Mn, Zn, Cu, Pb, and Cd contamination in sediments from three stations off the Thoothukudi coast.Risk assessment based on trace element concentration of sediments from Van Island,off Thoothukudi coast, was conducted by Krishnakumar et al. (2017). These authors arrived at a risk assessment map based on concentrations of Fe, Cr, Mn, Ni, Cu, Zn, and Pb in the sediments. A similar work was carried out for the Koswari Island by Krishnakumar et al. (2017). Karikalan et al. (2014)analysed the concentration of Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, and Cd of surface sediments of Thoothukudi. They found enrichment of these elements in the sediments. In surrounding areas north of Thoothukudi, in the Park Strait,Kasilingam et al. (2016) measured the concentrations of Fe, Mn, Cr, Cu, Ni, Cd, Pb, and Zn. They arrived at various pollution ratios and concluded that human-induced sources have contributed to the enrichment of these elements. Others such as Krishnakumar et al. (2015) studied the metal concentrations of the corals in the Gulf of Munnar. Magesh et al. (2011) evaluated the trace element contamination in sediments of the Tamiraparani estuary that is situated north of Thoothukudi city. Periodical monitoring of the environmental components of Thoothukudi is required to understand the changes that happen over time. Recently, the city has garnered attention with people protestingthe industries there. In this study, the focus is confined to the Thoothukudi city region. Further, sediments are derived from the surrounding terrigenous environment. Therefore, the soils in the study area also needs to be analysed as they eventually contribute to the characteristics of the sediments. Empirical analyses on each of the components and as a composite whole for the region will enable an understanding of the contamination levels.

II. METHODOLOGY

Five soil samples including were collected from different parts of the city. Each sample was collected after careful removal of the overgrowth and dry organic accumulus. Each sample represents the top soil from 0 to 10 cm of the specific sampling location. Thoothukudi city has a large lake called Korampallam. Three grab samples of sediments from different parts of the lake were collected. Along the Thoothukudi coast, 2 grab samples of near shore marine sediments were collected, andfour marine sediment samples were collected from the open sea. One marine sediment sample was collected from the shores of Van island away from the coast line of Thoothukudi. The locations of all the sampling sites were logged using a hand-held GPS (Garmin eTrex). The study area and the sample locations are shown in Fig.1. The study area falls between longitudes 78°15′ 20.49″ E and 77° 58′ 6.96″ E and latitudes 8° 54′ 7.17″ N and 8° 40′ 43.76″ N.

Fig.1. Google Earth snapshot of study area with sample locations

The samples were packed in polyethylene bags and marked appropriately. Energy Dispersive isotope-source X-ray fluorescence (XRF) was used by Boyle (2000) for rapid elemental analysis of sediment samples, wherein Si, Ti, Ca, K, Fe, Mn, and S were measured among other elements in the samples. In this study, one part of each sample was air dried and sent for Energy Dispersive X Ray Fluorescence analysis using an ED-XRF Shimadzu EDX 720model for the analysis of the elements

Si, Al, Fe, Ca, K, S, Ti, and Mn. One gram of a representative fraction of each sample was digested using HNO_3: HCl; 1:3 v/v and 6 ml of HF which was kept in a hot water bath for 3 h and then the digested precipitate acquired was made up to 100 ml. The solution was analysed for Cr, Ni, Cu, Zn, and Pb by an Inductively Coupled Plasma Optical Emission Spectrometer (model Perkin Elmar Optima 5300 DV ICP-OES).

III. RESULTS AND DISCUSSION

The results of the analyses are presented in Table 1.

Table 1. Elemental concentrations of various elements in soils and sediments

A. *Geo-accumulation Index (I_{geo})*

Geo-accumulation index defined by Muller (1979) and modified by Taylor and McLennan (1995) were calculated using the following equation.

$$I_{geo} = log_2 \frac{Cn}{1.5\ Bn}$$

where Cn= concentration of the element as measured in the samples and Bn is the geochemical background concentration which is considered as the crustal average. The crustal average concentrations given by Taylor (1964) were considered the geochemical background. The geochemical background is multiplied by 1.5 to account for fluctuations in the environment and minor anthropogenic influences. The computed geo-accumulation values for the soil and sediment samples are presented in Table 2.

Table 2. Geo-accumulation indices of various elements in soils and sediments

I_{geo} values are classified as <0–unpolluted, 0 to 1–unpolluted to moderately polluted, 1 to 2–moderately polluted, 2 to 3–moderately polluted to strongly polluted, 3 to 4–strongly polluted, and >5–extremely polluted. It can be seen from Table 2 that with respect to the element S, all the soil samples and the lake sediment sample L3and the marine sediment samples M3, M4, M5, and M6 are extremely polluted and all the other soil and sediment samples are strongly polluted to extremely polluted. With respect to the heavy metal Pb, the marine sediment M4 shows that it is strongly polluted to extremely polluted, M1 is strongly polluted, samples M2, M4, M5, M6, and M7and lake sediment L2, and soil S3 are moderately polluted to strongly polluted.The marine sediment samples M1 and M2 indicate that they are moderately polluted to strongly polluted for Ca. The soil sample S5 was found to be moderately polluted to strongly polluted for Ti. The element Ca in soil sample S3and lake sediments L1 and L3, Cu in L1 and Pb in marine sediment M3 were found to be moderately polluted. All the other elements in the other samples were in the unpolluted or unpolluted to moderately polluted range. Highest concern towards contamination were indicated by the elements S and Pb.

B. *Enrichment Factors*

Enrichment factors are useful indices that help in understanding the quantum of contamination of an environmental component.The crustal average values provided by Taylor (1964) were chosen as the background.Al was chosen as the normalising element as it is stable when compared with Fe in natural Eh–pH conditions. Thus, enrichment factor (EF) is defined as

$$\frac{(\frac{Element}{Al})\text{sample}}{(\frac{Element}{Al})\text{background}}$$

The computed enrichment factors are provided in Table 3.

Table 3.Enrichment factors of various elements in soils and sediments

Enrichment factor indicates the level of enrichment of an element with respect to the crustal background concentrations of respective elements provided by Taylor (1964). If the EF is 0 to 1 it indicates background concentration, 1 to 2 minimal enrichment, 2 to 5 moderate enrichment, 5 to 20 significant enrichment, 20 to 40 very high enrichment and > 40 extremely high enrichment. In general, if the EF values are greater than 10, they are considered as from a non-crustal anthropogenic source. Table 3 indicates that S in all the soil and lake sediment samples shows extremely high enrichment except in soil sample S5 where it shows significant enrichment. Ca in both the near shore marine sediment samples show significant enrichment. This is probably because of the accumulation of dead corals along the shore owing to the influx of sewage water from the Thoothukudi city and thermal pollution caused by the thermal power plant that is adjoining the sea. Marine sediments M3 and M2, lake sediment L1, and soil sample S3 show moderate enrichment of Ca. Lake sediment L2 and marine sediment M5 show minimal enrichment of Ca.As far as the enrichment of Si is concerned, marine sediments M1, M3, M4, M5, M6, and M7 show significant enrichment of anthropogenic origin. This is perhaps caused by the influx of silicates from the ash produced by the thermal power plant. Even the other sediment sample M2 has an EF value of 4.36. Fe, K, and Mnshow no enrichment in all the samples. Ti shows moderate enrichment in soil sample S4 and lake sample L1 and significant enrichment in soil sample S5. This is probably because of the enhanced Ti content in the local soils of Thoothukudi region (Pillai and Moorthy, 2013) and hence not of anthropogenic origin. All the lake sediments showed minimal enrichment of Cr which was insignificant in all the soil and marine sediment samples. Ni showed moderate enrichment in soil sample S3 and minimal or no enrichment in all other samples. Cu is moderately enriched in soil samples S3 and S4 and lake sediment L1. Zn is moderately enriched in L1 and is not significant in all the other samples. Pb is significantly enriched in soil sample S3 and lake sample L2 and moderately enriched in soil sample S4 and lake samples L1 and L3. Overall,the only environmental stress in marine sediments seems to be from Si and Ca which are caused probably by influx from the thermal power plant and the death of corals due to sewage contamination caused by the city. Pb, Cu, and S are the causes of concern in the soils and lake sediments.

C. *Pollution Load Indices*

Pollution load index (PLI) was suggested by Tomlinson (1980) to provide an easy understanding of the pollution load present within a site, a zone or a region. Kasilingam et al, (2016) utilised PLI for assessing the pollution loads in sediments in the Palk Strait that is situated north of Thoothukudi city. Contamination factors for each element is computed by the formula $CF = \frac{\text{concentration of element in sample}}{\text{concentration of element in background}}$.

The background concentrations were taken from Taylor (1964). The top five contamination factors among the metals Fe, Ti, Mn, Cr, Ni, Cu, Zn, and Pb were chosen to arrive at the PLI for the site. Hence, $PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times \dots CFn}$, where CF is equal to contamination factor and n = 5. A composite PLI for soil samples can be arrived by $\sqrt[n]{(soil\ site1 \times soil\ site2 \times soil\ site3 \times \dots soil\ siten}$.

Similar PLI calculations can be done for lake and marine sediments as well. The overall PLI for the region can be computed by using the composite PLIs for soil and lake and marine sediment samples using the formula $\sqrt[3]{PLIsoil \times PLIlake\ sediment \times PLImarine\ sediment}$.

Kasilingam et al. (2016) have suggested that a PLI value of 0 indicates background concentration, 0 to 1 unpolluted, 1 to 2 unpolluted to moderately polluted, 2 to 3 moderately polluted, 3 to 4 moderately to highly polluted, 4 to 5 highly polluted, and >5 very highly polluted. The PLI values for various samples and their composite values are presented in Table 4.

Table 4. Pollution Load Indices

From Table 4the soil sample S3 is moderately polluted, samples S1, S4, and S5 are unpolluted to moderately polluted. The overall PLI for soil is 1.44 indicating that the soil component is unpolluted to moderately polluted. The lake sediment sample L2 is moderately polluted and samples L1 and L3 are unpolluted to moderately polluted. The overall PLI for lake sediment component is 1.86 indicating unpolluted to moderately polluted. With respect to the marine sediment samples, the PLI values indicate that samples M1, M4, and M6 are moderately polluted whereas all the other samples (M2, M3, M5, and M7) are unpolluted to moderately polluted. The overall PLI for the marine sediment component is 1.91 indicating that it is unpolluted to moderately polluted. The overall composite PLI for the Thoothukudi city region is 1.87 indicating that the region is unpolluted to moderately polluted.

IV. CONCLUSIONS

Thoothukudi city and its environmental components such as soil and lake and marine sediments are under increasing stress owing to urbanisation and industrial activities. Based on the geo-accumulation indices, it is evident that pollution in terms of S and Pb are of highest concern in all the components. From the enrichment factors it can be concluded that Ca enrichment in the near shore sedimentsamples indicate accumulation of dead corals due to the influx of sewage and thermal pollution. Si enrichment is probably caused by coal ash released from the thermal power plants. Tienrichment in soils is because of the naturally high Ti content in the soils of the region due to geochemical reasons. Heavy metals Pb and Cu are causes of concern in soils and lake sediments.Pollution load indices for individual components indicatethat they are unpolluted to moderately polluted. The pollution load index for the Thoothukudi city region indicates that it is unpolluted to moderately polluted.

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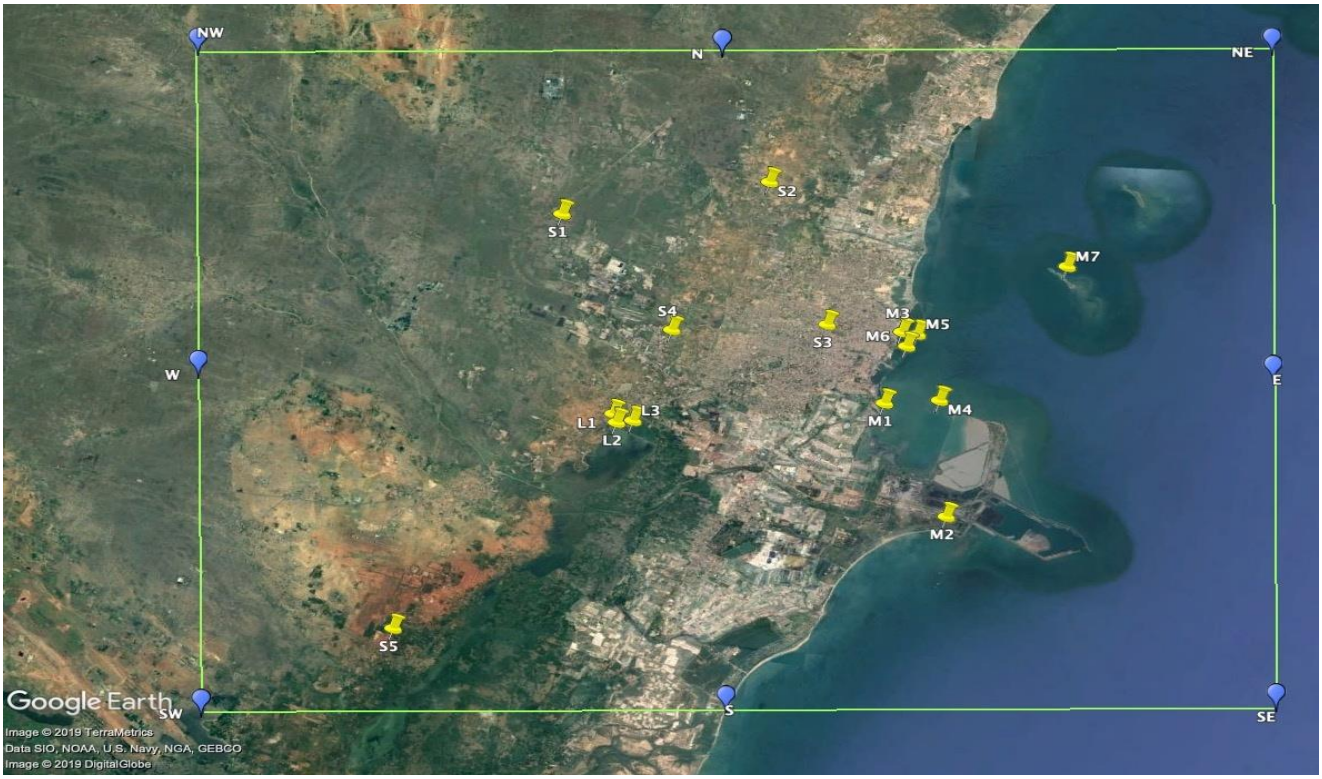

Fig. 1. Google Earth snapshot of study area with sample locations

Table 1. Elemental concentrations of various elements in soils and sediments

	SOIL					LAKE SEDIMENTS			MARINE SEDIMENTS						
ELEMENT/ Sample No.	**S1**	**S2**	**S3**	**S4**	**S5**	**L1**	**L2**	**L3**	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**
Si (%)	28.26	34.30	27.86	36.58	25.06	26.86	31.24	23.07	11.54	9.12	34.94	34.11	36.11	36.74	37.69
Al (%)	9.36	9.38	6.68	6.52	13.52	6.92	8.12	7.83	1.64	2.09	3.47	1.74	3.14	3.22	5.47
Fe (%)	6.89	1.50	2.04	1.03	6.41	2.31	2.02	5.08	1.11	1.62	0.86	0.32	0.54	0.44	2.18
Ca (%)	4.06	0.76	13.23	0.91	0.08	14.27	6.82	15.73	46.30	49.49	7.46	10.15	5.37	2.64	0.39
K (%)	1.44	2.05	1.64	1.32	0.42	1.63	1.69	1.50	0.98	1.20	1.64	1.10	1.69	1.61	1.50

S (%)	1.37	1.33	1.55	1.73	0.69	1.09	1.17	1.37	1.82	1.20	2.29	1.33	1.83	1.64	1.15
Ti (%)	0.95	0.29	0.72	0.91	5.45	1.13	0.55	1.06	0.30	0.29	0.27	0.00	0.40	0.50	0.68
Mn (%)	0.10	0.02	0.04	0.02	0.05	0.04	0.04	0.09	0.12	0.08	0.00	0.00	0.00	0.01	0.05
Cr (ppm)	12.21	20.13	28.08	15.08	8.03	135.12	173.33	155.05	256.05	196.21	185.44	94.04	66.11	139.33	102.01
Ni(ppm)	63.09	89.51	141.11	72.13	76.87	94.37	142.07	35.31	98.35	102.72	123.38	102.08	80.58	104.14	90.93
Cu(ppm)	35.12	82.72	160.04	121.59	63.06	178.62	88.73	103.98	61.61	42.08	39.06	36.43	20.91	72.82	64.48
Zn(ppm)	22.32	85.01	54.23	91.34	83.29	122.53	74.29	93.28	136.01	86.99	87.62	128.09	132.46	136.93	43.18
Pb (ppm)	12.06	8.63	85.67	35.76	13.06	36.02	74.04	25.19	182.39	140.47	59.06	325.04	127.07	142.17	89.98

Table 2. Geo-accumulation indices of various elements in soils and sediments

	SOIL					**LAKE SEDIMENTS**			**MARINE SEDIMENTS**						
ELEMENT/ Sample No.	S1	S2	S3	S4	S5	L1	L2	L3	M1	M2	M3	M4	M5	M6	M7
Si (%)	-0.58	-0.30	-0.60	-0.21	-0.75	-0.65	-0.43	-0.87	-1.87	-2.21	-0.27	-0.31	-0.23	-0.20	-0.16
Al (%)	-0.40	-0.40	-0.89	-0.92	0.13	-0.84	-0.60	-0.66	-2.91	-2.56	-1.83	-2.83	-1.98	-1.94	-1.18
Fe (%)	-0.29	-2.49	-2.05	-3.04	-0.40	-1.87	-2.06	-0.73	-2.93	-2.38	-3.30	-4.72	-3.98	-4.25	-1.95
Ca (%)	-0.62	-3.03	1.09	-2.77	-6.23	1.20	0.13	1.34	2.89	2.99	0.26	0.70	-0.21	-1.24	-4.00
K (%)	-1.12	-0.62	-0.94	-1.24	-2.89	-0.94	-0.89	-1.06	-1.67	-1.38	-0.93	-1.51	-0.89	-0.96	-1.06
S (%)	5.14	5.10	5.32	5.47	4.14	4.80	4.90	5.13	5.54	4.95	5.88	5.09	5.55	5.39	4.88
Ti (%)	0.15	-1.58	-0.25	0.09	2.67	0.40	-0.64	0.31	-1.51	-1.55	-1.66	NA	-1.10	-0.78	-0.32
Mn (%)	-0.47	-2.70	-1.87	-3.25	-1.45	-1.98	-1.80	-0.63	-0.30	-0.91	NA	NA	NA	-3.98	-1.57
Cr (ppm)	-3.62	-2.90	-2.42	-3.31	-4.22	-0.15	0.21	0.05	0.77	0.39	0.31	-0.67	-1.18	-0.11	-0.56
Ni(ppm)	-0.83	-0.33	0.33	-0.64	-0.55	-0.25	0.34	-1.67	-0.19	-0.13	0.13	-0.14	-0.48	-0.11	-0.31
Cu(ppm)	-1.23	0.00	0.96	0.56	-0.39	1.11	0.11	0.33	-0.42	-0.97	-1.08	-1.18	-1.98	-0.18	-0.36
Zn(ppm)	-2.23	-0.30	-0.95	-0.20	-0.33	0.22	-0.50	-0.17	0.37	-0.27	-0.26	0.29	0.34	0.38	-1.28
Pb (ppm)	-0.64	-1.12	2.19	0.93	-0.52	0.94	2.10	0.21	3.28	2.91	1.66	4.12	2.76	2.92	2.26

Table 3. Enrichment factors of various elements in soils and sediments

	S1	**S2**	**S3**	**S4**	**S5**	**L1**	**L2**	**L3**	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**
Si (%)	0.88	1.07	1.22	1.64	0.54	1.13	1.12	0.86	7.03	4.36	10.07	19.59	11.51	11.40	6.90
Al (%)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Fe (%)	1.08	0.23	0.45	0.23	0.69	0.49	0.36	0.95	0.67	0.78	0.25	0.18	0.17	0.14	0.40
Ca (%)	0.86	0.16	3.93	0.28	0.01	4.09	1.67	3.98	28.22	23.64	2.15	5.83	1.71	0.82	0.07
K (%)	0.61	0.86	0.97	0.80	0.12	0.93	0.82	0.75	0.60	0.57	0.47	0.63	0.54	0.50	0.27
S (%)	46.47	45.01	73.63	84.15	16.08	49.82	45.46	55.28	1.11	0.57	0.66	0.76	0.58	0.51	0.21
Ti (%)	1.46	0.44	1.55	2.01	5.82	2.35	0.97	1.95	0.18	0.14	0.08	0.00	0.13	0.15	0.12
Mn (%)	0.95	0.20	0.51	0.20	0.33	0.45	0.44	1.02	0.07	0.04	0.00	0.00	0.00	0.00	0.01
Cr (ppm)	0.11	0.18	0.35	0.19	0.05	1.61	1.75	1.63	0.02	0.01	0.01	0.01	0.00	0.00	0.00
Ni(ppm)	0.74	1.04	2.32	1.21	0.62	1.49	1.92	0.49	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Cu(ppm)	0.56	1.31	3.59	2.78	0.70	3.85	1.62	1.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn(ppm)	0.28	1.07	0.95	1.64	0.72	2.07	1.07	1.40	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Pb (ppm)	0.84	0.56	8.38	3.54	0.63	3.43	6.00	2.10	0.01	0.01	0.00	0.02	0.00	0.00	0.00

Table 4. Pollution Load Indices

	SOIL					**LAKE SEDIMENTS**			**MARINE SEDIMENT**						
	S1	**S2**	**S3**	**S4**	**S5**	**L1**	**L2**	**L3**	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**
PLI Site	1.12	0.93	2.05	1.65	1.73	1.94	2.01	1.70	2.59	1.97	1.66	2.09	1.57	2.23	1.49
PLI Component	1.44					1.87			1.91						

PLI Region	1.71