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ORIGINAL ARTICLE

**STUDIES ON THE SURFACE SEDIMENT CHARACTERISTICS OF TUTICORIN, SOUTH
EAST COAST OF INDIA**

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ABSTRACT

The Tuticorin coast is a coral platform of the south east coast of India. To understand its environmental conditions, geochemical enrichment of trace elements (Mn, Cr, Cu, Ni, Co, Pb, Zn, and Cd) were analyzed for two seasons. Geochemical fractionation confirmed that the metals are lithogenic origin, were mainly derived by detrital processes. The sediments in the study area are sandy with abundant calcareous matter, which determines the total and acid leachable elements. The presence of trace metals depicts the input Cr, Pb, Cd, Cu, and Zn through industrial activities. Factor analysis supports the higher discharge of acid leachable elements and its association with CaCO₃. The present study discusses the geochemical variations of trace metal, their possible source of contamination and monitoring program.

Keywords: Tuticorin, trace element, Organic carbon, CaCO₃

1. INTRODUCTION

Technological development of large scale industries along the coastal water zone affect the entire zone through anthropogenic inputs and natural natural chemical form of trace elements is no longer recognizable. The content of trace elements that have been modified bio geochemically in the coastal waters are in turn transported to the open ocean and the original thereby original composition of sea water is altered (Ackroyd et al 1986; Sagger et al 1997). The geochemistry of dissolved trace metals are controlled by a complex interplay of hydrodynamic factors, industrial, municipal waste water discharges, and biogeochemical processes.

A detailed investigation in the aquatic regions of industrial zones of Tamil Nadu State a study was undertaken from 2002, which represents the enrichment of trace metals in sediments in Tuticorin coast, Bay of Bengal.

The present study focuses on physico chemical conditions, level of dissolved trace metals in marine environment off Tuticorin, south east coast of India. The results will also be useful for pollution monitoring program along the coastal region and also to check the level of dissolved trace metals.

2. MATERIALS AND METHODS

Study Area

The present study covers Tuticorin area, which is situated in the coastal stretch of the East coast, Tamil Nadu and the study area was selected based on the industrial activity, land use, oceanographic conditions and geology.

The physiographical features present a raised beach with a sand bar parallel to the coastline north of Tiruchendur. Beach, coastal ridges, cliff coastline, sand dunes, beach terraces, spits, salt marshes and teri sands are some of the geomorphic features observed in the study area.

The sediments of the Gulf of Mannar surrounding Tuticorin coast consist of calcareous sand and gravels, derived from coral/algal reefs and benthic macro fauna and other terrigenous detritus depending on the local source. The sediments in the present study area are a heterogeneous mixture mainly composed of quartz sand, biogenic carbonate and shell fragments.

Sampling stations

The area of investigation in the Bay of Bengal and sampling locations are shown in the (Figure 1). Total number of ten surface sediment samples were collected in a transect pattern in Tuticorin using Petersen grab sampler. The samples were collected using the coastal research vessel 'Sagar Paschimi' in collaboration with National Institute of Ocean Technology, Chennai.

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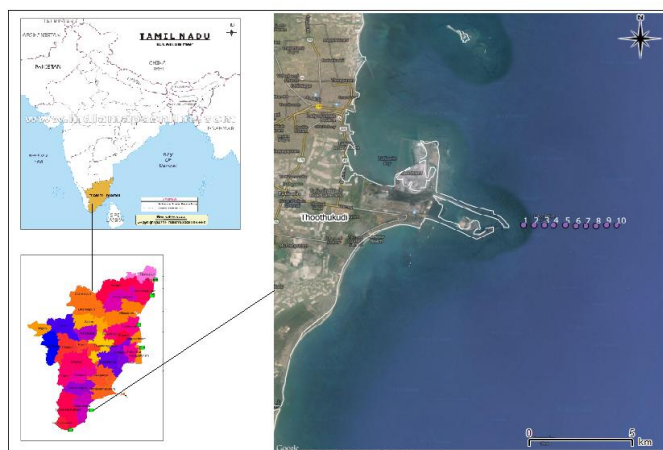


Figure 1. Map showing the Study area and sampling locations

Geochemical analysis of sediments

Geochemical analysis of sediments involves procedures for their decomposition and related chemical measurements. Samples were collected from 2 transects. The samples were analyzed for acid leachable trace elements study after proper preliminary treatment. All the elemental analyses were carried out on total unfractionated sediment samples. This means that no separation of specific sediment sizes was performed prior to the chemical analyses. To determine acid leachable trace metal concentrations of collected sediment samples, method by Loring and Rantala, 1992 is followed.

Sand silt and clay determination by Pipette method

Inexpensive size analysis of naturally occurring fine sediments or of material obtained from wet sieving of sediment containing significant fines is most satisfactorily achieved by the use of the pipette method (Krumbein and Pettijohn, 1938; Galehouse, 1971 and Folk, 1974). This technique relies on the fact that in a dilute suspension, particle settles through a column of water at velocities which are dependent up on their size. As particles decrease in sizes they become increasingly cohesive as surface ionic charges grow on relative significance (McManus, 1988). To determine the size of the flocculated sediments it is necessary to introduce a dispersing agent. Sodium Hexa-metaphosphate is the commonest dispersing agent used for sedimentation analysis.

A 20 g portion of each sample is treated with dilute 4 N HCl to remove carbonate materials and is washed through a 230 ASTM sieve until clear solution passed through. A pinch of sodium-hexa-meta-phosphate (dispersant) is added to isolate clay bounded strongly with silt. The washings are collected carefully in a container and transferred to a 1000 ml measuring jar of de-ionized water. Care is taken to keep the washing to a minimum, so that it did not exceed 1000 ml, and thoroughly mixed by means of manual stirrer which travels from the base to the top of the fluid column. As suspension begins, a timing device is started. Pipette is inserted slowly into the fluid so that its inlet is 20 cm below the surface of fluid and a volume of 20 ml is withdrawn after 1 minute. In each case the pipette is gently inserted and withdrawn from the fluids in order to minimize disturbances. Withdrawn aliquot transferred to pre-weighed beaker and dried at 90°C.

Then weight of the withdrawn sample is measured to the nearest milligram. In calculating the weight of sediment retained in each withdrawn aliquot, allowance also given for the dispersant.

The other raw sub-sample are separated as sand (>63 μ m) and mud (<63 μ m) fractions through wet sieving with the help of 230 ASTM mesh. The separated sand fraction is dried and calculated separately as sand fraction. The mud fraction of each sample is collected in a 1 litre graduated measuring jar and filled with distilled water. The suspension in the measuring jar is then well agitated using a stirring device, in order to obtain a uniform distribution of particles. As soon as the agitation is stopped, the time is noted and after exactly 2 hours and 3 minutes, a 20 cc pipette is inserted up to a depth of 10 cm in the solution and from that level the sample is withdrawn with uniform suction. The pipette out sample is transferred to a 50 cc beaker and dried in an oven. Care is taken to prevent boiling and splattering. Later, the material retained on the sieve is dried and weighed as the sand fraction. The silt and clay that are collected in washings are further discriminated as silt and clay fractions by the pipette method. After complete drying the weights of sand, silt and clay are converted into weight percentages and plotted on a trilinear diagram after Trefethen (1950).

Calcium carbonate (CaCO_3)

Calcium carbonate contents are determined by digesting the sample in HCl according to the procedures of Muller (1979) as follows: 5 g of sediment sample in 150 ml of beaker is added 100 ml of 1 N HCl (87.28 ml of con. HCl make up to 1 l with distilled water) and mixed thoroughly for 1 hour. Then mixture is allowed to settle down and overlying acidic solution is siphoned of (20 ml) into a conical flask. After adding 6-8 drops of Bromothymol Blue indicator. The solution is titrated against 1N NaOH and the disappearance of blue color is noted as end point. Blank titration is also carried out using same procedure.

Organic Matter (OM)

The readily oxidizable organic carbon content is determined by oxidizing the sediments in $\text{K}_2\text{Cr}_2\text{O}_7$ and Sulphuric Acid and then titrated with Ferrous Ammonium Sulphate solution by using Diphenylamine indicator to get clear end point as discussed in detail by Gaudette et al. (1974).

0.5 g of dried and powdered sediment sample is placed in a 500 ml conical flask. Exactly 10 ml of 1 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution and 20 ml of concentrated H_2SO_4 with Ag_2SO_4 (dissolved 2.5 g Ag_2SO_4) in 1 L of H_2SO_4 are added with the help of burette and mixed the mixture by gently rotating the flask for 1 minute. The mixture is allowed to stand for 30 minutes. After 30 minutes, 200 ml of distilled water; 10 ml of 85% HPO_3 and 0.2 g NaF are added sequentially. Then, 15 drops (0.5 ml) of the diphenylamine indicator are added to the sample flask. Finally, the solution mixture is back titrated with 0.5 N Ferrous Ammonium Sulphate solutions to a one-drop brilliant green end point. A blank without sediment is run along with each new batch of the samples.

Acid leachable trace metal analysis

The acid leachable fraction extracts almost the whole degree of fraction of elements simply absorbed by sediments

depicting the contamination of an area (Agemian and Chau, 1976; Taliadouri, 1995). Extraction of acid leachable metals was done by taking 5 g of dry sediment sample in a 100 ml plastic bottle in which 75 ml of 0.5 N HCl was added and after mechanically shaking for 16 h it is filtered with Whatman Grade "A" filter paper. The filtered solution was analyzed for acid leachable Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn and Cd in flame atomic absorption spectroscopy (GBC 920 *plus*) and graphite furnace was in use for determination of Cd due to the low level.

Chemicals of high purity (Merck, Germany) were used and standard solutions were prepared from 1000 mg/L stock solution of each metal. Analysis of triplicates for every fifth sample suggests that precision of analysis lies in the following coefficient of variation Fe 3.1%, Mn 1.5%, Cr 3.4%, Cu 1.9%, Ni 2.4%, Co 2.4%, Pb 2.1%, Zn 3.9% and Cd 3.1%.

3. RESULTS AND DISCUSSION

The sediments of the Gulf of Mannar surrounding Tuticorin coast consist of calcareous sand and gravels, derived from coral/algal reefs and benthic macro fauna and other terrigenous detritus depending on the local source. The sediments in the present study area are a heterogeneous mixture mainly composed of quartz sand, biogenic carbonate and shell fragments.

A total of 10 surface sediment samples were collected in two transects (5 samples in each transect) perpendicular to the coast. The textural characters, calcium carbonate, organic matter distribution and the sediment type in surface are given in Table 1 and the sample stations are shown in Figure 1. Sand content (Figure 2) dominates in the Tuticorin region with sand content ranging between 59.55% and 99.07% with an average of 88.78% indicating a relatively higher energy regime that prevents sedimentation of fine-grained particles and silt between 0.43% and 39.95% with an average of 10.56% (Table 1). Clay content is less than 2%. Sand dominated regions were observed in the entire study area except T8. The silty nature could be due to the formation of a spit and construction of a jetty for the Tuticorin harbor, which shelters the area from the action of currents, which transport the sediments. The increase in sand content in the entire study area indicates that currents from the abrasion zone transport the finer sediments once they reach the coastal zone (Szefer and Skwarzec, 1988). Moreover, the coarse grained nature of the coastal region reflects the turbulent conditions of deposition. However, increase in fine sediments along the coast in certain samples is an indication of fresh water input with finer particles that settle to the bottom when current and wind speeds reduce (Thomson-Becker and Luoma, 1985).

Distribution of CaCO₃ in the gulf indicates a calcium carbonate range from 1.25 to 21.75 % with an average of 9.63 %. The high terrigenous input of CaCO₃ from a land source is indicated by 21.75% of CaCO₃ at T7. The high CaCO₃ values indicate that the major source of carbonate materials is the shell fragments and input from adjacent land mass where Tertiary lime stones and calcareous sandstones extend in the study area (Ray and others 1990; Armstrong Aldrin Sam 1998). Relatively high values of carbonates in

the studied samples may be due to the strong currents leading to non-deposition of terrigenous materials (Rao 1978).

Distribution of organic carbon in the samples is influenced to a significant degree by the diluting effect of CaCO₃ present in the study area. The distributions of OC show that the concentrations in the samples range from 2.43 % at station T7 to 4.98 % at station T8. CaCO₃ contents are lower and the dominance of mud at T8 also indicates that they are attached to finer particles.

Table 1 Sample locations, textural characters, calcium carbonate and organic matter distribution in surface sediments of the Tuticorin

Sample ID	Sand %	Silt %	Clay %	CaCO ₃ %	OM %	Sediment Type
T1	95.61	4.36	1.50	3.50	2.94	Sand
T2	98.33	0.67	1.00	8.50	3.26	Sand
T3	92.69	6.31	1.00	10.25	3.81	Sand
T4	97.96	1.54	0.50	18.75	3.15	Sand
T5	99.07	0.43	0.50	10.50	4.35	Sand
T6	97.07	2.43	0.50	9.75	3.28	Sand
T7	92.42	6.08	1.50	21.75	2.43	Sand
T8	59.55	39.95	0.50	2.50	4.98	Silty sand
T9	79.01	20.49	0.50	9.50	3.53	Sand
T10	76.12	23.38	0.50	1.25	2.79	Sand
Minimum	59.55	0.43	0.50	1.25	2.43	
Maximum	99.07	39.95	1.50	21.75	4.98	
Average	88.78	10.56	0.80	9.63	3.45	

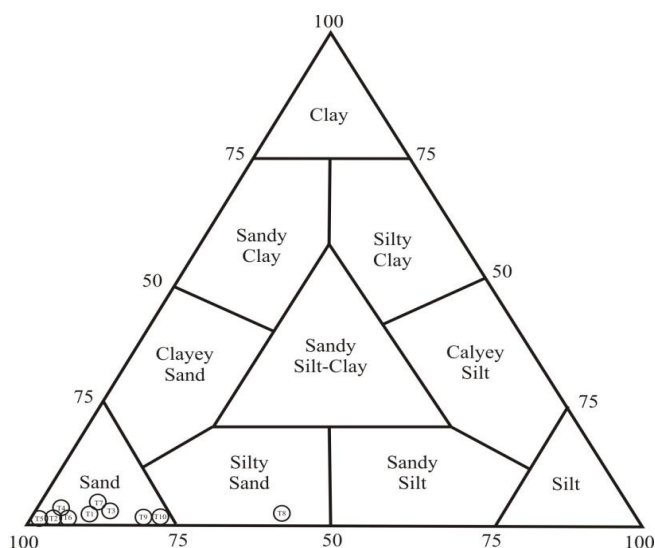


Figure 2 Ternary plots of sand-silt-clay components of surface sediments in Tuticorin. Field limits are from Shepard (1954)

The concentration of acid leachable trace metal distribution in surface sediments off the Tuticorin is given in the Table 2.

In the analyzed sample, the Fe concentration ranges from 120 $\mu\text{g g}^{-1}$ to 713 $\mu\text{g g}^{-1}$ with an average concentration of 362 $\mu\text{g g}^{-1}$. The minimum concentration is found in station T9 and the highest is found at T10. The Mn concentration varies from 52 $\mu\text{g g}^{-1}$ at station T5 to 150 $\mu\text{g g}^{-1}$ at T1. The Cr concentration ranges from the minimum of 7 $\mu\text{g g}^{-1}$ at T1 and the maximum of 16 $\mu\text{g g}^{-1}$ at T10 with an average concentration of 10 $\mu\text{g g}^{-1}$. The Cu concentration ranges from the minimum of 1 $\mu\text{g g}^{-1}$ at T1 and T2 and the maximum of 8 $\mu\text{g g}^{-1}$ at T10 with an average concentration of 3 $\mu\text{g g}^{-1}$. The Ni concentration varies from 6 $\mu\text{g g}^{-1}$ at station T10 to 167 $\mu\text{g g}^{-1}$ at T2. The Co concentration ranges from the minimum of 6 $\mu\text{g g}^{-1}$ at T3 and the maximum of 110 $\mu\text{g g}^{-1}$ at T4 with an average concentration of 63 $\mu\text{g g}^{-1}$.

Table 2 Acid leachable trace metal distribution in surface sediments of the Tuticorin

Sample ID	Concentrations in $\mu\text{g g}^{-1}$								
	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd
T1	384.0	150.0	7.0	1.0	112.0	9.0	4.0	3.0	0.2
T2	256.0	105.0	10.0	1.0	167.0	12.0	3.0	6.0	0.2
T3	504.0	92.0	12.0	2.0	155.0	6.0	2.0	8.0	0.1
T4	358.0	100.0	10.0	4.0	8.0	110.0	4.0	3.0	0.2
T5	291.0	52.0	9.0	2.0	7.0	77.0	3.0	2.0	0.2
T6	322.0	57.0	10.0	2.0	22.0	86.0	2.0	3.0	0.1
T7	493.0	60.0	11.0	4.0	8.0	101.0	3.0	3.0	0.2
T8	182.0	86.0	10.0	3.0	8.0	91.0	3.0	6.0	0.1
T9	120.0	59.0	9.0	2.0	9.0	79.0	2.0	3.0	0.1
T10	713.0	113.0	16.0	8.0	6.0	59.0	2.0	13.0	0.1
Minimum	120.0	52.0	7.0	1.0	6.0	6.0	2.0	2.0	0.1
Maximum	713.0	150.0	16.0	8.0	167.0	110.0	4.0	13.0	0.2
Average	362.3	87.4	10.4	2.9	50.2	63.0	2.8	5.0	0.1

Table 3 Correlation coefficient matrix (R^2) of acid leachable elements in surface sediments off the Tuticorin, southeast coast of India ($p < 0.05$)

	Sand	Silt	Clay	CaCO ₃	OM	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd
Sand	1.00													
Silt	-1.00	1.00												
Clay	0.35	-0.36	1.00											
CaCO ₃	0.52	-0.54	0.23	1.00										
OM	-0.45	0.45	-0.50	-0.36	1.00									
Fe	0.11	-0.12	0.26	-0.01	-0.56	1.00								
Mn	0.00	0.01	0.39	-0.46	-0.27	0.34	1.00							
Cr	-0.31	0.30	-0.25	-0.14	-0.23	0.75	0.02	1.00						
Cu	-0.39	0.39	-0.28	-0.06	-0.31	0.70	0.07	0.85	1.00					
Ni	0.37	-0.38	0.52	-0.18	-0.07	0.05	0.51	-0.14	-0.52	1.00				
Co	-0.24	0.23	-0.46	0.46	0.07	-0.18	-0.61	0.04	0.38	-0.91	1.00			
Pb	0.28	-0.27	0.37	0.23	-0.08	-0.16	0.47	-0.55	-0.22	0.06	0.05	1.00		
Zn	-0.44	0.44	-0.16	-0.53	-0.07	0.65	0.38	0.87	0.66	0.17	-0.34	-0.46	1.00	
Cd	0.64	-0.64	0.50	0.48	-0.31	-0.04	0.20	-0.45	-0.25	0.16	-0.03	0.80	-0.50	1.00

The Pb concentration ranges from the minimum of $2 \mu\text{g g}^{-1}$ at T3, T6, T9 and T10 and the maximum of $4 \mu\text{g g}^{-1}$ at T1 and T4 with an average concentration of $3 \mu\text{g g}^{-1}$. The Zn concentration varies from $2 \mu\text{g g}^{-1}$ at station T5 to $13 \mu\text{g g}^{-1}$ at T10. The Cd concentration is less than $0.2 \mu\text{g g}^{-1}$. The maximum concentrations are found at Station T10 for Fe, Cr, Cu and Zn.

The correlation coefficient matrix (R^2) of acid leachable elements in surface sediments off the Tuticorin, southeast coast of India ($p < 0.05$) is given in the table 3. The Fe shows very good correlation with Cr ($r=.75$). Cr shows good relationship with Cu ($r=.85$) and Zn ($r=.87$). Pb is strongly correlated with Cd ($r=.80$).

To test the elemental associations, the compositional data is subjected to Varimax factor loading. The first factor accounts for 35% of the total variance (Figure 3) and depicts the strong influence of Sand, Clay, CaCO₃, Pb and Cd. This explains the general coherence of transition metals probably resulting from a single source. The second factor accounts for 24% of

variance incorporating strong positive loading by Fe, Cr, Cu and Zn. The third factor accounts for 19% of the total variance and is loaded only by clay, Mn and Ni (Figure 3). These factor loading results are further supported by the elemental associations obtained by regression analysis.

Geoaccumulation index (I_{geo}) has been calculated for analyzed metals. In Figure 1, we show sample percentages in Muller's classes (Muller 1981) for Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn and Cd using the background values. Figure 3 shows that, for all the background values, 100% of samples fall in class 0 for Cr and Pb. Therefore, Tuticorin is not a contaminated area for these metals. For Fe, 90% of the samples fall in class 0 and 10% in class 1, by using our background values. For Mn, about 60% of samples are included in class 0 and 40% falls under class 1. Cu concentrations fall for 90% in class 0, for 10% in class 1, suggesting that the quality of sediments in this area is unpolluted to moderately polluted. Ni concentrations fall for 60% in class 0, for 10% in class 2 and 30% in class 4,

suggesting that the quality of sediments in this area is strongly polluted. Zn concentrations fall for 80% in class 0, for 20% in class 1, suggesting that the quality of sediments in this area is moderately polluted. Cd concentrations fall for 90% in class 1, for 10% in class 2, suggesting that the quality of sediments in this area is moderately polluted.

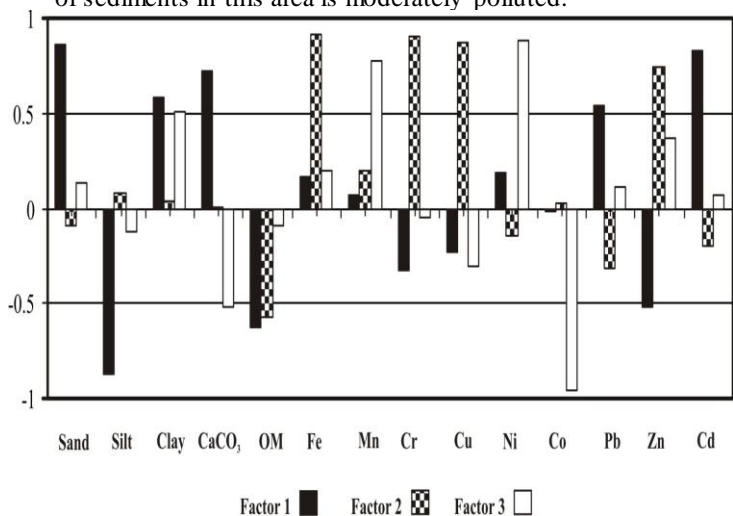


Figure 3 Results of factor analysis (R-mode) showing three primary factors (F1, F2 and F3) for surface sediments

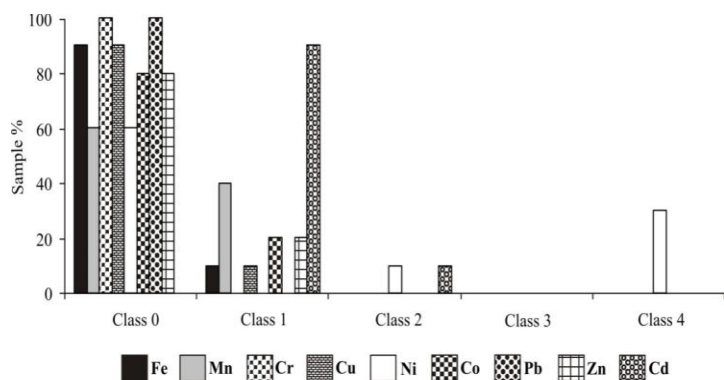


Figure 4 Percentage of samples in Muller's classes for Fe, Mn, Cr, Cu, Ni, Pb and Zn using the background values for Tuticorin

4.CONCLUSION

The major conclusions derived from this study are given below.

The heavy metal concentration for the environmentally sensitive area (Tuticorin) has been evaluated and compared.

- The sediments in Tuticorin are mostly sandy silt and silty sand. The correlation matrix exhibits poor correlation between these components and minor metals indicating an insignificant role of CaCO₃ and OM in enriching minor metals.
- In Tuticorin, Ni and Cd falls under class 2 (moderately polluted), Ni falls under class 4 (strongly polluted) suggesting this area is enriched with respect to Ni.
- The order of enrichment in Tuticorin is as follows: Ni > Cd > Mn, Pb, Co > Fe, Cr, Cu and Zn.

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