

Chemistry of Trace Metals in the Riverine Sediments of Kortalaiyar River, Tamilnadu, India

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Abstract: *The growing competition in the quantitative and qualitative demand of water from domestic, industrial and economic sector seek the approach to water resource management. Rivers are the carriers of the contaminants due to the flocculation of metals in the sediments. The scope of the present study is to evaluate the contamination level in Kortalaiyar River which plays a vital role in the water supply, food security and economic development of the Chennai city. Sediment samples and water samples were collected from 30 locations starting from Poondi Lake to Ennore creek to analyze the variations in the trace metals and major metals which includes the heavy metals too. The geochemical analysis was carried out for Pre Monsoon and Post Monsoon seasons for two consecutive years. The trace metals and the major metals analyzed were correlated and studied using Pearson's correlation matrix. The level of contamination is figured out to be maximum near the Ennore creek where the river forms estuary with the Sea.*

Keywords: Kortalaiyar River, Ennore Creek, Pearson's Correlation matrix, Trace metals, Major metals, Estuary

1. Introduction

Rivers are considered as one the major sources of water due to the availability of fresh water. The sediments present in the river is closely related to the level of pollution in it. Sediments form a natural buffer and filter system and often play an important role in the storage and release of nutrients in the aquatic ecosystems. Pollution of the environment is reflected by levels of contamination of rivers, lakes and other reservoirs. There are sites of accumulation of impurities coming from human activity, due to dissolution, precipitation and adsorption [1]. Sediments can also be defined as the material deposited at the bottom of rivers, which are silt and deposits [2]. During the last two centuries, heavy metals released by human activities have superimposed new pattern of metal distribution on those which are naturally occurring. Heavy metals are widely used in automobiles, mining industries, pesticides, house-holds appliances, dental amalgams, paints, photographic papers, photo chemicals etc [3]. A number of processes influence the sedimentary content and quality of river water. Sediments in water originate from surface erosion and contain mineral, bedrock erosion and organic components during the process of soil formation [4]. Sediment has important role in the nutrient cycle of aquatic environments. In some cases, sediment composition is responsible for the transport of essential nutrients as well as pollutants. Sediment analysis is increasingly important in evaluating qualities of the total ecosystem of a water body, in addition to the water sample analysis practiced for years [5].

Evaluation of the distribution and transfer of toxic metals between the sediment and water columns is of high significance. When heavy metals are introduced into the aquatic environment, they are redistributed throughout the water column. They may be deposited or accumulated in the sediments too [6]. Heavy metal concentration profiles in sediments can be used to identify the history and sources of pollution. The sources of major and minor elements in the aquatic sediment area may be the consequence of natural weathering, run-off from other water sources and atmospheric input or by anthropogenic impact. [7, 8].

2. Objectives

Urban and industrial activities in metropolitan cities all over the world have grown very rapidly in recent years and significant amount of contaminants are introduced in aquatic regions especially in the rivers. In many places, it started more than decades ago and the contamination level is increasing day-by day without any major process to control the level of pollution. This type of contamination disturbs the aquatic environment severely and also affects the adjacent area with major ecological degradation. A variety of physico-chemical effects takes place in aquatic region with major environmental changes with no effective monitoring system and it also makes it difficult to draw any major conclusions on the long-term effects of human activities. In the present study the geochemistry of Kortalaiyar river is studied to assess the anthropogenic input in the River.

The outcome of the study will help to assess the impacts of contamination and also to find suitable treatment techniques for the polluted sediments. Moreover, some remedial measures can also be proposed for strategic pollution control and management in the Kosasthalair River

3. Material and Methods

Study Area

Kortalaiyar River is one of the three rivers that flow in the Chennai metropolitan area. It is also known as Kosasthalair. The river has a length of 136 Km and it originates near Kaveripakkam in Vellore district and finally drains into the Bay of Bengal. It has a catchment area in North Arcot District with a branch near Kesavaram Anicut and flows into the city as Cooum River. The main Kortalaiyar river flows into Poondi reservoir. The water flows through Thiruvallur district from the Poondi reservoir, enters into the Chennai metropolitan area, and joins the sea at Ennore creek. The total catchment area of the river is 3,757 Km² and has a bed width range from 150 to 250 m. The discharge capacity of the river is 110,000m³/s and the expected flood discharge

capacity is about 125,000 m³/s. There are two check dams across the river, one at Tamaraipakkam and the other at Vallur. Tamaraipakkam anicut controls the excess discharge in the river. Vallur anicut is a small check dam near Minjur to control the water levels and to feed the irrigation channels in the area. Whenever the flood gates of Poondi reservoir are opened .a considerable volume of water drains into the sea through Kortalaiyar River near the Ennore Creek.

Sediment Sampling

The area for present study is 30 sampling points starting from Poondi reservoir (Lat 13°12'41.03"N, Long 79°52'10.18"E) to Ennore creek (Lat 13°13'53.72"N, Long 80°19'44.59"E).Thirty samples of surface sediments were collected in air dried Zip Lock covers for each season, Pre-Monsoon (PRM) and Post-Monsoon (POM) for two consecutive years from July 2011 to July 2013. The sediment samples were air dried at room temperature and then finely powdered using a Porcelain mortar and Pestle. It was sieved for further analysis. The metals, both major and trace, present in the sediment samples were analyzed by following USEPA SW 8462008.

4. Results and Discussion

The samples were analyzed to determine the presence of Major metals and Trace metals. The metals present in the sediments are Sodium, Aluminium, Silicon, Nitrogen, Phosphorous, Potassium, Boron , Barium, Calcium, Magnesium, Chromium, Nickel, Copper, Manganese, Iron, Zinc, Titanium , Cobalt , Lead and Cadmium. The concentration of these metals in the sediments may be accumulated in the water lying above it.

The presence of numerous metals in the water and sediment phases in a river can partially result in amelioration or enhancement of their bioavailability and toxicity [9].The associations of the various metals can be investigated by correlating the total concentration in the water and sediment phases. The total content does not describe the amount of

metal available to aquatic organisms and this may overestimate the real threat [10].Evaluation of seasonal interrelationships among metals in the water and sediment phase assists partially in explaining the bioavailability of the metals to the aquatic organisms.

Hence an attempt is made to study the geochemistry of Kortalaiyar River by correlating the concentration of various metals in the sediments. Two seasons namely, Pre-Monsoon (PRM) and Post-Monsoon (POM) has been studied to analyze the variation in the distribution pattern of the river under study. The difference in the concentration of metals in PRM and POM may be accounted to the rainfall pattern in Tamilnadu.

The correlation between the various metals is studied using Pearson's Correlation coefficient Matrix. It is found that in PRM and POM, there is close correlation between N, P and K among themselves and other metals. There is similarity in the correlation of these metals with heavy metals too. Nitrogen strongly correlates with Ni, Cu, Zn, Co, Pb and Cd. Pottasium resembles Nitrogen in the correlation pattern. Phosphorous shows strong correlation with Ni, Cu, Co and Pb. Since N, P and K have strong association with all other metals in the sediment, their existence as major metals have been justified.

Considering Iron, most of the heavy metals like Cr, Ni, Cu, Co, Pb, Cd etc tend to show close associations with it. This shows the distribution pattern with the local redox conditions [11]. Along the heavy metals, Fe is fairly correlated to N, K and Mg. Chromium shows strong correlation with Ni and Pb in PRM and POM. It also has significant association with N, P, K, Mg, Cu, Mn, Fe, Co, Cd. There is a very strong correlation between Cd, Zn, Cu, Pb, Co, Cr and Ni . Associations between metals are important, as they determine the bioavailability and potential toxicity to fish in an aquatic system [12 and 13].The correlation between Cr, Ni, Cu, Fe, Zn, Co, Pb and Cd in PRM and POM is tabulated in Table-1and Table-2 respectively.

Table 1

	<i>Cr</i>	<i>Ni</i>	<i>Cu</i>	<i>Fe</i>	<i>Zn</i>	<i>Co</i>	<i>Pb</i>	<i>Cd</i>
Cr	1							
Ni	0.917801	1						
Cu	0.589729	0.601509	1					
Fe	0.562264	0.510001	0.58735	1				
Zn	0.482912	0.598728	0.737999	0.601567	1			
Co	0.580286	0.667128	0.83711	0.644827	0.830499	1		
Pb	0.71575	0.882375	0.655849	0.406082	0.698781	0.755646	1	
Cd	0.587567	0.650264	0.8452	0.683404	0.865303	0.919428	0.731282	1

Table 2

	<i>Cr</i>	<i>Ni</i>	<i>Cu</i>	<i>Fe</i>	<i>Zn</i>	<i>Co</i>	<i>Pb</i>	<i>Cd</i>
Cr	1							
Ni	0.888091	1						
Cu	0.607862	0.618604	1					
Fe	0.593601	0.515367	0.600627	1				
Zn	0.408673	0.532496	0.705217	0.457458	1			
Co	0.572198	0.632986	0.882466	0.671461	0.765027	1		
Pb	0.743031	0.876631	0.720348	0.537072	0.680284	0.757168	1	
Cd	0.597853	0.661992	0.917495	0.649492	0.802439	0.950816	0.772077	1

The variation of these metals in the PRM and POM is shown in Figure-1 and Figure-2 respectively.

The Pearson Correlation Coefficient (r) measures the strength and direction of linear relationships between two or more random variables and ranges from -1 to 1 [14, 15, 16]. In the present study r is used to describe the interrelationships between the elements analyzed at a significance level (p) of < 0.01 . It is evident from the correlation matrix that there exists a close proximity between the heavy metals. The metals show synergistic and ameliorative effects in the sediment phase, more so for the water-sediment interface. Although intermetallic correlation associations does not imply the direct cause and effect relations, they indicate that these elements travel in the same

pathways through the aquatic system as the metals with which they are correlated [17]. [18] State that positive correlation between metals show an association or interaction between the metals in a particular study area, but that on the other hand, these metals might have similar sources of input. A strong correlation between two heavy metals may be an occurrence of strong dependence of both the metals on the same causal factor [9]. The significant seasonal differences in intermetallic relations indicate that metal mobility and association in both the water and sediment interface also depends on the limnochemistry, hydrodynamics (especially water volume) and particularly the temperature of the water phase [19].

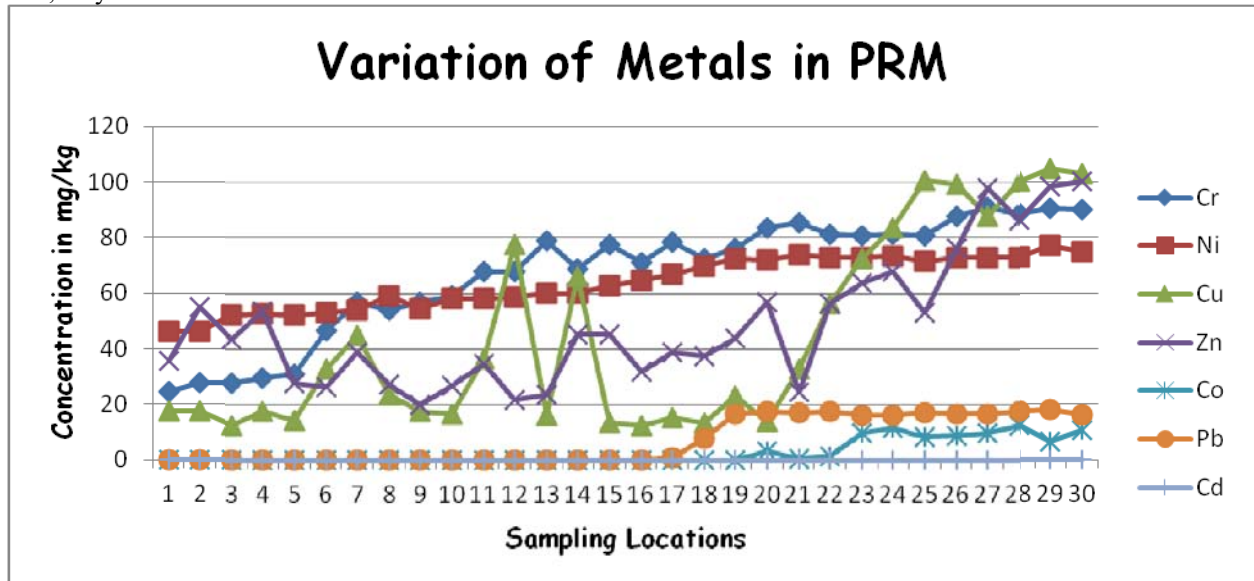


Figure 1

Factors that determine the metal mobility in the sediment-water phase include decomposition-resuspension; sorption adsorption and complexation- decomplexation [20]. These processes are governed by pH, salinity and redox conditions [21]. Metals occur in various species or complexes both in the water and sediment phase. In the sediments that are unpolluted, the metals are mainly bound to silicates and

other primary minerals. These species are relatively immobile and are usually not available to living organisms. Whereas in polluted sediments, heavy metals are more mobile and are bound to different phases of the sediment. Therefore, most of the metals discharged into the river are found in the bottom sediments [22].

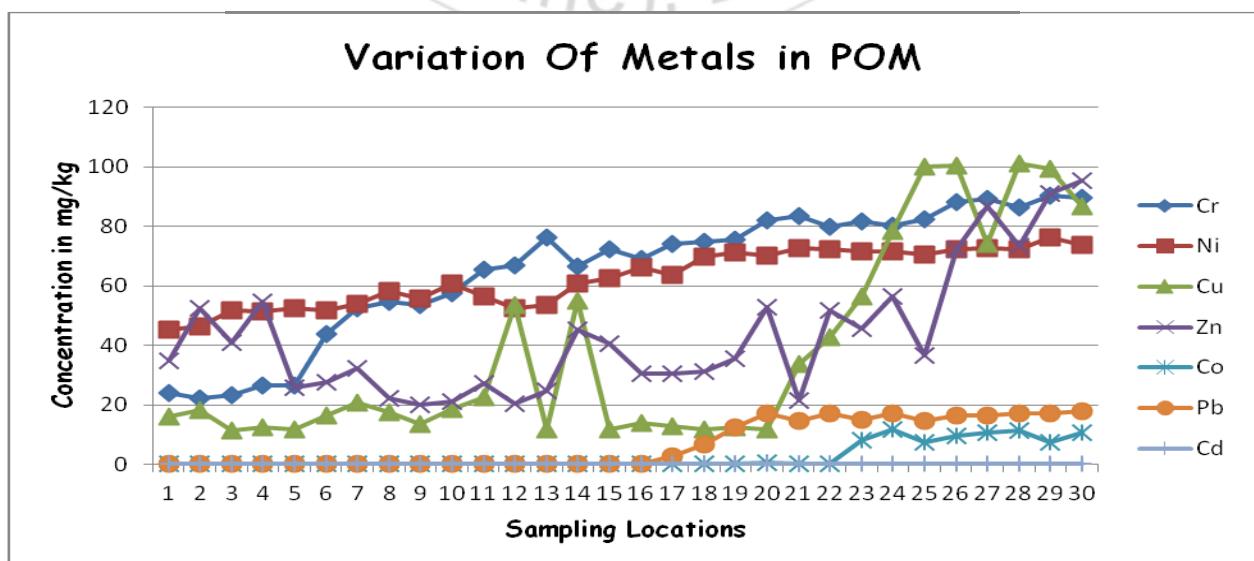


Figure 2

However, the metals that are accumulated might be carried from sediments into the water by natural process as well as man-made process, which may pose as a risk to the aquatic ecosystem. Biogeochemical and ecotoxicological significance of the metals present in the water phase of lotic systems depend widely on its presence, fractional content, co precipitation, concentration, reflux, desorption and decomplexation from the sediment phase, as well as its reactivity in the presence of other metals present in a multisolution [9].

In PRM, Zinc shows close association with Mg, Cu, Co, Cd where as in POM, it shows good correlation with K also. The higher concentration of Zinc in sediment may be attributed to the presence of unused remains of Zinc sulphate in fertilizers [23]. Maximum concentration of Zn in sediments nearby Ennore is probably due to the discharges of effluents from the petrochemical, painting industries [24]. Zinc can enter the aquatic environment from a number of sources, including industrial discharges, sewage, effluent and runoff [25].

Titanium shows a very uncommon pattern of distribution in the Kortalaiyar river. In PRM, Ti is moderately correlated to Mg and Fe. It is negatively correlated to P, Ba and Ni. In POM, it is seen that Ti does not show close association with any metal and it is negatively related to P and Ni. Titanium is non-toxic, because of its poor absorption and retention in living organisms [26]. Potential anthropogenic sources of Ti in the environment include paint pigments.

The elements with different chemical properties may appear with similar distribution patterns in the sediments due to the fact that they are linked to the same carrier particle with similar sedimentological properties. The type of carrier particle and the way in which elements are bound to it determine the element's geochemical fraction in sediments [27, 28].

A factor of interest is the finding of enriched levels of metal content near the estuary that the River makes with the Ennore Creek. It is one of the most industrially developed area in Chennai. Ennore is on the northeast coast of Chennai [29]. Ennore coast consists of alluvial tracts and beach dunes, tidal flats and creek in the eastern part. Ennore comprises of lagoons, with salt marshes and backwaters, which are submerged under water during high tide and form an arm of the sea opening in to the Bay of Bengal [30]. Ennore creek was once encompassed with rich biodiversity and in due course of time has been totally wiped out by the petrochemical complex by pumping their effluents into the Ennore Creek. Consequently the natural wealth is eroded to mere sewage channel and the biological productivity of the coast has come down[31]

It is surrounded by many industries like Thermal power station, fertilizers and Petrochemical industry. Hence the point sources of pollution are mainly from North Chennai Thermal Power Plant, Ennore Port activities, other nearby industries and untreated urban wastes from Chennai Metropolitan [32]. The concentration of the major and trace metals are found to be very high in Ennore creek and its nearby areas like Manali. The sediment samples in the location 24 to 30 is recorded as the most polluted area along the flow line of the Kortalaiyar river.

5. Conclusion

The geochemical analysis of the kortalaiyar river has made us aware of the metal concentration in the river. The presence of heavy metals in the sediments indicate the proximity to high contamination level in the near future. The correlation studies reveal the relationship between each metal thereby predicting the possible source of contamination. The strong correlation between the major metals and the trace metals indicate the enrichment of these metals in due course of time. Overall, the data also signifies the need for a regular approach towards monitoring on enrichment of trace metals and the present study is part of a larger regular monitoring program in the aquatic environments of south India. This type of development plans and remedial measures can serve as an example and will help to reduce the level of enrichment in the aquatic environment especially in major populated industrialized cities. Kortalaiyar River is one of the important aquatic regions within city limits and special contaminant monitoring programs can be implemented as long-term measures.

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